CHAPTER 12

Acids and Bases

Opening Essay

Formerly there were rather campy science-fiction television shows in which the hero was always being threatened with death by being plunged into a vat of boiling acid: "Mwa ha ha, Buck Rogers [or whatever the hero's name was], prepare to meet your doom by being dropped into a vat of boiling acid!" (The hero always escapes, of course.) This may have been interesting drama but not very good chemistry. If the villain knew his/her/its science, the hero would have been dropped into a vat of boiling base.

Recall that the active component of a classic acid is the H^+ ion, while the active part of a classic base is the OH^- ion. Both ions are related to water in that all H^+ ion needs to become a water molecule is an OH^- ion, while all an OH^- ion needs to become water is an H^+ ion. Consider the relative masses involved: an ion of mass 1 needs an ion of mass 17 to make water, while an ion of mass 17 needs an ion of mass 1 to make water. Which process do you think will be easier?

In fact, bases are more potentially dangerous than acids because it is much easier for an OH^- ion to rip off an H^+ ion from surrounding matter than it is for an H^+ ion to rip off an OH^- ion. Certain household chemicals, such as some brands of cleanser, can be very concentrated bases, which makes them among the most potentially hazardous substances found around the home; if spilled on the skin, the strong caustic compound can immediately remove H^+ ions from the flesh, resulting in chemical burns. Compare that to the fact that we occasionally purposefully ingest substances such as citrus fruits, vinegar, and wine—all of which contain acids. (Of course, some parts of the body, such as the eyes, are extremely sensitive to acids as well as bases.) It seems that our bodies are more capable of dealing with acids than with bases.

On the left is a common acid, and on the right is a common base. Which one is more potentially hazardous?

© *Thinkstock*

So a note to all the villains out there: get your chemistry right if you want to be successful!

Acids and bases are important classes of chemical compounds. They are part of the foods and beverages we ingest, they are present in medicines and other consumer products, and they are prevalent in the world around us. In this chapter, we will focus on acids and bases and their chemistry.

1. ARRHENIUS ACIDS AND BASES

LEARNING OBJECTIVES

1. **Identify an Arrhenius acid and an Arrhenius base.**
2. **Write the chemical reaction between an Arrhenius acid and an Arrhenius base.**

Arrhenius acid

A compound that increases the hydrogen ion concentration in aqueous solution.

hydronium ion

The actual chemical species that represents a hydrogen ion.

Historically, the first chemical definition of an acid and a base was put forward by Svante Arrhenius, a Swedish chemist, in 1884. An **Arrhenius acid** is a compound that increases the H^+ ion concentration in aqueous solution. The H^+ ion is just a bare proton, and it is rather clear that bare protons are not floating around in an aqueous solution. Instead, chemistry has defined the **hydronium ion** (H_3O^+) as the actual chemical species that represents an H^+ ion. H^+ ions and H_3O^+ ions are often considered interchangeable when writing chemical equations (although a properly balanced chemical equation should also include the additional H_2O). Classic Arrhenius acids can be considered ionic compounds in which H^+ is the cation. Table 12.1 lists some Arrhenius acids and their names.

TABLE 12.1 Some Arrhenius Acids

Formula	Name
$HC_2H_3O_2$ (also written CH_3COOH)	acetic acid
$HClO_3$	chloric acid
HCl	hydrochloric acid
HBr	hydrobromic acid
HI	hydriodic acid
HF	hydrofluoric acid
HNO_3	nitric acid
$H_2C_2O_4$	oxalic acid
$HClO_4$	perchloric acid
H_3PO_4	phosphoric acid
H_2SO_4	sulfuric acid
H_2SO_3	sulfurous acid

Arrhenius base

A compound that increases the hydroxide ion concentration in aqueous solution.

An **Arrhenius base** is a compound that increases the OH^- ion concentration in aqueous solution. Ionic compounds of the OH^- ion are classic Arrhenius bases.

EXAMPLE 1

Identify each compound as an Arrhenius acid, an Arrhenius base, or neither.

1. HNO_3
2. CH_3OH
3. $Mg(OH)_2$

Solution

1. This compound is an ionic compound between H^+ ions and NO_3^- ions, so it is an Arrhenius acid.
2. Although this formula has an OH in it, we do not recognize the remaining part of the molecule as a cation. It is neither an acid nor a base. (In fact, it is the formula for methanol, an organic compound.)
3. This formula also has an OH in it, but this time we recognize that the magnesium is present as Mg^{2+} cations. As such, this is an ionic compound of the OH^- ion and is an Arrhenius base.

Test Yourself

Identify each compound as an Arrhenius acid, an Arrhenius base, or neither.

1. KOH
2. H_2SO_4
3. C_2H_6

Answer

1. Arrhenius base
2. Arrhenius acid
3. neither

Acids have some properties in common. They turn litmus, a plant extract, red. They react with some metals to give off H_2 gas. They react with carbonate and hydrogen carbonate salts to give off CO_2 gas. Acids that are ingested typically have a sour, sharp taste. (The name *acid* comes from the Latin word *acidus*, meaning "sour.") Bases also have some properties in common. They are slippery to the touch, turn litmus blue, and have a bitter flavor if ingested.

Acids and bases have another property: they react with each other to make water and an ionic compound called a salt. A **salt**, in chemistry, is any ionic compound made by combining an acid with a base. A reaction between an acid and a base is called a **neutralization reaction** and can be represented as follows:

$$\text{acid} + \text{base} \rightarrow H_2O + \text{salt}$$

The stoichiometry of the balanced chemical equation depends on the number of H^+ ions in the acid and the number of OH^- ions in the base.

salt

Any ionic compound that is formed from a reaction between an acid and a base.

neutralization reaction

The reaction of an acid and a base to produce water and a salt.

EXAMPLE 2

Write the balanced chemical equation for the neutralization reaction between H_2SO_4 and KOH. What is the name of the salt that is formed?

Solution

The general reaction is as follows:

$$H_2SO_4 + KOH \rightarrow H_2O + \text{salt}$$

Because the acid has two H^+ ions in its formula, we need two OH^- ions to react with it, making two H_2O molecules as product. The remaining ions, K^+ and SO_4^{2-}, make the salt potassium sulfate (K_2SO_4). The balanced chemical reaction is as follows:

$$H_2SO_4 + 2KOH \rightarrow 2H_2O + K_2SO_4$$

Test Yourself

Write the balanced chemical equation for the neutralization reaction between HCl and $Mg(OH)_2$. What is the name of the salt that is formed?

Answer

$2HCl + Mg(OH)_2 \rightarrow 2H_2O + MgCl_2$; magnesium chloride

KEY TAKEAWAYS

- An Arrhenius acid is a compound that increases the H^+ ion concentration in aqueous solution.
- An Arrhenius base is a compound that increases the OH^- ion concentration in aqueous solution.
- The reaction between an Arrhenius acid and an Arrhenius base is called neutralization and results in the formation of water and a salt.

EXERCISES

1. Define *Arrhenius acid*.
2. Define *Arrhenius base*.
3. What are some general properties of Arrhenius acids?
4. What are some general properties of Arrhenius bases?
5. Identify each substance as an Arrhenius acid, an Arrhenius base, or neither.
   a. NaOH
   b. C_2H_5OH
   c. H_3PO_4
6. Identify each substance as an Arrhenius acid, an Arrhenius base, or neither.
   a. $C_6H_{12}O_6$
   b. HNO_2
   c. $Ba(OH)_2$
7. Write the balanced chemical equation for the neutralization reaction between KOH and $H_2C_2O_4$. What is the salt?
8. Write the balanced chemical equation for the neutralization reaction between $Sr(OH)_2$ and H_3PO_4. What is the salt?
9. Write the balanced chemical equation for the neutralization reaction between HCl and $Fe(OH)_3$. What is the salt?
10. Write the balanced chemical equation for the neutralization reaction between H_2SO_4 and $Cr(OH)_3$. What is the salt?
11. $CaCl_2$ would be the product of the reaction of what acid and what base?
12. $Zn(NO_3)_2$ would be product of the reaction of what acid and what base?
13. $BaSO_4$ would be product of the reaction of what acid and what base?
14. Na_3PO_4 would be product of the reaction of what acid and what base?

ANSWERS

1. a compound that increases the H^+ concentration in water

3. sour taste, react with metals, and turn litmus red

5. a. Arrhenius base
   b. neither
   c. Arrhenius acid
7. $2KOH + H_2C_2O_4 \rightarrow 2H_2O + K_2C_2O_4$; $K_2C_2O_4$
9. $3HCl + Fe(OH)_3 \rightarrow 3H_2O + FeCl_3$; $FeCl_3$
11. HCl and $Ca(OH)_2$
13. H_2SO_4 and $Ba(OH)_2$

2. BRØNSTED-LOWRY ACIDS AND BASES

LEARNING OBJECTIVES

1. **Identify a Brønsted-Lowry acid and a Brønsted-Lowry base.**
2. **Identify conjugate acid-base pairs in an acid-base reaction.**

The Arrhenius definition of acid and base is limited to aqueous (that is, water) solutions. Although this is useful because water is a common solvent, it is limited to the relationship between the H^+ ion and the OH^- ion. What would be useful is a more general definition that would be more applicable to other chemical reactions and, importantly, independent of H_2O.

