Chapter

8

Acids and Bases

In this chapter, you will be able to

- experimentally determine the empirical properties, including pH, of acids and bases;
- design and conduct an experiment to determine the effect of dilution on pH;
- explain acids and bases, using both Arrhenius and Brønsted-Lowry theories;
- describe and explain the difference between strong and weak acids and bases;
- use the terms: ionization, dissociation, strong acid/base, weak acid/base, hydronium ion, proton transfer, conjugate acid/base, titration, titrant, and endpoint;
- write balanced chemical equations for reactions involving acids and bases;
- develop the skills involved in titration and solve stoichiometry problems using titration evidence;
- describe examples of solutions for which the concentration must be known and exact.

Acid indigestion, commercial antacid remedies for indigestion, pH-balanced shampoos—you don't have to look far in a drugstore to find labels referring to acids or acidity. Many people think that all acids are corrosive, and therefore dangerous, because solutions of acids react with many substances. Yet boric acid is used as an eyewash. Can this be as dangerous as it sounds?

References in the popular media offer no insight into what acids and bases are, or what they do. In fact, such references usually emphasize only one perspective, such as the environmental damage caused by an acid or the cleaning power of a base. As a result, popular ideas are often confusing. An amateur gardener who has just read an article describing the destruction of conifer forests by acid rain may be puzzled by instructions on a package of evergreen fertilizer stating that evergreens are acid-loving plants (**Figure 1**).

This chapter takes a historical approach, presenting evidence and following the development of theories about the substances we call acids and bases. These theories are used to explain and predict the behaviour of acids and bases.

Reflect on your Learning

1. What are some properties of acids?
2. How can you explain these properties of acids?
3. What are some properties of bases?
4. How can you explain these properties of bases?
5. How do your explanations in questions 2 and 4 account for the evidence that acids react with bases?

8.1 Understanding Acids and Bases

The story of acids and bases is progressive: It is unfolding like a detective story. Our understanding of acids and bases has changed over time as we have extended our concepts to include more and more acids and bases. Early scientists described acids, for example, as compounds that produce hydrogen gas when reacted with an active metal. These scientists realized that acids (at least, some acids) contain hydrogen atoms. To other investigators, acids were substances that contain oxygen and that react with limestone to produce carbon dioxide.

Later, investigators discovered that acids in aqueous solution change blue litmus to red and conduct electricity. These observations did not fit with the earlier definitions of acids. A new explanation was needed.

Acids and bases share some properties with molecular and ionic substances, and have some properties that are unique.

Table 1 shows that pure liquid samples of both ionic compounds and bases conduct electricity. Similarly, aqueous solutions of both ionic compounds and bases conduct electricity. In some way, bases seem to be similar to ionic compounds. What is it about ionic compounds that enables them to conduct electricity? According to Arrhenius, ionic compounds separate into ions when they are liquid or in solution. Can we assume that the same is true of bases? Perhaps they, too, separate into ions. The presence of mobile ions would explain the conductivity.

Table 1: Properties of Pure and Aqueous Substances

Substance	Conductivity			Litmus
	Solid	Liquid	Aqueous	Aqueous
most molecular compounds	no	no	no	no effect
most ionic compounds	no	yes	yes	no effect
acids	no	no	yes	blue to red
bases	no	yes	yes	red to blue

Do all bases release the same ion in aqueous solution? Many bases are ionic compounds that contain a hydroxide, OH^-, which could be released in solution. It seems likely that this ion gives a base its characteristics. After all, sodium chloride, NaCl, is not a base but sodium hydroxide, NaOH, is. Going by the evidence we have at this stage, we can conclude that bases are ionic hydroxides that release mobile hydroxide ions in solution.

$$NaOH_{(s)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$$
$$Ca(OH)_{2(s)} \rightarrow Ca^{2+}_{(aq)} + 2\ OH^-_{(aq)}$$

Table 1 also shows that molecular substances, including acids, do not conduct electricity in their pure states. However, acids (unlike other molecular substances) become conductors when dissolved in water. Arrhenius explained that molecular substances do not conduct electricity because they contain only electrically neutral particles called molecules. Can we conclude, therefore, that acids in their pure forms contain neutral molecules and not ions, but that acids in solution contain ions? This is certainly what the evidence suggests. It seems that acids are somehow different in structure and/or composition from other molecular substances.

DID YOU KNOW ?

Liquid Ionic Compounds

How hot does an ionic compound have to be, before we can test it for conductivity? Because of the strong ionic bonds, it has to be heated to extremely high temperatures (700 –1000°C). When the ionic bonds are broken, the ions are free to move around and the substance can conduct electricity.

By studying the composition of substances that turn blue litmus red in an aqueous solution, scientists found that acids seem to contain hydrogen atoms. This led scientists to write the chemical formula for acids as $HA_{(aq)}$ (**Table 2**). The electrical conductivity of these acidic solutions led to the theory that acids ionize in water to release hydrogen ions, $H^+_{(aq)}$. Acids, then, according to the evidence, are hydrogen-containing compounds that ionize in water to produce hydrogen ions.