In 1923, Danish chemist Johannes Brønsted and English chemist Thomas Lowry independently proposed new definitions for acids and bases, ones that focus on proton transfer. A **Brønsted-Lowry acid** is any species that can donate a proton (H^+) to another molecule. A **Brønsted-Lowry base** is any species that can accept a proton from another molecule. In short, a Brønsted-Lowry acid is a proton donor (PD), while a Brønsted-Lowry base is a proton acceptor (PA).

Brønsted-Lowry acid

Any species that can donate a proton to another molecule.

Brønsted-Lowry base

Any species that can accept a proton from another molecule.

It is easy to see that the Brønsted-Lowry definition covers the Arrhenius definition of acids and bases. Consider the prototypical Arrhenius acid-base reaction:

$$\underset{\text{acid}}{H^+(aq)} + \underset{\text{base}}{OH^-(aq)} \rightarrow H_2O(\ell)$$

The acid species and base species are marked. The proton, however, is (by definition) a proton donor (labeled PD), while the OH^- ion is acting as the proton acceptor (labeled PA):

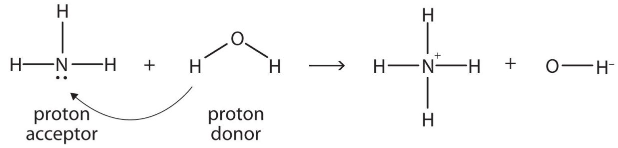
$$\underset{\text{PD}}{H^+(aq)} + \underset{\text{PA}}{OH^-(aq)} \rightarrow H_2O(\ell)$$

The proton donor is a Brønsted-Lowry acid, and the proton acceptor is the Brønsted-Lowry base:

$$\underset{\text{BL acid}}{H^+(aq)} + \underset{\text{BL base}}{OH^-(aq)} \rightarrow H_2O(\ell)$$

Thus H^+ is an acid by both definitions, and OH^- is a base by both definitions.

Ammonia (NH_3) is a base even though it does not contain OH^- ions in its formula. Instead, it generates OH^- ions as the product of a proton-transfer reaction with H_2O molecules; NH_3 acts like a Brønsted-Lowry base, and H_2O acts like a Brønsted-Lowry acid:



A reaction with water is called **hydrolysis**; we say that NH_3 hydrolyzes to make NH_4^+ ions and OH^- ions.

hydrolysis

A reaction with water.

Even the dissolving of an Arrhenius acid in water can be considered a Brønsted-Lowry acid-base reaction. Consider the process of dissolving HCl(g) in water to make an aqueous solution of hydrochloric acid. The process can be written as follows:

$$HCl(g) + H_2O(\ell) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

amphiprotic

A substance that can act as a proton donor or a proton acceptor.

HCl(g) is the proton donor and therefore a Brønsted-Lowry acid, while H_2O is the proton acceptor and a Brønsted-Lowry base. These two examples show that H_2O can act as both a proton donor and a proton acceptor, depending on what other substance is in the chemical reaction. A substance that can act as a proton donor or a proton acceptor is called **amphiprotic**. Water is probably the most common amphiprotic substance we will encounter, but other substances are also amphiprotic.

EXAMPLE 3

Identify the Brønsted-Lowry acid and the Brønsted-Lowry base in this chemical equation.

$$C_6H_5OH + NH_2^- \rightarrow C_6H_5O^- + NH_3$$

Solution

The C_6H_5OH molecule is losing an H^+; it is the proton donor and the Brønsted-Lowry acid. The NH_2^- ion (called the amide ion) is accepting the H^+ ion to become NH_3, so it is the Brønsted-Lowry base.

Test Yourself

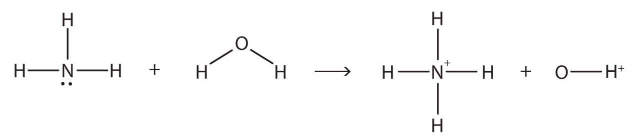
Identify the Brønsted-Lowry acid and the Brønsted-Lowry base in this chemical equation.

$$Al(H_2O)_6^{3+} + H_2O \rightarrow Al(H_2O)_5(OH)^{2+} + H_3O^+$$

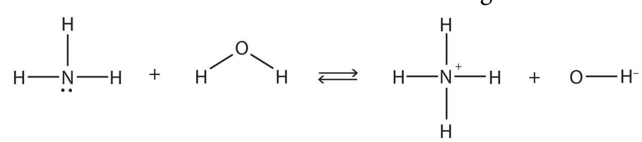
Answer

Brønsted-Lowry acid: $Al(H_2O)_6^{3+}$; Brønsted-Lowry base: H_2O

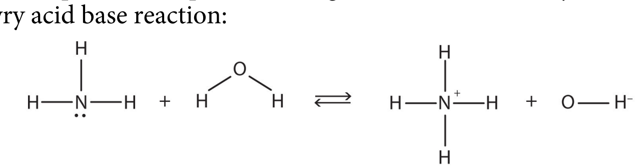
In the reaction between NH_3 and H_2O,



the chemical reaction does not go to completion; rather, the reverse process occurs as well, and eventually the two processes cancel out any additional change. At this point, we say the chemical reaction is at *equilibrium*. Both processes still occur, but any net change by one process is countered by the same net change by the other process; it is a *dynamic*, rather than a *static*, equilibrium. Because both reactions are occurring, it makes sense to use a double arrow instead of a single arrow:

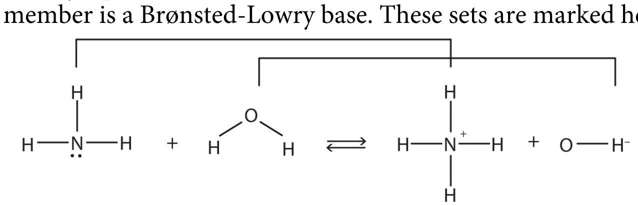


What do you notice about the reverse reaction? The NH_4^+ ion is donating a proton to the OH^- ion, which is accepting it. This means that the NH_4^+ ion is acting as the proton donor, or Brønsted-Lowry acid, while OH^- ion, the proton acceptor, is acting as a Brønsted-Lowry base. The reverse reaction is also a Brønsted-Lowry acid base reaction:



BL base BL acid BL acid BL base

This means that both reactions are acid-base reactions by the Brønsted-Lowry definition. If you consider the species in this chemical reaction, two sets of similar species exist on both sides. Within each set, the two species differ by a proton in their formulas, and one member of the set is a Brønsted-Lowry acid, while the other member is a Brønsted-Lowry base. These sets are marked here:



BL base BL acid BL acid BL base

The two sets—NH_3/NH_4^+ and H_2O/OH^-—are called **conjugate acid-base pairs**. We say that NH_4^+ is the conjugate acid of NH_3, OH^- is the conjugate base of H_2O, and so forth. Every Brønsted-Lowry acid-base reaction can be labeled with two conjugate acid-base pairs.

conjugate acid-base pair

Two species whose formulas differ by only a hydrogen ion.

EXAMPLE 4

Identify the conjugate acid-base pairs in this equilibrium.

$$(CH_3)_3N + H_2O \text{ ? } (CH_3)_3NH^+ + OH^-$$

Solution

One pair is H_2O and OH^-, where H_2O has one more H^+ and is the conjugate acid, while OH^- has one less H^+ and is the conjugate base. The other pair consists of $(CH_3)_3N$ and $(CH_3)_3NH^+$, where $(CH_3)_3NH^+$ is the conjugate acid (it has an additional proton) and $(CH_3)_3N$ is the conjugate base.

Test Yourself

Identify the conjugate acid-base pairs in this equilibrium.

$$NH_2^- + H_2O \text{ ? } NH_3 + OH^-$$

Answer

H_2O (acid) and OH^- (base); NH_2^- (base) and NH_3 (acid)

Chemistry Is Everywhere: Household Acids and Bases

Many household products are acids or bases. For example, the owner of a swimming pool may use muriatic acid to clean the pool. Muriatic acid is another name for HCl(aq). In Chapter 4, Section 5, vinegar was mentioned as a dilute solution of acetic acid [$HC_2H_3O_2$(aq)]. In a medicine chest, one may find a bottle of vitamin C tablets; the chemical name of vitamin C is ascorbic acid ($HC_6H_7O_6$).

One of the more familiar household bases is NH_3, which is found in numerous cleaning products. NH_3 is a base because it increases the OH^- ion concentration by reacting with H_2O:

$$NH_3(aq) + H_2O(\ell) \rightarrow NH_4^+(aq) + OH^-(aq)$$

Many soaps are also slightly basic because they contain compounds that act as Brønsted-Lowry bases, accepting protons from H_2O and forming excess OH^- ions. This is one explanation for why soap solutions are slippery.

Perhaps the most dangerous household chemical is the lye-based drain cleaner. Lye is a common name for NaOH, although it is also used as a synonym for KOH. Lye is an extremely caustic chemical that can react with grease, hair, food particles, and other substances that may build up and clog a water pipe. Unfortunately, lye can also attack body tissues and other substances in our bodies. Thus when we use lye-based drain cleaners, we must be very careful not to touch any of the solid drain cleaner or spill the water it was poured into. Safer, nonlye drain cleaners (like the one in the accompanying figure) use peroxide compounds to react on the materials in the clog and clear the drain.

Drain cleaners can be made from a reactive material that is less caustic than a base.

Source: Photo used by permission of Citrasolv, LLC.

KEY TAKEAWAYS

- A Brønsted-Lowry acid is a proton donor; a Brønsted-Lowry base is a proton acceptor.
- Acid-base reactions include two sets of conjugate acid-base pairs.

EXERCISES

1. Define *Brønsted-Lowry acid*. How does it differ from an Arrhenius acid?
2. Define *Brønsted-Lowry base*. How does it differ from an Arrhenius base?
3. Write the dissociation of hydrogen bromide in water as a Brønsted-Lowry acid-base reaction and identify the proton donor and proton acceptor.
4. Write the dissociation of nitric acid in water as a Brønsted-Lowry acid-base reaction and identify the proton donor and proton acceptor.
5. Pyridine (C_5H_5N) acts as a Brønsted-Lowry base in water. Write the hydrolysis reaction for pyridine and identify the Brønsted-Lowry acid and Brønsted-Lowry base.
6. The methoxide ion (CH_3O^-) acts as a Brønsted-Lowry base in water. Write the hydrolysis reaction for the methoxide ion and identify the Brønsted-Lowry acid and Brønsted-Lowry base.
7. Identify the Brønsted-Lowry acid and Brønsted-Lowry base in this chemical equation.

$$H_3PO_4 + OH^- \rightarrow H_2PO_4^- + H_2O$$

8. Identify the Brønsted-Lowry acid and Brønsted-Lowry base in this chemical equation.

$$H_2C_2O_4 + 2F^- \rightarrow 2HF + C_2O_4^{2-}$$

9. Predict the products of this reaction, assuming it undergoes a Brønsted-Lowry acid-base reaction.

$$HC_2H_3O_2 + C_5H_5N \rightarrow ?$$

10. Predict the products of this reaction, assuming it undergoes a Brønsted-Lowry acid-base reaction.

$$(C_2H_5)_3N + H_2O \rightarrow ?$$

11. What is the conjugate acid of H_2O? of NH_3?

12. What is the conjugate acid of $H_2PO_4^-$? of NO_3^-?
13. What is the conjugate base of HSO_4^-? of H_2O?
14. What is the conjugate base of H_3O^+? of H_2SO_4?
15. Identify the conjugate acid-base pairs in this reaction.

$$HSO_4^- + PO_4^{3-} \rightarrow SO_4^{2-} + HPO_4^{2-}$$

16. Identify the conjugate acid-base pairs in this reaction.

$$HClO_3 + (C_2H_5)_3N \rightarrow ClO_3^- + (C_2H_5)_3NH^+$$

17. Identify the conjugate acid-base pairs in this reaction.

$$NH_3 + C_6H_5O^- \rightarrow C_6H_5OH + NH_2^-$$

18. Identify the conjugate acid-base pairs in this reaction.

$$C_5H_5NH^+ + C_2O_4^{2-} \rightarrow C_5H_5N + HC_2O_4^-$$

ANSWERS

1. A Brønsted-Lowry acid is a proton donor. It does not necessarily increase the H^+ concentration in water.
3. $HBr + H_2O \rightarrow H_3O^+ + Br^-$; PD: HBr; PA: H_2O
5. $C_5H_5N + H_2O \rightarrow C_5H_5NH^+ + OH^-$; PD: H_2O; PA: C_5H_5N
7. BL acid: H_3PO_4; BL base: OH^-
9. $C_2H_3O_2^-$ and $C_5H_5NH^+$
11. H_3O^+; NH_4^+
13. SO_4^{2-}; OH^-
15. HSO_4^- and SO_4^{2-}; PO_4^{3-} and HPO_4^{2-}
17. NH_3 and NH_2^-; $C_6H_5O^-$ and C_6H_5OH

3. ACID-BASE TITRATIONS

LEARNING OBJECTIVES

1. **Describe a titration experiment.**
2. **Explain what an indicator does.**
3. **Perform a titration calculation correctly.**

The reaction of an acid with a base to make a salt and water is a common reaction in the laboratory, partly because so many compounds can act as acids or bases. Another reason that acid-base reactions are so prevalent is because they are often used to determine quantitative amounts of one or the other. Performing chemical reactions quantitatively to determine the exact amount of a reagent is called a **titration**. A titration can be performed with almost any chemical reaction for which the balanced chemical equation is known. Here, we will consider titrations that involve acid-base reactions.

In a titration, one reagent has a known concentration or amount, while the other reagent has an unknown concentration or amount. Typically, the known reagent (the **titrant**) is added to the unknown quantity and is dissolved in solution. The unknown amount of substance (the **analyte**) may or may not be dissolved in solution (but usually is). The titrant is added to the analyte using a precisely calibrated volumetric delivery tube called a burette (also spelled buret; see Figure 12.1). The burette has markings to determine how much volume of solution has been added to the analyte. When the reaction is complete, it is said to be at the **equivalence point**; the number of moles of titrant can be calculated from the concentration and the volume, and the balanced chemical equation can be used to determine the number of moles (and then concentration or mass) of the unknown reactant.

titration

A chemical reaction performed quantitatively to determine the exact amount of a reagent.

titrant

The reagent of known concentration.

analyte

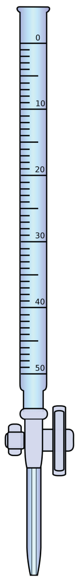
The reagent of unknown concentration.

equivalence point

The point of the reaction when all the analyte has been reacted with the titrant.

FIGURE 12.1
Equipment for Titrations

A burette is a type of liquid dispensing system that can accurately indicate the volume of liquid dispensed.



For example, suppose 25.66 mL (or 0.02566 L) of 0.1078 M HCl was used to titrate an unknown sample of NaOH. What mass of NaOH was in the sample? We can calculate the number of moles of HCl reacted:

$$\#\text{ mol HCl} = (0.02566\text{ L})(0.1078\text{ M}) = 0.002766\text{ mol HCl}$$

We also have the balanced chemical reaction between HCl and NaOH:

$$\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$$

So we can construct a conversion factor to convert to number of moles of NaOH reacted:

$$0.002766\ \cancel{\text{mol HCl}} \times \frac{1\text{ mol NaOH}}{1\ \cancel{\text{mol HCl}}} = 0.002766\text{ mol NaOH}$$

Then we convert this amount to mass, using the molar mass of NaOH (40.00 g/mol):

$$0.002766\ \cancel{\text{mol NaOH}} \times \frac{40.00\text{ g NaOH}}{1\ \cancel{\text{mol NaOH}}} = 0.1106\text{ g NaOH}$$

This is type of calculation is performed as part of a titration.

EXAMPLE 5

What mass of $Ca(OH)_2$ is present in a sample if it is titrated to its equivalence point with 44.02 mL of 0.0885 M HNO_3? The balanced chemical equation is as follows:

$$2\text{HNO}_3 + \text{Ca(OH)}_2 \rightarrow \text{Ca(NO}_3)_2 + 2\text{H}_2\text{O}$$

Solution

In liters, the volume is 0.04402 L. We calculate the number of moles of titrant:

$$\#\text{ moles HNO}_3 = (0.04402\text{ L})(0.0885\text{ M}) = 0.00390\text{ mol HNO}_3$$

Using the balanced chemical equation, we can determine the number of moles of $Ca(OH)_2$ present in the analyte:

$$0.00390\ \cancel{\text{mol HNO}_3} \times \frac{1\text{ mol Ca(OH)}_2}{2\ \cancel{\text{mol HNO}_3}} = 0.00195\text{ mol Ca(OH)}_2$$

Then we convert this to a mass using the molar mass of $Ca(OH)_2$:

$$0.00195\ \cancel{\text{mol Ca(OH)}_2} \times \frac{74.1\text{ g Ca(OH)}_2}{1\ \cancel{\text{mol Ca(OH)}_2}} = 0.144\text{ g Ca(OH)}_2$$

Test Yourself

What mass of $H_2C_2O_4$ is present in a sample if it is titrated to its equivalence point with 18.09 mL of 0.2235 M NaOH? The balanced chemical reaction is as follows:

$$\text{H}_2\text{C}_2\text{O}_4 + 2\text{NaOH} \rightarrow \text{Na}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O}$$

Answer

0.182 g

How does one know if a reaction is at its equivalence point? Usually, the person performing the titration adds a small amount of an **indicator**, a substance that changes color depending on the acidity or basicity of the solution. Because different indicators change colors at different levels of acidity, choosing the correct one is important in performing an accurate titration.

indicator

A substance whose color change indicates the equivalence point of a titration.

KEY TAKEAWAYS

- A titration is the quantitative reaction of an acid and a base.
- Indicators are used to show that all the analyte has reacted with the titrant.