Table 2: Properties of Hydrogen Compounds

Empirical formula	Litmus test	Molecular formula
$CH_2O_{3(aq)}$	blue to red	H_2CO_3
$CH_{4(aq)}$	no change	CH_4
$SH_{2(aq)}$	blue to red	H_2S
$PH_{3(aq)}$	no change	PH_3
$NHO_{3(aq)}$	blue to red	HNO_3

$$HCl_{(g)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$
$$HNO_{3(aq)} \rightarrow H^+_{(aq)} + NO^-_{3(aq)}$$

Arrhenius extended his theory of ions to explain some of the properties of acids and bases. According to Arrhenius, we can write an equation showing that **bases** dissociate into individual positive and negative ions in solution. He proposed that aqueous hydroxide ions were responsible for the properties of basic solutions, such as turning red litmus paper blue. The **dissociation** of bases is similar to that of any other ionic compound, as shown in the following dissociation equation for barium hydroxide.

$$Ba(OH)_{2(s)} \rightarrow Ba^{2+}_{(aq)} + 2\ OH^-_{(aq)}$$

According to the evidence in **Table 1**, acids are electrolytes in solution even though as pure substances, they are molecular compounds. Acids, such as $HCl_{(g)}$ and $H_2SO_{4(l)}$, do not show their acidic properties until they dissolve in water. Since acids in solution are electrolytes, Arrhenius' theory suggests that acid solutions must contain ions. However, the pure solute is molecular; it is made up only of neutral molecules. How, then, can its solution contain ions? Obviously, **acids** do not simply dissolve to form a solution of molecules. According to Arrhenius, after acids dissolve as individual molecules, they then ionize into hydrogen ions and negative ions in solution.

In the case of acids, Arrhenius assumed that the water somehow causes the acid molecules to ionize, but he didn't propose an explanation for this. (We now believe that water molecules help to pull the molecules apart—to ionize the acid.) A typical example of an acid is hydrogen chloride gas dissolving in water to form hydrochloric acid. We can describe this process with an **ionization** equation.

$$HCl_{(g)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

So, although HCl is a molecular compound, it appears to behave in solution as if it were ionic. It ionizes into ions, which are capable of conducting electricity in solution. We explain the properties of acids by saying that all acids produce hydrogen ions in solution, and define acids as substances that ionize in water to increase the hydrogen ion concentration.

DID YOU KNOW ?

Formulas of Acids

The 19th century idea was that acids are salts (compounds) of hydrogen. For example, scientists would say that $HCl_{(aq)}$ is the hydrogen salt of $NaCl_{(aq)}$. This led to the practice of writing hydrogen first in the formulas of substances known to form acidic solutions, such as $H_2SO_{4(aq)}$ and $HCl_{(aq)}$.

base: (according to the Arrhenius theory) an ionic hydroxide that dissociates in water to produce hydroxide ions

dissociation: the separation of ions that occurs when an ionic compound dissolves in water

acid: (according to the Arrhenius theory) a compound that ionizes in water to form hydrogen ions

ionization: any process by which a neutral atom or molecule is converted into an ion

The Arrhenius theory was a major advance in understanding chemical substances and solutions. Arrhenius also provided the first comprehensive theory of acids and bases. The empirical and theoretical definitions of acids and bases are summarized in **Table 3**.

Table 3: Acids, Bases, and Neutral Substances

Type of substance	Empirical definition	Theoretical definition
acids	• in solution, turn blue litmus red • are electrolytes • in solution, neutralize bases	• these hydrogen-containing compounds ionize to produce $H^+_{(aq)}$ ions • $H^+_{(aq)}$ ions react with $OH^-_{(aq)}$ ions to produce water
bases	• in solution, turn red litmus blue • are electrolytes • in solution, neutralize acids	• ionic hydroxides dissociate to produce $OH^-_{(aq)}$ ions • $OH^-_{(aq)}$ ions react with $H^+_{(aq)}$ ions to produce water
neutral substances	• in solution, do not affect litmus • some are electrolytes • some are nonelectrolytes	• no $H^+_{(aq)}$ or $OH^-_{(aq)}$ ions are formed • some exist as ions in solution • some exist as molecules in solution

Sample Problem 1

Write dissociation or ionization equations (as appropriate) for the dissolving of the following chemicals in water. Label each equation as either dissociation or ionization.

(a) potassium chloride (a salt substitute)

(b) hydroiodic acid (a strong acid)

Solution

(a) $KCl_{(s)} \rightarrow K^+_{(aq)} + Cl^-_{(aq)}$ (dissociation)

(b) $HI_{(aq)} \rightarrow H^+_{(aq)} + I^-_{(aq)}$ (ionization)

As Sample Problem 1 shows, ionic substances dissociate in water, but acids ionize.

Acids as pure substances are molecular and, as such, may be solids, liquids, or gases at SATP (standard ambient temperature and pressure). When you are writing ionization equations for acids, you may not always know the initial state of matter. If you do know the state, use (s), (l), or (g) subscripts; if you do not know the pure state of the acid, use (aq). This is correct for now, as all the acids you will be using in this course are in aqueous solution. For example,

$$HCl_{(g)} \text{ or } HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^+_{(aq)} \quad \text{(a gaseous acid)}$$
$$HC_2H_3O_{2(l)} \text{ or } HC_2H_3O_{2(aq)} \rightarrow H^+_{(aq)} + C_2H_3O^-_{2(aq)} \quad \text{(a liquid acid)}$$
$$H_2C_2O_{4(s)} \text{ or } H_2C_2O_{4(aq)} \rightarrow H^+_{(aq)} + HC_2O^-_{4(aq)} \quad \text{(a solid acid)}$$

Recall that chemicals that turn blue litmus red have acid formulas that begin with H.