EXERCISES

1. Define *titration*.
2. What is the difference between the titrant and the analyte?
3. True or false: An acid is always the titrant. Explain your answer.
4. True or false: An analyte is always dissolved before reaction. Explain your answer.
5. If 55.60 mL of 0.2221 M HCl was needed to titrate a sample of NaOH to its equivalence point, what mass of NaOH was present?
6. If 16.33 mL of 0.6664 M KOH was needed to titrate a sample of $HC_2H_3O_2$ to its equivalence point, what mass of $HC_2H_3O_2$ was present?
7. It takes 45.66 mL of 0.1126 M HBr to titrate 25.00 mL of $Ca(OH)_2$ to its equivalence point. What is the original concentration of the $Ca(OH)_2$ solution?
8. It takes 9.77 mL of 0.883 M H_2SO_4 to titrate 15.00 mL of KOH to its equivalence point. What is the original concentration of the KOH solution?

ANSWERS

1. a chemical reaction performed in a quantitative fashion
3. False; a base can be a titrant, or the reaction being performed may not even be an acid-base reaction.
5. 0.494 g
7. 0.1028 M

4. STRONG AND WEAK ACIDS AND BASES AND THEIR SALTS

LEARNING OBJECTIVES

1. **Define a strong and a weak acid and base.**
2. **Recognize an acid or a base as strong or weak.**
3. **Determine if a salt produces an acidic or a basic solution.**

Except for their names and formulas, so far we have treated all acids as equals, especially in a chemical reaction. However, acids can be very different in a very important way. Consider HCl(aq). When HCl is dissolved in H_2O, it completely dissociates into H^+(aq) and Cl^-(aq) ions; all the HCl molecules become ions:

$$HCl \xrightarrow{100\%} H^+(aq) + Cl^-(aq)$$

Any acid that dissociates 100% into ions is called a **strong acid**. If it does not dissociate 100%, it is a **weak acid**. $HC_2H_3O_2$ is an example of a weak acid:

$$HC_2H_3O_2 \xrightarrow{\sim 5\%} H^+(aq) + C_2H_3O_2^-(aq)$$

Because this reaction does not go 100% to completion, it is more appropriate to write it as an equilibrium:

$$HC_2H_3O_2 \; ? \; H^+(aq) + C_2H_3O_2^-(aq)$$

strong acid

Any acid that is 100% dissociated into ions in aqueous solution.

weak acid

Any acid that is less than 100% dissociated into ions in aqueous solution.

strong base

Any base that is 100% dissociated into ions in aqueous solution.

weak base

Any base that is less than 100% dissociated into ions in aqueous solution.

As it turns out, there are very few strong acids, which are given in Table 12.2. If an acid is not listed here, it is a weak acid. It may be 1% ionized or 99% ionized, but it is still classified as a weak acid.

The issue is similar with bases: a **strong base** is a base that is 100% ionized in solution. If it is less than 100% ionized in solution, it is a **weak base**. There are very few strong bases (see Table 12.2); any base not listed is a weak base. All strong bases are OH^- compounds. So a base based on some other mechanism, such as NH_3 (which does not contain OH^- ions as part of its formula), will be a weak base.

TABLE 12.2 Strong Acids and Bases

Acids	Bases
HCl	LiOH
HBr	NaOH
HI	KOH
HNO_3	RbOH
H_2SO_4	CsOH
$HClO_3$	$Mg(OH)_2$
$HClO_4$	$Ca(OH)_2$
	$Sr(OH)_2$
	$Ba(OH)_2$

EXAMPLE 6

Identify each acid or base as strong or weak.

1. HCl
2. $Mg(OH)_2$
3. C_5H_5N

Solution

1. Because HCl is listed in Table 12.2, it is a strong acid.
2. Because $Mg(OH)_2$ is listed in Table 12.2, it is a strong base.
3. The nitrogen in C_5H_5N would act as a proton acceptor and therefore can be considered a base, but because it does not contain an OH compound, it cannot be considered a strong base; it is a weak base.

Test Yourself

Identify each acid or base as strong or weak.

1. RbOH
2. HNO_2

Answers

1. strong base
2. weak acid

EXAMPLE 7

Write the balanced chemical equation for the dissociation of $Ca(OH)_2$ and indicate whether it proceeds 100% to products or not.

Solution

This is an ionic compound of Ca^{2+} ions and OH^- ions. When an ionic compound dissolves, it separates into its constituent ions:

$$Ca(OH)_2 \rightarrow Ca^{2+}(aq) + 2OH^-(aq)$$

Because $Ca(OH)_2$ is listed in Table 12.2, this reaction proceeds 100% to products.

Test Yourself

Write the balanced chemical equation for the dissociation of hydrazoic acid (HN_3) and indicate whether it proceeds 100% to products or not.

Answer

The reaction is as follows:

$$HN_3 \rightarrow H^+(aq) + N_3^-(aq)$$

It does not proceed 100% to products because hydrazoic acid is not a strong acid.

Certain salts will also affect the acidity or basicity of aqueous solutions because some of the ions will undergo hydrolysis, just like NH_3 does to make a basic solution. The general rule is that salts with ions that are part of strong acids or bases will not hydrolyze, while salts with ions that are part of weak acids or bases will hydrolyze.

Consider NaCl. When it dissolves in an aqueous solution, it separates into Na^+ ions and Cl^- ions:

$$NaCl \rightarrow Na^+(aq) + Cl^-(aq)$$

Will the $Na^+(aq)$ ion hydrolyze? If it does, it will interact with the OH^- ion to make NaOH:

$$Na^+(aq) + H_2O \rightarrow NaOH + H^+(aq)$$

However, NaOH is a strong base, which means that it is 100% ionized in solution:

$$NaOH \rightarrow Na^+(aq) + OH^-(aq)$$

The free $OH^-(aq)$ ion reacts with the $H^+(aq)$ ion to remake a water molecule:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O$$

The net result? There is no change, so there is no effect on the acidity or basicity of the solution from the $Na^+(aq)$ ion. What about the Cl^- ion? Will it hydrolyze? If it does, it will take an H^+ ion from a water molecule:

$$Cl^-(aq) + H_2O \rightarrow HCl + OH^-$$

However, HCl is a strong acid, which means that it is 100% ionized in solution:

$$HCl \rightarrow H^+(aq) + Cl^-(aq)$$

The free $H^+(aq)$ ion reacts with the $OH^-(aq)$ ion to remake a water molecule:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O$$

The net result? There is no change, so there is no effect on the acidity or basicity of the solution from the $Cl^-(aq)$ ion. Because neither ion in NaCl affects the acidity or basicity of the solution, NaCl is an example of a **neutral salt**.

neutral salt

An ionic compound that does not affect the acidity of its aqueous solution.

Things change, however, when we consider a salt like $NaC_2H_3O_2$. We already know that the Na^+ ion won't affect the acidity of the solution. What about the acetate ion? If it hydrolyzes, it will take an H^+ from a water molecule:

$$C_2H_3O_2^-(aq) + H_2O \rightarrow HC_2H_3O_2 + OH^-(aq)$$

basic salt

An ionic compound whose aqueous solution is slightly basic.

acid salt

An ionic compound whose aqueous solution is slightly acidic.

Does this happen? Yes, it does. Why? *Because $HC_2H_3O_2$ is a weak acid.* Any chance a weak acid has to form, it will (the same with a weak base). As some $C_2H_3O_2^-$ ions hydrolyze with H_2O to make the molecular weak acid, OH^- ions are produced. OH^- ions make solutions basic. Thus $NaC_2H_3O_2$ solutions are slightly basic, so such a salt is called a **basic salt**.

There are also salts whose aqueous solutions are slightly acidic. NH_4Cl is an example. When NH_4Cl is dissolved in H_2O, it separates into NH_4^+ ions and Cl^- ions. We have already seen that the Cl^- ion does not hydrolyze. However, the NH_4^+ ion will:

$$NH_4^+(aq) + H_2O \rightarrow NH_3(aq) + H_3O^+(aq)$$

Recall from Section 1 that H_3O^+ ion is the hydronium ion, the more chemically proper way to represent the H^+ ion. This is the classic acid species in solution, so a solution of $NH_4^+(aq)$ ions is slightly acidic. NH_4Cl is an example of an **acid salt**. The molecule NH_3 is a weak base, and it will form when it can, just like a weak acid will form when it can.

So there are two general rules: (1) If an ion derives from a strong acid or base, it will not affect the acidity of the solution. (2) If an ion derives from a weak acid, it will make the solution basic; if an ion derives from a weak base, it will make the solution acidic.

EXAMPLE 8

Identify each salt as acidic, basic, or neutral.

1. KCl
2. KNO_2
3. NH_4Br

Solution

1. The ions from KCl derive from a strong acid (HCl) and a strong base (KOH). Therefore, neither ion will affect the acidity of the solution, so KCl is a neutral salt.
2. Although the K^+ ion derives from a strong base (KOH), the NO_2^- ion derives from a weak acid (HNO_2). Therefore the solution will be basic, and KNO_2 is a basic salt.
3. Although the Br^- ions derive from a strong acid (HBr), the NH_4^+ ion derives from a weak base (NH_3), so the solution will be acidic, and NH_4Br is an acidic salt.