The Arrhenius Concept of Acids and Bases

In 1887 Svante Arrhenius created a theory of ions to explain the electrical conductivity of solutions. Arrhenius explained that ionic compounds form solutions that conduct electricity because these compounds dissociate as they dissolve to release an anion and a cation. For example, potassium hydrogen sulfate forms an electrically conductive solution because it dissolves as two ions.

$$KHSO_{4(s)} \rightarrow K^+_{(aq)} \text{ or } HSO^-_{4(aq)}$$

Scientists had previously agreed that acids were hydrogen compounds. Arrhenius added to this theory by suggesting that acids are hydrogen compounds that ionize to increase the hydrogen ion concentration of a solution. For example, hydrogen chloride gas dissolves in water and ionizes almost completely to increase the hydrogen ion concentration.

$$HCl_{(g)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

Arrhenius was also able to explain in a theoretical way why bases have their characteristic properties. He suggested that bases are ionic hydroxides that dissolve in water to increase the hydroxide ion concentration of the solution. For example, potassium hydroxide dissociates in water to increase the hydroxide ion concentration.

$$KOH_{(s)} \rightarrow K^+_{(aq)} + OH^-_{(aq)}$$

SUMMARY The Arrhenius Theoretical Definitions

acid → $H^+_{(aq)}$ + anion

base → cation + $OH^-_{(aq)}$

other ionic compounds → ions but no $H^+_{(aq)}$ or $OH^-_{(aq)}$

Investigation 8.4.1

Testing Arrhenius' Acid–Base Definitions

INQUIRY SKILLS

- ○ Questioning
- ○ Hypothesizing
- ● Predicting
- ● Planning
- ● Conducting
- ● Recording
- ● Analyzing
- ● Evaluating
- ● Communicating

The purpose of this investigation is to test the Arrhenius definitions of acids and bases. As part of this investigation, you are asked to make a Prediction. Do not base your Prediction on experience or a personal hypothesis—use only the Arrhenius theoretical definitions. Assume that the Arrhenius concept restricts dissociation and ionization: Bases dissociate to produce $OH^-_{(aq)}$ and a cation; and acids ionize to produce $H^+_{(aq)}$ and an anion.

You are expected to design an experiment to classify a number of common substances in solution (see **Materials**) as acidic, basic, or neutral. (Refer to Chapter 2 if you need help writing the formulas for each of the substances.) Complete a report, including the **Prediction**, **Experimental Design**, **Analysis**, and **Evaluation**.

and that $NaNO_{3(aq)}$ is neutral. However, by Arrhenius's definitions, we would predict all of the following compounds to be neutral, but they are not:

- compounds of **hydrogen polyatomic ions** ($NaHCO_{3(aq)}$ and $NaHSO_{4(aq)}$)
- oxides of metals and nonmetals ($CaO_{(aq)}$ and $CO_{2(g)}$)
- compounds that are neither oxides nor hydroxides (e.g., $NH_{3(aq)}$ and $Na_2CO_{3(aq)}$), but yet are bases
- compounds that contain no hydrogen (e.g., $Al(NO_3)_{3(aq)}$), but yet are acids

Clearly, the Arrhenius theoretical definitions of acid and base need to be revised or replaced.

hydrogen polyatomic ion: a bi-ion; a polyatomic ion with an available hydrogen (e.g., hydrogen carbonate (bicarbonate) ion, hydrogen sulfite (bisulfite) ion)

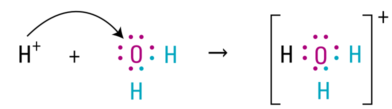

Figure 2
The Lewis (electron dot) diagram for a hydrogen ion has no electrons. A water molecule is believed to have two lone pairs of electrons, as shown in its Lewis diagram. The hydrogen ion (proton) is believed to bond to one of these lone pairs of electrons to produce the H_3O^+ ion.

Figure 3
By passing infrared light through solutions of acids, Paul Giguère of the Université Laval, Quebec City, obtained clear evidence for the existence of hydronium ions in solution.

A theoretical concept has two major purposes: to explain current evidence and to predict the results of new experiments. While the first purpose is useful, it is not valued as much as the ability to predict results. Theoretical progress is made when theories not only explain what is known but also allow valid predictions to be made about new situations.

We need to revise Arrhenius' acid–base definitions to explain the exceptions listed above. The new theory involves two key ideas: collisions with water molecules and the nature of the hydrogen ion. Since all substances tested are in aqueous solution, then particles will constantly be colliding with, and may also react with, the water molecules present.