Test Yourself

Identify each salt as acidic, basic, or neutral.

1. $(C_5H_5NH)Cl$
2. Na_2SO_3

Answers

1. acidic
2. basic

Some salts are composed of ions that come from both weak acids and weak bases. The overall effect on an aqueous solution depends on which ion exerts more influence on the overall acidity. We will not consider such salts here.

KEY TAKEAWAYS

- Strong acids and bases are 100% ionized in aqueous solution.
- Weak acids and bases are less than 100% ionized in aqueous solution.
- Salts of weak acids or bases can affect the acidity or basicity of their aqueous solutions.

EXERCISES

1. Differentiate between a strong acid and a weak acid.
2. Differentiate between a strong base and a weak base.

3. Identify each as a strong acid or a weak acid. Assume aqueous solutions.
   a. HF
   b. HCl
   c. HC_2O_4
4. Identify each as a strong base or a weak base. Assume aqueous solutions.
   a. NaOH
   b. $Al(OH)_3$
   c. $C_4H_9NH_2$
5. Write a chemical equation for the ionization of each acid and indicate whether it proceeds 100% to products or not.
   a. HNO_3
   b. HNO_2
   c. HI_3
6. Write a chemical equation for the ionization of each base and indicate whether it proceeds 100% to products or not.
   a. NH_3
   b. $(CH_3)_3N$
   c. $Mg(OH)_2$
7. Write the balanced chemical equation for the reaction of each acid and base pair.
   a. $HCl + C_5H_5N$
   b. $H_2C_2O_4 + NH_3$
   c. $HNO_2 + C_7H_9N$
8. Write the balanced chemical equation for the reaction of each acid and base pair.
   a. $H_3C_5H_5O_7 + Mg(OH)_2$
   b. $HC_3H_3O_3 + (CH_3)_3N$
   c. $HBr + Fe(OH)_3$
9. Identify each salt as neutral, acidic, or basic.
   a. NaBr
   b. $Fe(NO_3)_2$
   c. $Fe(NO_3)_3$
10. Identify each salt as neutral, acidic, or basic.
    a. NH_4I
    b. $C_2H_5NH_3Cl$
    c. KI
11. Identify each salt as neutral, acidic, or basic.
    a. $NaNO_2$
    b. $NaNO_3$
    c. NH_4NO_3
12. Identify each salt as neutral, acidic, or basic.
    a. $KC_2H_3O_2$
    b. $KHSO_4$
    c. $KClO_3$
13. Write the hydrolysis reaction that occurs, if any, when each salt dissolves in water.
    a. K_2SO_3
    b. KI
    c. NH_4ClO_3
14. Write the hydrolysis reaction that occurs, if any, when each salt dissolves in water.
    a. $NaNO_3$
    b. CaC_2O_4
    c. C_5H_5NHCl
15. When NH_4NO_2 dissolves in H_2O, both ions hydrolyze. Write chemical equations for both reactions. Can you tell if the solution will be acidic or basic overall?
16. When pyridinium acetate ($C_5H_5NHC_2H_3O_2$) dissolves in H_2O, both ions hydrolyze. Write chemical equations for both reactions. Can you tell if the solution will be acidic or basic overall?
17. A lab technician mixes a solution of 0.015 M $Mg(OH)_2$. Is the resulting OH^- concentration greater than, equal to, or less than 0.015 M? Explain your answer.
18. A lab technician mixes a solution of 0.55 M HNO_3. Is the resulting H^+ concentration greater than, equal to, or less than 0.55 M? Explain your answer.

ANSWERS

1. A strong acid is 100% ionized in aqueous solution, whereas a weak acid is not 100% ionized.
3. a. weak acid
   b. strong acid
   c. weak acid
5. a. $HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq)$; proceeds 100%
   b. $HNO_2(aq) \rightarrow H^+(aq) + NO_2^-(aq)$; does not proceed 100%
   c. $HI_3(aq) \rightarrow H^+(aq) + I_3^-(aq)$; does not proceed 100%
7. a. $HCl + C_5H_5N \rightarrow Cl^- + C_5H_5NH^+$
   b. $H_2C_2O_4 + 2NH_3 \rightarrow C_2O_4^{2-} + 2NH_4^+$
   c. $HNO_2 + C_7H_9N \rightarrow NO_2^- + C_7H_9NH^+$
9. a. neutral
   b. acidic
   c. acidic
11. a. basic
    b. neutral
    c. acidic
13. a. $SO_3^{2-} + H_2O \rightarrow HSO_3^- + OH^-$
    b. no reaction
    c. $NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$

15. $NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$; $NO_2^- + H_2O \rightarrow HNO_2 + OH^-$; it is not possible to determine whether the solution will be acidic or basic.

17. greater than 0.015 M because there are two OH^- ions per formula unit of $Mg(OH)_2$

5. AUTOIONIZATION OF WATER

LEARNING OBJECTIVES

1. **Describe the autoionization of water.**
2. **Calculate the concentrations of H^+ and OH^- in solutions, knowing the other concentration.**

We have already seen that H_2O can act as an acid or a base:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \text{ (}H_2O\text{ acts as an acid)}$$

$$HCl + H_2O \rightarrow H_3O^+ + Cl^- \text{ (}H_2O\text{ acts as a base)}$$

It may not surprise you to learn, then, that within any given sample of water, some H_2O molecules are acting as acids, and other H_2O molecules are acting as bases. The chemical equation is as follows:

$$H_2O + H_2O \rightarrow H_3O^+ + OH^-$$

autoionization of water

Water molecules act as acids (proton donors) and bases (proton acceptors) with each other to a tiny extent in all aqueous solutions.

This occurs only to a very small degree: only about 6 in 10^8 H_2O molecules are participating in this process, which is called the **autoionization of water**. At this level, the concentration of both H^+(aq) and OH^-(aq) in a sample of pure H_2O is about 1.0×10^{-7} M. If we use square brackets—[ ]—around a dissolved species to imply the molar concentration of that species, we have

$$[H^+] = [OH^-] = 1.0 \times 10^{-7} \text{ M}$$

for *any* sample of pure water because H_2O can act as both an acid and a base. The product of these two concentrations is 1.0×10^{-14}:

$$[H^+] \times [OH^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

In acids, the concentration of H^+(aq)—$[H^+]$—is greater than 1.0×10^{-7} M, while for bases the concentration of OH^-(aq)—$[OH^-]$—is greater than 1.0×10^{-7} M. However, the *product* of the two concentrations—$[H^+][OH^-]$—is *always* equal to 1.0×10^{-14}, no matter whether the aqueous solution is an acid, a base, or neutral:

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

autoionization constant of water

The product of the hydrogen ion and hydroxide ion concentrations.

This value of the product of concentrations is so important for aqueous solutions that it is called the **autoionization constant of water** and is denoted K_w:

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

This means that if you know $[H^+]$ for a solution, you can calculate what $[OH^-]$ has to be for the product to equal 1.0×10^{-14}, or if you know $[OH^-]$, you can calculate $[H^+]$. This also implies that as one concentration goes up, the other must go down to compensate so that their product always equals the value of K_w.

EXAMPLE 9

What is $[OH^-]$ of an aqueous solution if $[H^+]$ is 1.0×10^{-4} M?

Solution

Using the expression and known value for K_W,

$$K_W = [H^+][OH^-] = 1.0 \times 10^{-14} = (1.0 \times 10^{-4})[OH^-]$$

We solve by dividing both sides of the equation by 1.0×10^{-4}:

$$[OH^-] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-4}} = 1.0 \times 10^{-10}\ M$$

It is assumed that the concentration unit is molarity, so $[OH^-]$ is 1.0×10^{-10} M.

Test Yourself

What is $[H^+]$ of an aqueous solution if $[OH^-]$ is 1.0×10^{-9} M?

Answer

1.0×10^{-5} M

When you have a solution of a particular acid or base, you need to look at the formula of the acid or base to determine the number of H^+ or OH^- ions in the formula unit because $[H^+]$ or $[OH^-]$ may not be the same as the concentration of the acid or base itself.

EXAMPLE 10

What is $[H^+]$ in a 0.0044 M solution of $Ca(OH)_2$?

Solution

We begin by determining $[OH^-]$. The concentration of the solute is 0.0044 M, but because $Ca(OH)_2$ is a strong base, there are two OH^- ions in solution for every formula unit dissolved, so the actual $[OH^-]$ is two times this, or 2×0.0044 M = 0.0088 M. Now we can use the K_W expression:

$$[H^+][OH^-] = 1.0 \times 10^{-14} = [H^+](0.0088\ M)$$

Dividing both sides by 0.0088:

$$[H^+] = \frac{1.0 \times 10^{-14}}{(0.0088)} = 1.1 \times 10^{-12}\ M$$

$[H^+]$ has decreased significantly in this basic solution.

Test Yourself

What is $[OH^-]$ in a 0.00032 M solution of H_2SO_4? (Hint: assume both H^+ ions ionize.)