It is highly unlikely that the particle we call an aqueous hydrogen ion, $H^+_{(aq)}$, actually exists in an acidic solution. If such a particle were to come near polar water molecules, it would bond strongly to one or more of the molecules (**Figure 2**), that is, it would be hydrated. There is no evidence for the existence of unhydrated hydrogen ions in aqueous solution. However, the Canadian scientist Paul Giguère has done experiments that provide clear evidence for the existence of hydrated protons (**Figure 3**). The simplest representation of a hydrated proton is $H_3O^+_{(aq)}$, commonly called the **hydronium ion** (**Figure 4**).

hydronium ion: a hydrated hydrogen ion (proton), conventionally represented as $H_3O^+_{(aq)}$

Figure 4
The hydronium ion is represented as a pyramidal structure. The oxygen atom is the apex and the three identical hydrogen atoms form the base of the pyramid.

We can now explain the formation of acidic solutions by strong acids such as $HCl_{(aq)}$ as a reaction with water, forming hydronium ions (**Figure 5**).

$$HCl_{(g)} + H_2O_{(l)} \xrightarrow{>99\%} H_3O^+_{(aq)} + Cl^-_{(aq)}$$

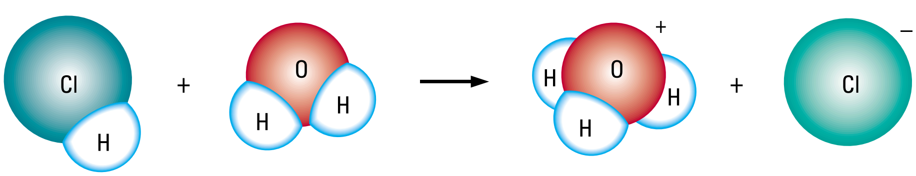

Figure 5
When gaseous hydrogen chloride dissolves in water, the HCl molecules are thought to collide and react with water molecules to form hydronium and chloride ions.

A strong acid, such as HCl, is considered to react completely with water. In other words, the collisions with water molecules are very successful, producing a 100% reaction. What about weak acids? Because they have lesser acidic properties,

DID YOU KNOW ?

pH

How does this new theory about acids affect our concept of pH? Fortunately, the mathematical definition of pH works equally well with hydronium ions as it did with hydrogen ions.

there must be fewer hydronium ions produced from the same volume and concentration of solution compared with strong acids. Therefore, the collisions of weak acid molecules with water cannot be very successful. Based on pH measurements, 0.10 mol/L acetic acid, a common weak acid, is only successful in forming hydronium ions in 1.3% of its collisions with water molecules.

$$HC_2H_3O_{2(aq)} + H_2O_{(l)} \xrightarrow{1.3\%} H_3O^+_{(aq)} + C_2H_3O^-_{2(aq)}$$

In general, *acidic solutions form when substances react with water to form hydronium ions.*

The concept of acids reacting with water to produce hydronium ions is a small adjustment in thinking when explaining or predicting the behaviour of typical acids. In most contexts, we can think of acids as either ionizing to produce hydrogen ions or reacting with water to produce hydronium ions.

Strong and Weak Bases

Evidence indicates that there are both strong bases (e.g., sodium hydroxide) and weak bases (e.g., ammonia). For equal concentrations of solutions, strong bases have high electrical conductivity and very high pH (>>7), whereas weak bases have low electrical conductivity and pH closer to 7. We can explain the behaviour of strong bases: They dissociate to increase the hydroxide ion concentration in an aqueous solution. Further evidence indicates that all ionic hydroxides are **strong bases**: 100% of the dissolved ionic hydroxides dissociates to release hydroxide ions.

strong base: (according to the Arrhenius theory and the "reaction-with-water" theory) an ionic hydroxide that dissociates 100% in water to produce hydroxide ions

weak base: (according to the "reaction-with-water" theory) a chemical that reacts less than 50% with water to produce hydroxide ions

What about **weak bases**? How can we explain their properties? The pure compounds (e.g., $NH_{3(g)}$) do not contain hydroxide ions, so they cannot dissociate to release hydroxide ions. Nevertheless, solutions of weak bases appear to contain hydroxide ions in a higher concentration than does pure water. Where do they come from? Clearly, this question cannot be answered by the Arrhenius definition of bases. We need to revise his theory to include a new concept: that weak base molecules or ions react with water to produce hydroxide ions. This remains consistent with the explanation for strong bases and for strong and weak acids. Weak bases do not react 100% with water. Evidence indicates that they commonly react less than 10%. This means that they produce fewer hydroxide ions than a similar amount of a strong base, which accounts for the weaker basic properties of weak bases.

Recall from Section 8.1 that ionic hydroxides produce basic solutions by simple dissociation. We know that ionic hydroxides, such as barium hydroxide, are strong bases.

$$Ba(OH)_{2(s)} \rightarrow Ba^{2+}_{(aq)} + 2\ OH^-_{(aq)} \qquad \text{(a strong base)}$$

Here, there is no need to consider a reaction with water because we know that ionic hydroxides, such as $Ba(OH)_2$, dissociate to produce hydroxide ions. However, there are many common examples of bases that are not ionic hydroxides, such as ammonia (window cleaner) and sodium carbonate (washing soda). Most bases, other than soluble ionic hydroxides, are weak bases. Weak bases may be either ionic or molecular compounds in their pure state.