Answer

1.6×10^{-11} M

For strong acids and bases, $[H^+]$ and $[OH^-]$ can be determined directly from the concentration of the acid or base itself because these ions are 100% ionized by definition. However, for weak acids and bases, this is not so. The degree, or percentage, of ionization would need to be known before we can determine $[H^+]$ and $[OH^-]$.

EXAMPLE 11

A 0.0788 M solution of $HC_2H_3O_2$ is 3.0% ionized into H^+ ions and $C_2H_3O_2^-$ ions. What are $[H^+]$ and $[OH^-]$ for this solution?

Solution

Because the acid is only 3.0% ionized, we can determine $[H^+]$ from the concentration of the acid. Recall that 3.0% is 0.030 in decimal form:

$$[H^+] = 0.030 \times 0.0788 = 0.00236 \text{ M}$$

With this $[H^+]$, then $[OH^-]$ can be calculated as follows:

$$[OH^-] = \frac{1.0 \times 10^{-14}}{0.00236} = 4.2 \times 10^{-12} \text{ M}$$

This is about 30 times higher than would be expected for a strong acid of the same concentration.

Test Yourself

A 0.0222 M solution of pyridine (C_5H_5N) is 0.44% ionized into pyridinium ions ($C_5H_5NH^+$) and OH^- ions. What are $[OH^-]$ and $[H^+]$ for this solution?

Answer

$[OH^-] = 9.77 \times 10^{-5}$ M; $[H^+] = 1.02 \times 10^{-10}$ M

KEY TAKEAWAY

- In any aqueous solution, the product of $[H^+]$ and $[OH^-]$ equals 1.0×10^{-14}.

EXERCISES

1. Does $[H^+]$ remain constant in all aqueous solutions? Why or why not?
2. Does $[OH^-]$ remain constant in all aqueous solutions? Why or why not?
3. What is the relationship between $[H^+]$ and K_W? Write a mathematical expression that relates them.
4. What is the relationship between $[OH^-]$ and K_W? Write a mathematical expression that relates them.
5. Write the chemical equation for the autoionization of water and label the conjugate acid-base pairs.
6. Write the reverse of the reaction for the autoionization of water. It is still an acid-base reaction? If so, label the acid and base.
7. For a given aqueous solution, if $[H^+] = 1.0 \times 10^{-3}$ M, what is $[OH^-]$?
8. For a given aqueous solution, if $[H^+] = 1.0 \times 10^{-9}$ M, what is $[OH^-]$?
9. For a given aqueous solution, if $[H^+] = 7.92 \times 10^{-5}$ M, what is $[OH^-]$?
10. For a given aqueous solution, if $[H^+] = 2.07 \times 10^{-11}$ M, what is $[H^+]$?
11. For a given aqueous solution, if $[OH^-] = 1.0 \times 10^{-5}$ M, what is $[H^+]$?
12. For a given aqueous solution, if $[OH^-] = 1.0 \times 10^{-12}$ M, what is $[H^+]$?
13. For a given aqueous solution, if $[OH^-] = 3.77 \times 10^{-4}$ M, what is $[H^+]$?
14. For a given aqueous solution, if $[OH^-] = 7.11 \times 10^{-10}$ M, what is $[H^+]$?
15. What are $[H^+]$ and $[OH^-]$ in a 0.344 M solution of HNO_3?
16. What are $[H^+]$ and $[OH^-]$ in a 2.86 M solution of HBr?
17. What are $[H^+]$ and $[OH^-]$ in a 0.00338 M solution of KOH?
18. What are $[H^+]$ and $[OH^-]$ in a 6.02×10^{-4} M solution of $Ca(OH)_2$?
19. If HNO_2 is dissociated only to an extent of 0.445%, what are $[H^+]$ and $[OH^-]$ in a 0.307 M solution of HNO_2?
20. If $(C_2H_5)_2NH$ is dissociated only to an extent of 0.077%, what are $[H^+]$ and $[OH^-]$ in a 0.0955 M solution of $(C_2H_5)_2NH$?

ANSWERS

1. $[H^+]$ varies with the amount of acid or base in a solution.
3. $[H^+] = \frac{K_w}{[OH^-]}$
5. $H_2O + H_2O \rightarrow H_3O^+ + OH^-$; H_2O/H_3O^+ and H_2O/OH^-
7. 1.0×10^{-11} M
9. 1.26×10^{-10} M
11. 1.0×10^{-9} M
13. 2.65×10^{-11} M
15. $[H^+] = 0.344$ M; $[OH^-] = 2.91 \times 10^{-14}$ M
17. $[OH^-] = 0.00338$ M; $[H^+] = 2.96 \times 10^{-12}$ M
19. $[H^+] = 0.00137$ M; $[OH^-] = 7.32 \times 10^{-12}$ M

6. THE PH SCALE

LEARNING OBJECTIVES

1. **Define *pH*.**
2. **Determine the pH of acidic and basic solutions.**

As we have seen, $[H^+]$ and $[OH^-]$ values can be markedly different from one aqueous solution to another. So chemists defined a new scale that succinctly indicates the concentrations of either of these two ions.

pH is a logarithmic function of $[H^+]$:

$$pH = -\log[H^+]$$

pH is usually (but not always) between 0 and 14. Knowing the dependence of pH on $[H^+]$, we can summarize as follows:

- If $pH < 7$, then the solution is acidic.
- If $pH = 7$, then the solution is neutral.
- If $pH > 7$, then the solution is basic.

This is known as the **pH scale**. You can use pH to make a quick determination whether a given aqueous solution is acidic, basic, or neutral.

pH

The negative logarithm of the hydrogen ion concentration.

pH scale

The range of values from 0 to 14 that describes the acidity or basicity of a solution.

EXAMPLE 12

Label each solution as acidic, basic, or neutral based only on the stated pH.

1. milk of magnesia, pH = 10.5
2. pure water, pH = 7
3. wine, pH = 3.0

Solution

1. With a pH greater than 7, milk of magnesia is basic. (Milk of magnesia is largely $Mg(OH)_2$.)
2. Pure water, with a pH of 7, is neutral.
3. With a pH of less than 7, wine is acidic.

Test Yourself

Identify each substance as acidic, basic, or neutral based only on the stated pH.

1. human blood, pH = 7.4
2. household ammonia, pH = 11.0
3. cherries, pH = 3.6

Answers

1. basic
2. basic
3. acidic

Table 12.3 gives the typical pH values of some common substances. Note that several food items are on the list, and most of them are acidic.

TABLE 12.3 Typical pH Values of Various Substances*

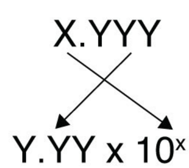
Substance	pH
stomach acid	1.7
lemon juice	2.2
vinegar	2.9
soda	3.0
wine	3.5
coffee, black	5.0
milk	6.9
pure water	7.0
blood	7.4
seawater	8.5
milk of magnesia	10.5
ammonia solution	12.5
1.0 M NaOH	14.0
***Actual values may vary depending on conditions.**	

pH is a *logarithmic* scale. A solution that has a pH of 1.0 has 10 times the $[H^+]$ as a solution with a pH of 2.0, which in turn has 10 times the $[H^+]$ as a solution with a pH of 3.0 and so forth.

Using the definition of pH, it is also possible to calculate $[H^+]$ (and $[OH^-]$) from pH and vice versa. The general formula for determining $[H^+]$ from pH is as follows:

$$[H^+] = 10^{-pH}$$

You need to determine how to evaluate the above expression on your calculator. Ask your instructor if you have any questions. The other issue that concerns us here is significant figures. Because the number(s) before the decimal point in a logarithm relate to the power on 10, the number of digits *after* the decimal point is what determines the number of significant figures in the final answer:



EXAMPLE 13

What are $[H^+]$ and $[OH^-]$ for an aqueous solution whose pH is 4.88?

Solution

We need to evaluate the expression

$$[H^+] = 10^{-4.88}$$

Depending on the calculator you use, the method for solving this problem will vary. In some cases, the "−4.88" is entered and a "10^X" key is pressed; for other calculators, the sequence of keystrokes is reversed. In any case, the correct numerical answer is as follows:

$$[H^+] = 1.3 \times 10^{-5}\ M$$

Because 4.88 has two digits after the decimal point, $[H^+]$ is limited to two significant figures. From this, $[OH^-]$ can be determined:

$$[OH^-] = \frac{1 \times 10^{-14}}{1.3 \times 10^{-5}} = 7.7 \times 10^{-10}\ M$$

Test Yourself

What are $[H^+]$ and $[OH^-]$ for an aqueous solution whose pH is 10.36?

Answer

$[H^+] = 4.4 \times 10^{-11}$ M; $[OH^-] = 2.3 \times 10^{-4}$ M

There is an easier way to relate $[H^+]$ and $[OH^-]$. We can also define **pOH** similar to pH:

pOH

The negative logarithm of the hydroxide ion concentration.

$$pOH = -\log[OH^-]$$

(In fact, p"anything" is defined as the negative logarithm of that anything.) This also implies that

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

A simple and useful relationship is that for any aqueous solution,

$$pH + pOH = 14$$

This relationship makes it simple to determine pH from pOH or pOH from pH and then calculate the resulting ion concentration.

EXAMPLE 14

The pH of a solution is 8.22. What are pOH, $[H^+]$, and $[OH^-]$?

Solution

Because the sum of pH and pOH equals 14, we have

$$8.22 + \text{pOH} = 14$$

Subtracting 8.22 from 14, we get

$$\text{pOH} = 5.78$$

Now we evaluate the following two expressions:

$$[H^+] = 10^{-8.22}$$

$$[OH^-] = 10^{-5.78}$$

So

$$[H^+] = 6.0 \times 10^{-9}\ M$$

$$[OH^-] = 1.7 \times 10^{-6}\ M$$

Test Yourself

The pOH of a solution is 12.04. What are pH, $[H^+]$, and $[OH^-]$?

Answer

pH = 1.96; $[H^+] = 1.1 \times 10^{-2}$ M; $[OH^-] = 9.1 \times 10^{-13}$ M

KEY TAKEAWAYS

- pH is a logarithmic function of $[H^+]$.
- $[H^+]$ can be calculated directly from pH.
- pOH is related to pH and can be easily calculated from pH.

EXERCISES

1. Define *pH*. How is it related to pOH?
2. Define *pOH*. How is it related to pH?
3. What is the pH range for an acidic solution?
4. What is the pH range for a basic solution?
5. What is $[H^+]$ for a neutral solution?
6. What is $[OH^-]$ for a neutral solution? Compare your answer to Exercise 6. Does this make sense?
7. Which substances in Table 12.3 are acidic?
8. Which substances in Table 12.3 are basic?
9. What is the pH of a solution when $[H^+]$ is 3.44×10^{-4} M?
10. What is the pH of a solution when $[H^+]$ is 9.04×10^{-13} M?
11. What is the pH of a solution when $[OH^-]$ is 6.22×10^{-7} M?
12. What is the pH of a solution when $[OH^-]$ is 0.0222 M?
13. What is the pOH of a solution when $[H^+]$ is 3.44×10^{-4} M?
14. What is the pOH of a solution when $[H^+]$ is 9.04×10^{-13} M?
15. What is the pOH of a solution when $[OH^-]$ is 6.22×10^{-7} M?
16. What is the pOH of a solution when $[OH^-]$ is 0.0222 M?
17. If a solution has a pH of 0.77, what is its pOH, $[H^+]$, and $[OH^-]$?
18. If a solution has a pOH of 13.09, what is its pH, $[H^+]$, and $[OH^-]$?

ANSWERS

1. pH is the negative logarithm of $[H^+]$ and is equal to 14 – pOH.
3. pH < 7
5. 1.0×10^{-7} M
7. Every entry above pure water is acidic.
9. 3.46
11. 7.79
13. 10.54
15. 6.21
17. pOH = 13.23; $[H^+] = 1.70 \times 10^{-1}$ M; $[OH^-] = 5.89 \times 10^{-14}$ M

7. BUFFERS

LEARNING OBJECTIVES

1. **Define *buffer*.**
2. **Correctly identify the two components of a buffer.**

As indicated in Section 4, weak acids are relatively common, even in the foods we eat. But we occasionally encounter a strong acid or base, such as stomach acid, which has a strongly acidic pH of 1.7. By definition, strong acids and bases can produce a relatively large amount of H^+ or OH^- ions and consequently have marked chemical activities. In addition, very small amounts of strong acids and bases can change the pH of a solution very quickly. If 1 mL of stomach acid [approximated as 0.1 M HCl(aq)] were added to the bloodstream and no correcting mechanism were present, the pH of the blood would decrease from about 7.4 to about 4.7—a pH that is not conducive to continued living. Fortunately, the body has a mechanism for minimizing such dramatic pH changes.

The mechanism involves a **buffer**, a solution that resists dramatic changes in pH. Buffers do so by being composed of certain pairs of solutes: either a weak acid plus a salt derived from that weak acid or a weak base plus a salt of that weak base. For example, a buffer can be composed of dissolved $HC_2H_3O_2$ (a weak acid) and $NaC_2H_3O_2$ (the salt derived from that weak acid). Another example of a buffer is a solution containing NH_3 (a weak base) and NH_4Cl (a salt derived from that weak base).

buffer

A solution that resists dramatic changes in pH.

Let us use an $HC_2H_3O_2/NaC_2H_3O_2$ buffer to demonstrate how buffers work. If a strong base—a source of $OH^-(aq)$ ions—is added to the buffer solution, those OH^- ions will react with the $HC_2H_3O_2$ in an acid-base reaction:

$$HC_2H_3O_2(aq) + OH^-(aq) \rightarrow H_2O(\ell) + C_2H_3O_2^-(aq)$$

Rather than changing the pH dramatically by making the solution basic, the added OH^- ions react to make H_2O, so the pH does not change much.

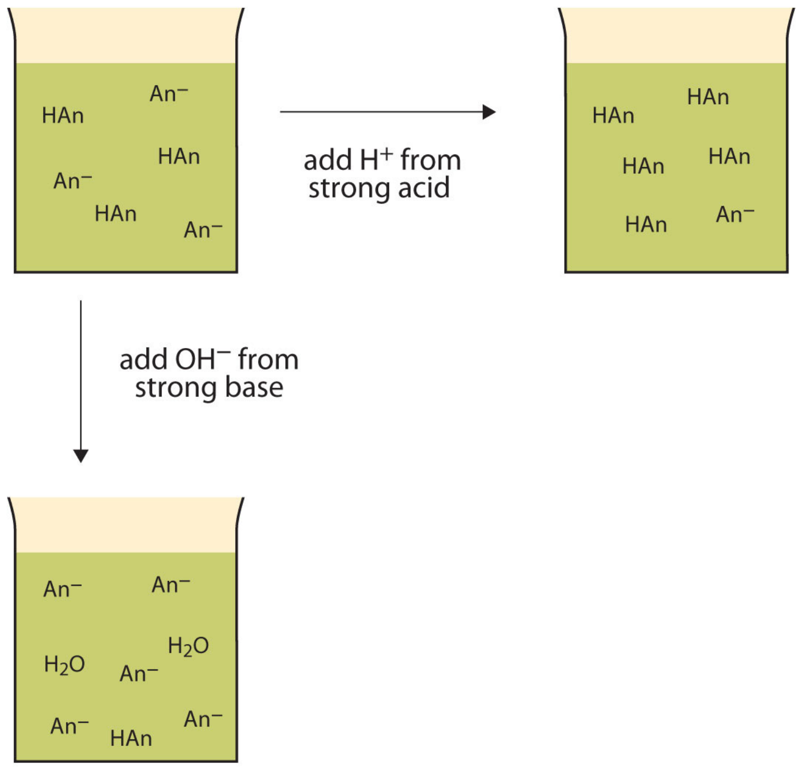
If a strong acid—a source of H^+ ions—is added to the buffer solution, the H^+ ions will react with the anion from the salt. Because $HC_2H_3O_2$ is a weak acid, it is not ionized much. This means that if lots of H^+ ions and $C_2H_3O_2^-$ ions are present in the same solution, they will come together to make $HC_2H_3O_2$:

$$H^+(aq) + C_2H_3O_2^-(aq) \rightarrow HC_2H_3O_2(aq)$$

Rather than changing the pH dramatically and making the solution acidic, the added H^+ ions react to make molecules of a weak acid. Figure 12.2 illustrates both actions of a buffer.

FIGURE 12.2 The Actions of Buffers

Buffers can react with both strong acids (top) and strong bases (side) to minimize large changes in pH.



Buffers made from weak bases and salts of weak bases act similarly. For example, in a buffer containing NH_3 and NH_4Cl, NH_3 molecules can react with any excess H^+ ions introduced by strong acids:

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

while the $NH_4^+(aq)$ ion can react with any OH^- ions introduced by strong bases:

$$NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(aq) + H_2O(\ell)$$

EXAMPLE 15

Which combinations of compounds can make a buffer solution?

1. $HCHO_2$ and $NaCHO_2$
2. HCl and NaCl
3. CH_3NH_2 and CH_3NH_3Cl
4. NH_3 and NaOH

Solution

1. $HCHO_2$ is formic acid, a weak acid, while $NaCHO_2$ is the salt made from the anion of the weak acid (the formate ion [CHO_2^-]). The combination of these two solutes would make a buffer solution.
2. HCl is a strong acid, not a weak acid, so the combination of these two solutes would not make a buffer solution.
3. CH_3NH_2 is methylamine, which is like NH_3 with one of its H atoms substituted with a CH_3 group. Because it is not listed in Table 12.2, we can assume that it is a weak base. The compound CH_3NH_3Cl is a salt made from that weak base, so the combination of these two solutes would make a buffer solution.
4. NH_3 is a weak base, but NaOH is a strong base. The combination of these two solutes would not make a buffer solution.

Test Yourself

Which combinations of compounds can make a buffer solution?