Ammonia and sodium carbonate each form basic aqueous solutions as demonstrated by a litmus paper test. This equation for ammonia shows the theory to explain the evidence:

$$NH_{3(aq)} + H_2O_{(l)} \xrightarrow{<50\%} OH^-_{(aq)} + NH^+_{4(aq)} \qquad \text{(a weak base)}$$

The presence of hydroxide ions explains the basic solution, and the less than 100% reaction explains the weak base properties. (Note that both atoms and charge are conserved in the balanced equation.)

Sodium carbonate is an ionic compound with high solubility. According to the Arrhenius theory, sodium carbonate dissociates in water to produce aqueous ions of sodium and carbonate.

$$Na_2CO_{3(s)} \rightarrow 2\ Na^+_{(aq)} + CO^{2-}_{3(aq)}$$

The sodium ion cannot be responsible for the basic properties of the solution, because many sodium compounds (e.g., $NaCl_{(aq)}$) form neutral solutions. The basic character of carbonate solutions can be explained as resulting from their reaction with water.

$$CO^{2-}_{3(aq)} + H_2O_{(l)} \xrightarrow{<50\%} OH^-_{(aq)} + HCO^-_{3(aq)}$$

Note again that hydroxide ions explain the basic properties and that atoms and charge are conserved in the balanced equation.

We now have explanations for the production of hydroxide ions by bases: Strong bases (commonly ionic hydroxides) dissociate to produce hydroxide ions; and weak bases react with water to increase the hydroxide ion concentration. This theory is sometimes called the revised Arrhenius theory.

Sample Problem 1

A forensic technician tested the pH of a sodium cyanide solution and found that it had a pH greater than 7. Explain this evidence using chemical equations.

Solution

$$NaCN_{(s)} \rightarrow Na^+_{(aq)} + CN^-_{(aq)}$$

$$CN^-_{(aq)} + H_2O_{(l)} \xrightarrow{<50\%} OH^-_{(aq)} + HCN_{(aq)}$$

The cyanide ion produces hydroxide ions in reaction with water, so is a weak base. As a weak base, we expect the reaction to be less than 50% and the solution to have a pH greater than 7 but not, say, greater than 13.

SUMMARY Strong and Weak Acids and Bases

	Strong acids	Weak acids	Strong bases	Weak bases
empirical	very low pH (<<7)	medium to low pH (<7)	very high pH (>>7)	medium to high pH (>7)
	high conductivity	low conductivity	high conductivity	low conductivity
	fast reaction rate	slow reaction rate	fast reaction rate	slow reaction rate
solute	molecular	molecular and polyatomic ion	ionic hydroxide	molecular and polyatomic ion*
theoretical (Arrhenius)	completely ionized to form $H^+_{(aq)}$	partially ionized to form $H^+_{(aq)}$	completely dissociated into $OH^-_{(aq)}$	—
theoretical (revised Arrhenius)	completely reacted with water to form $H_3O^+_{(aq)}$	partially reacted with water to form $H_3O^+_{(aq)}$	completely dissociated to form form $OH^-_{(aq)}$	partially reacted with water to form $OH^-_{(aq)}$

* Except the hydroxide ion, $OH^-_{(aq)}$

Figure 6
Johannes Brønsted created new theoretical definitions for acids and bases based upon proton transfer.

Practice

Understanding Concepts

12. What were some of the early ideas about the chemistry of acids? What evidence eventually showed that these ideas were false?
13. How well does the original Arrhenius theory predict and explain acids and bases?
14. What is the more recent replacement for the idea of a hydrogen ion causing acidic properties? State its name and formula.
15. Write chemical equations to explain the pH of a 0.1 mol/L solution of each substance.
    (a) $HCN_{(aq)}$; pH = 5
    (b) $HNO_{3(aq)}$; pH = 1
    (c) $Na_2SO_{4(aq)}$; pH = 8
    (d) $Sr(OH)_{2(aq)}$; pH = 13
16. In the previous question, identify the strong and weak acids and bases.

The Brønsted–Lowry Concept

Acid and base definitions, revised to include the ideas of the hydronium ion and reaction with water, are more effective in describing, explaining, and predicting the behaviour of acids and bases than are Arrhenius' original definitions. However, chemical research has shown that even these revised definitions are still too restrictive. Reactions of acids and bases do not always involve water. Also, evidence indicates that some entities that form basic solutions (such as $HCO^-_{3(aq)}$) can actually neutralize the solution of a stronger base. A broader concept is needed to describe, explain, and predict these properties of acids and bases.

New theories in science usually result from looking at the evidence in a way that has not occurred to other observers. A new approach to acids and bases was developed in 1923 by Johannes Brønsted (1879–1947) of Denmark (**Figure 6**) and independently by Thomas Lowry (1874–1936) of England. These scientists focused on the role of an acid and a base in a reaction rather than on the acidic or basic properties of their aqueous solutions. An acid, such as aqueous hydrogen chloride, functions in a way opposite to a base, such as aqueous ammonia. According to the Brønsted-Lowry concept, hydrogen chloride donates a proton (H^+) to a water molecule,

H^+

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

and ammonia accepts a proton from a water molecule.

H^+

$$NH_{3(aq)} + H_2O_{(l)} \rightarrow OH^-_{(aq)} + NH^+_{4(aq)}$$

Water does not have to be one of the reactants. For example, the hydronium ions present in a hydrochloric acid solution can react directly with dissolved ammonia molecules.

H^+

$$\underset{\text{acid}}{H_3O^+_{(aq)}} + \underset{\text{base}}{NH_{3(aq)}} \rightarrow H_2O_{(l)} + NH^+_{4(aq)}$$

We can describe this reaction as NH_3 molecules removing protons from H_3O^+ ions. Hydronium ions act as the **acid**, and ammonia molecules act as the **base**. Water is present as the solvent, but not as a primary reactant. In fact, water does not even have to be present, as evidenced by the reaction of hydrogen chloride and ammonia gases (**Figure 7**).

H^+

$$\underset{\text{acid}}{HCl_{(g)}} + \underset{\text{base}}{NH_{3(g)}} \rightarrow NH_4Cl_{(s)}$$

Figure 7
One hazard of handling concentrated solutions of ammonia and hydrochloric acid is gas fumes. The photograph shows ammonia gas and hydrogen chloride gas escaping from their open bottles, and reacting to form a white cloud of very tiny crystals of $NH_4Cl_{(s)}$.

acid: (according to the Brønsted-Lowry concept) a proton donor

base: (according to the Brønsted-Lowry concept) a proton acceptor

amphiprotic: a substance capable of acting as an acid or a base in different chemical reactions; an entity that can gain or lose a proton (sometimes called amphoteric)

A substance can be classified as a Brønsted-Lowry acid or base only for a specific reaction. It is not a general property of a substance. This point is important—a substance may gain protons in one reaction, but lose them in another reaction with another substance. (For example, in the reaction of HCl with water shown above, water acts as the Brønsted-Lowry base; whereas, in the reaction of NH_3 with water, water acts as the Brønsted-Lowry acid.) A substance that appears to act as a Brønsted-Lowry acid in some reactions and as a Brønsted-Lowry base in other reactions is called **amphiprotic**. The hydrogen carbonate ion ($HCO^-_{3(aq)}$) in baking soda (**Figure 8**) is amphiprotic, like every other hydrogen polyatomic ion. Hydrogen polyatomic ions, as their name suggests, are polyatomic ions containing hydrogen. Examples of amphiprotic substances include $HCO^-_{3(aq)}$, $H_2O_{(l)}$, $HSO^-_{3(aq)}$, $H_2PO^-_{4(aq)}$, and $HPO^{2-}_{4(aq)}$.

Note that amphiprotic entities can either gain or lose a proton, as shown by the following reactions. First let's see what happens when the bicarbonate ion is added to the solution of a strong acid, which will contain hydronium ions.

H^+

$$\underset{\text{base}}{HCO^-_{3(aq)}} + \underset{\text{acid}}{H_3O^+_{(aq)}} \rightarrow H_2CO_{3(aq)} + H_2O_{(l)} \qquad \text{(neutralizes a strong acid)}$$

Now let's look at the reaction of the bicarbonate ion with the solution of a strong base, which will contain hydroxide ions.

H^+

$$\underset{\text{acid}}{HCO^-_{3(aq)}} + \underset{\text{base}}{OH^-_{(aq)}} \rightarrow CO^{2-}_{3(aq)} + H_2O_{(l)} \qquad \text{(neutralizes a strong base)}$$

In both cases, the bicarbonate ion moves the pH of the solutions toward 7.

According to the Brønsted-Lowry concept, acid–base reactions involve the transfer of a proton. Therefore, the products formed in these reactions must differ from the reactants by a proton (H^+). If you look again at the equations above, you can see that this is true.

As another example, when acetic acid reacts with water, an acidic solution (containing hydronium ions) is formed.

H^+

$$\underset{\text{acid}}{HC_2H_3O_{2(aq)}} + \underset{\text{base}}{H_2O_{(l)}} \rightarrow C_2H_3O^-_{2(aq)} + H_3O^+_{(aq)}$$

Figure 8
Baking soda (sodium hydrogen carbonate, $NaHCO_3$) is a common household substance that is useful for many purposes other than baking. You can use it to neutralize both spilled acids and bases, and it can also be used as an extinguisher for small fires.

The acetate ion product is simply what is left after an acetic acid molecule loses its proton. The hydronium ion product is what is formed as a result of a water molecule gaining a proton. Any proton that is lost can, in principle, be regained and any proton that is gained can be lost in some other reaction. Therefore, we can consider the acetate ion to be a potential Brønsted-Lowry base: It could act as a base in another reaction. A product formed as a result of an acid losing a proton is called a **conjugate base**. Similarly, the hydronium ion is a potential Brønsted-Lowry acid: It could act as an acid in another reaction. A product resulting from a base gaining a proton is called a **conjugate acid**.

conjugate base: the base formed by removing a proton (H^+) from an acid

conjugate acid: the acid formed by adding a proton (H^+) to a base

conjugate acid–base pair

$$\underset{\text{acid}}{HC_2H_3O_{2(aq)}} + \underset{\text{base}}{H_2O_{(l)}} \rightarrow \underset{\text{conjugate base}}{C_2H_3O_2{}^-{}_{(aq)}} + \underset{\text{conjugate acid}}{H_3O^+_{(aq)}}$$

conjugate acid–base pair

conjugate acid–base pair: an acid–base pair that differs by one proton (H^+)

A pair of substances that differ only by a proton is called a **conjugate acid–base pair** (Table 3).