1. $NaHCO_3$ and NaCl
2. H_3PO_4 and NaH_2PO_4
3. NH_3 and $(NH_4)_3PO_4$
4. NaOH and NaCl

Answers

1. no
2. yes
3. yes
4. no

Buffers work well only for limited amounts of added strong acid or base. Once either solute is completely reacted, the solution is no longer a buffer, and rapid changes in pH may occur. We say that a buffer has a certain **capacity**. Buffers that have more solute dissolved in them to start with have larger capacities, as might be expected.

capacity

The amount of strong acid or base a buffer can counteract.

Human blood has a buffering system to minimize extreme changes in pH. One buffer in blood is based on the presence of HCO_3^- and H_2CO_3 [the second compound is another way to write $CO_2(aq)$]. With this buffer present, even if some stomach acid were to find its way directly into the bloodstream, the change in the pH of blood would be minimal. Inside many of the body's cells, there is a buffering system based on phosphate ions.

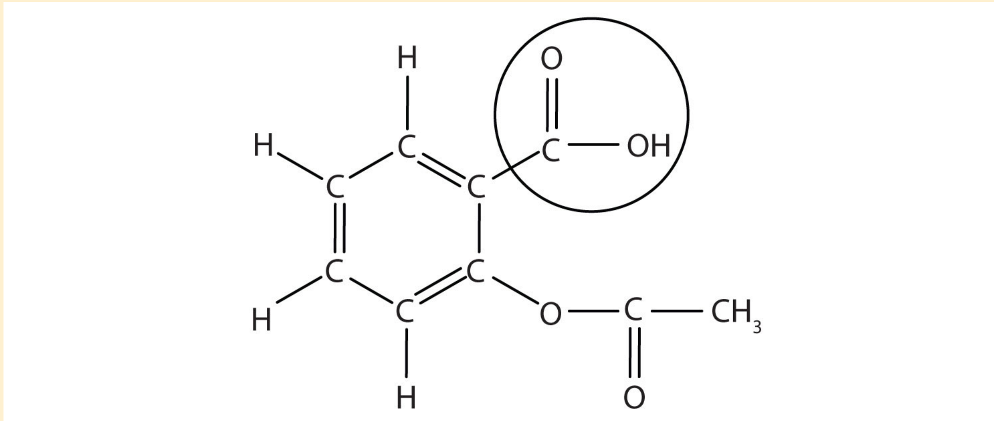
Food and Drink App: The Acid That Eases Pain

Although medicines are not exactly "food and drink," we do ingest them, so let's take a look at an acid that is probably the most common medicine: acetylsalicylic acid, also known as aspirin. Aspirin is well known as a pain reliever and antipyretic (fever reducer).

The structure of aspirin is shown in the accompanying figure. The acid part is circled; it is the H atom in that part that can be donated as aspirin acts as a Brønsted-Lowry acid. Because it is not given in Table 12.2, acetylsalicylic acid is a weak acid. However, it is still an acid, and given that some people consume relatively large amounts of aspirin daily, its acidic nature can cause problems in the stomach lining, despite the stomach's defenses against its own stomach acid.

The Molecular Structure of Aspirin

The circled atoms are the acid part of the molecule.



Because the acid properties of aspirin may be problematic, many aspirin brands offer a "buffered aspirin" form of the medicine. In these cases, the aspirin also contains a buffering agent—usually MgO—that regulates the acidity of the aspirin to minimize its acidic side effects.

As useful and common as aspirin is, it was formally marketed as a drug starting in 1899. The US Food and Drug Administration (FDA), the governmental agency charged with overseeing and approving drugs in the United States, wasn't formed until 1906. Some have argued that if the FDA had been formed before aspirin was introduced, aspirin may never have gotten approval due to its potential for side effects—gastrointestinal bleeding, ringing in the ears, Reye's syndrome (a liver problem), and some allergic reactions. However, recently aspirin has been touted for its effects in lessening heart attacks and strokes, so it is likely that aspirin is here to stay.

KEY TAKEAWAY

- A buffer is a solution that resists sudden changes in pH.

EXERCISES

1. Define *buffer*. What two related chemical components are required to make a buffer?
2. Can a buffer be made by combining a strong acid with a strong base? Why or why not?
3. Which combinations of compounds can make a buffer? Assume aqueous solutions.
   a. HCl and NaCl
   b. HNO_2 and $NaNO_2$
   c. NH_4NO_3 and HNO_3
   d. NH_4NO_3 and NH_3
4. Which combinations of compounds can make a buffer? Assume aqueous solutions.
   a. H_3PO_4 and Na_3PO_4
   b. $NaHCO_3$ and Na_2CO_3
   c. $NaNO_3$ and $Ca(NO_3)_2$
   d. HN_3 and NH_3
5. For each combination in Exercise 3 that is a buffer, write the chemical equations for the reactions of the buffer components when a strong acid and a strong base is added.
6. For each combination in Exercise 4 that is a buffer, write the chemical equations for the reactions of the buffer components when a strong acid and a strong base is added.
7. The complete phosphate buffer system is based on four substances: H_3PO_4, $H_2PO_4^{-}$, HPO_4^{2-}, and PO_4^{3-}. What different buffer solutions can be made from these substances?
8. Explain why NaBr cannot be a component in either an acidic or a basic buffer.
9. Two solutions are made containing the same concentrations of solutes. One solution is composed of H_3PO_4 and Na_3PO_4, while the other is composed of HCN and NaCN. Which solution should have the larger capacity as a buffer?

10. Two solutions are made containing the same concentrations of solutes. One solution is composed of NH_3 and NH_4NO_3, while the other is composed of H_2SO_4 and Na_2SO_4. Which solution should have the larger capacity as a buffer?

ANSWERS

1. A buffer is the combination of a weak acid or base and a salt of that weak acid or base.
3. a. no
   b. yes
   c. no
   d. yes
5. 3b: strong acid: $NO_2^- + H^+ \rightarrow HNO_2$; strong base: $HNO_2 + OH^- \rightarrow NO_2^- + H_2O$; 3d: strong base: $NH_4^+ + OH^- \rightarrow NH_3 + H_2O$; strong acid: $NH_3 + H^+ \rightarrow NH_4^+$
7. Buffers can be made from three combinations: (1) H_3PO_4 and $H_2PO_4^-$, (2) $H_2PO_4^-$ and HPO_4^{2-}, and (3) HPO_4^{2-} and PO_4^{3-}. (Technically, a buffer can be made from any two components.)
9. The phosphate buffer should have the larger capacity.

8. END-OF-CHAPTER MATERIAL

ADDITIONAL EXERCISES

1. Write the balanced chemical equation between Zn metal and HCl(aq). The other product is $ZnCl_2$.
2. Write the neutralization reaction in which $ZnCl_2$, also found in Exercise 1, is the salt product.
3. Why isn't an oxide compound like CaO considered a salt? (Hint: what acid-base combination would be needed to make it if it were a salt?)
4. Metal oxides are considered basic because they react with H_2O to form OH compounds. Write the chemical equation for a reaction that forms a base when CaO is combined with H_2O.
5. Write the balanced chemical equation between aluminum hydroxide and sulfuric acid.
6. Write the balanced chemical equation between phosphoric acid and barium hydroxide.
7. Write the equation for the chemical reaction that occurs when caffeine ($C_8H_{10}N_4O_2$) acts as a Brønsted-Lowry base.
8. Citric acid ($C_6H_8O_7$) is the acid found in citrus fruits. It can lose a maximum of three H^+ ions in the presence of a base. Write the chemical equations for citric acid acting stepwise as a Brønsted-Lowry acid.
9. Can an amphiprotic substance be a strong acid and a strong base at the same time? Explain your answer.
10. Can an amphiprotic substance be a weak acid and a weak base at the same time? If so, explain why and give an example.
11. Under what conditions will the equivalence point of a titration be slightly acidic?
12. Under what conditions will the equivalence point of a titration be slightly basic?
13. Write the chemical equation for the autoionization of NH_3.
14. Write the chemical equation for the autoionization of HF.
15. What is the pOH range for an acidic solution?
16. What is the pOH range for a basic solution?
17. The concentration of commercial HCl is about 12 M. What is its pH and pOH?
18. The concentration of concentrated H_2SO_4 is about 18 M. Assuming only one H^+ comes off the H_2SO_4 molecule, what is its pH and pOH? What would the pH and pOH be if the second H^+ were also ionized?

ANSWERS

1. $Zn + 2HCl \rightarrow ZnCl_2 + H_2$
3. The O^{2-} ion would come from H_2O, which is not considered a classic acid in the Arrhenius sense.
5. $2Al(OH)_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 6H_2O$
7. $C_8H_{10}N_4O_2 + H_2O \rightarrow C_8H_{10}N_4O_2H^+ + OH^-$; the H^+ ion attaches to one of the N atoms in the caffeine molecule.
9. As a strong acid or base, an amphiprotic substance reacts 100% as an acid or a base, so it cannot be a base or an acid at the same time.
11. if the salt produced is an acidic salt
13. $NH_3 + NH_3 \rightarrow NH_4^+ + NH_2^-$
15. pOH > 7
17. pH = −1.08; pOH = 15.08