Table 3: Some Examples of Conjugate Acid–Base Pairs

Conjugate acid		Conjugate base
$H_2O_{(l)}$	and	$OH^-_{(aq)}$
$H_3O^+_{(aq)}$	and	$H_2O_{(l)}$
$HC_2H_3O_{2(aq)}$	and	$C_2H_3O^-_{2(aq)}$

SUMMARY Definitions of Acids and Bases

Arrhenius Definitions

- An acid ionizes in water to increase the hydrogen ion concentration.
- A base dissociates in water to increase the hydroxide ion concentration.
- A neutralization reaction involves the reaction of a hydrogen ion with a hydroxide ion.

Revised Arrhenius Definitions

- An acid reacts with water to increase the hydronium ion concentration.
- A base reacts with water to increase the hydroxide ion concentration.
- A neutralization reaction involves the reaction of a hydronium ion with a hydroxide ion.

Brønsted–Lowry Definitions

- An acid is a proton donor.
- A base is a proton acceptor.
- An acid–base neutralization reaction involves the transfer of one proton from the strongest acid present to the strongest base present.
- An amphiprotic substance is one that appears to act as a Brønsted-Lowry acid in some reactions and as a Brønsted-Lowry base in other reactions.
- A conjugate acid–base pair consists of two substances that differ only by one proton.

Practice

Understanding Concepts

17. According to the Brønsted-Lowry definitions, how are acids and bases different?
18. Classify each reactant in the following equations as a Brønsted-Lowry acid or base.
    (a) $HF_{(aq)} + SO_{3(aq)}^{2-} \rightarrow F_{(aq)}^{-} + HSO_{3(aq)}^{-}$
    (b) $CO_{3(aq)}^{2-} + HC_2H_3O_{2(aq)} \rightarrow C_2H_3O_{2(aq)}^{-} + HCO_{3(aq)}^{-}$
    (c) $H_3PO_{4(aq)} + OCl_{(aq)}^{-} \rightarrow H_2PO_{4(aq)}^{-} + HOCl_{(aq)}$
19. An aqueous hydrogen sulfate ion acts as the Brønsted-Lowry acid in the neutralization of a solution of hydrogen carbonate ions.
    (a) Write the chemical equation.
    (b) Identify two conjugate acid–base pairs.
20. What restrictions to acid–base reactions do the Brønsted-Lowry definitions remove?

Figure 9
Antoine Lavoisier

Changing Ideas on Acids and Bases

Usually chemists discover the empirical properties of substances long before a theory is developed to describe, explain, and predict their behaviour. For example, several of the distinguishing properties of acids and bases were known by the middle of the 17th century. Additional properties, such as pH and the nature of acid–base reactions, were discovered by the early 20th century.

Let's take an overview of the developing theory of acids and bases. It is a story that took place over several hundred years, thanks to the innovative thoughts and painstaking laboratory investigations of many great scientists.

Antoine Lavoisier (1743–1794) (**Figure 9**) assumed that oxygen was responsible for acid properties and that acids were combinations of oxides and water. For example, sulfuric acid, H_2SO_4, was described as hydrated sulfur trioxide, $SO_3{\cdot}H_2O$. There were immediate problems with this theory because some oxide solutions, such as CaO, are basic, and several acids, such as HCl, are not formed from oxides. This evidence led to the rejection of the oxygen theory, although we still use the generalization that nonmetallic oxides (e.g., SO_3) form acidic solutions.

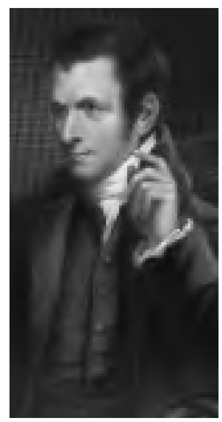

Figure 10
Sir Humphry Davy

Figure 11
Justus von Liebig

Sir Humphry Davy (1778–1829) (**Figure 10**) advanced a theory that the presence of hydrogen gave a compound acidic properties. Justus von Liebig (1803–1873) (**Figure 11**) later expanded this theory to include the idea that acids are salts (compounds) of hydrogen. This meant that acids could be thought of as ionic compounds in which hydrogen had replaced the metal ion. However, this theory did not explain why many compounds containing hydrogen have neutral properties (e.g., CH_4) or basic properties (e.g., NH_3).

Svante Arrhenius (1859–1927) (**Figure 12**) developed a theory in 1887 that provided the first useful theoretical definition of acids and bases. He described acids as substances that ionize in aqueous solution to form hydrogen ions, and bases as substances that dissociate to form hydroxide ions in solution. This theory explained the process of neutralization by assuming that $H_{(aq)}^{+}$ and $OH_{(aq)}^{-}$ ions combine to form $H_2O_{(l)}$. The various strengths of acids were explained in terms of the degree (percentage) of ionization, but Arrhenius's theory is limited to aqueous solutions and cannot explain the properties of many common substances.

Figure 12
Svante Arrhenius

DID YOU KNOW ?

Prove Me Wrong!

In science, no theory can be proven. Well-established, accepted theories have a substantial quantity of supporting evidence. On the other hand, a theory can be disproven by a single, significant, reproducible observation. In Einstein's words: "No amount of experimentation can ever prove me right; a single experiment can prove me wrong."

Paul Giguère of the Université Laval, Quebec, found evidence that, in a solution, hydrogen ions are bonded to water molecules. The simplest representation of an aqueous hydrogen ion is $H_3O^+_{(aq)}$, commonly known as a hydronium ion. The concept of the hydronium ion was used to revise the Arrhenius definitions of acids and bases. Now acids could be described as substances that react with water to form hydronium ions, and bases could be described as substances that dissociate or react with water to form hydroxide ions. This revised Arrhenius theory is still limited to aqueous solutions but it does provide an explanation for the properties of aqueous solutions of nonmetal oxides, metal oxides, and polyatomic anions.

Johannes Brønsted (1879–1947) of Denmark and Thomas Lowry (1874–1936) of England independently developed a theory that focused on the role of acids and bases in a reaction rather than on the properties of their aqueous solutions. They defined acids as substances that donate protons (H^+) and bases as substances that accept protons in a chemical reaction. In the Brønsted-Lowry concept, a substance can only be defined as an acid or a base for a specific reaction. Ions such as hydrogen carbonate, $HCO^-_{3(aq)}$, or hydrogen sulfite, $HSO^-_{3(aq)}$, can act as acids in one reaction and as bases in another.

Changes in Knowledge

History indicates that it is unwise to assume that any scientific concept is the final word. Whenever scientists assume that they understand a subject, two things usually happen. Conceptual knowledge tends to remain static for a while, because little falsifying evidence exists or because any falsifying evidence is ignored. Then, when enough falsifying evidence accumulates, a revolution in thinking occurs within the scientific community in which the current concept is drastically revised or entirely replaced. The experience of the Swedish chemist Svante Arrhenius gives some insight into the difficulty scientists have in getting new ideas accepted.

While Arrhenius was attending the University of Uppsala near his home, he became intrigued by the question of why some aqueous solutions conduct electricity, but others do not. This problem had puzzled chemists ever since Sir Humphry Davy and Michael Faraday experimented over half a century earlier by passing electric currents through chemical substances.

Faraday believed that an electric current produces particles of electricity, which he called ions, in some solutions. He could not explain what ions were, or why they did not form in aqueous sugar or alcohol solutions.

As a university student, Arrhenius noticed that conducting solutions differed from non-conducting solutions in terms of another important property. The freezing point of any aqueous solution is lower than the freezing point of pure water; the more solute that is dissolved in the water, the more the freezing point is lowered (depressed). Arrhenius found that the freezing point depression of electrolytes in solution was always two or three times lower than that of non-electrolytes, in solutions of the same concentration. He concluded that when a solution such as pure table salt, NaCl, dissolves, it does not separate into NaCl molecules in solution but rather into two types of particles. Since the NaCl solution also conducts electricity, he reasoned that the particles must be electrically charged. In Arrhenius' view, the conductivity and freezing point evidence indicated that pure substances that form electrolytes are composed of charged ions, not neutral atoms. The stage was now set for a scientific controversy. Faraday was an established, respected scientist and his explanation agreed with Dalton's model of indivisible, neutral atoms. Arrhenius was an unknown university student and his theory contradicted Dalton's widely accepted model.

Despite strong supporting evidence, Arrhenius's creative idea was rejected by most of the scientific community, including his teachers. When Arrhenius presented his theory and its supporting evidence as part of his doctoral thesis, the examiners questioned him for four gruelling hours. They grudgingly passed him, but with the lowest possible mark.

For over a decade, only a few people supported Arrhenius' theory. Gradually, more supporting evidence accumulated, including J.J. Thomson's discovery of the electron in 1897. Soon, Arrhenius's theory of ions became widely accepted as the simplest and most logical explanation of the nature of electroytes. In 1903 Arrhenius won the Nobel Prize for the same thesis that had nearly failed him in his PhD examination years earlier.

Arrhenius' struggle to have his ideas accepted is not so unusual. Ideally, scientists are completely open-minded, but they are people, and many people resist change. We are sometimes reluctant to accept new ideas that conflict radically with familiar ones.

DID YOU KNOW?

Scientific Concepts

"Creating a new theory is not like destroying an old barn and erecting a skyscraper in its place. It is rather like climbing a mountain, gaining new and wider views, discovering unexpected connections between our starting point and its rich environment. But the point from which we started out still exists and can be seen, although it appears smaller and forms a tiny part of our broad view gained by the mastery of the obstacles on our adventurous way up."

Albert Einstein (1879–1955)
German-born American theoretical physicist

Explore an Issue

Role Play: Evaluating New Ideas in Science

You are a member of the PhD examination committee for Svante Arrhenius. Is his experimental work reliable? Were his experiments well designed and carefully repeated? Is his interpretation of the experimental results valid? Is his reasoning logical and based on the evidence?

(a) Read the short summary of Arrhenius' work above, and research more detailed information in other references.

(b) Choose a role and prepare to question Arrhenius, played by your teacher, on his PhD thesis. You might consider the following roles:
- a senior professor at the university who firmly believes in Dalton's theory that atoms are indivisible, neutral particles;
- a scientist who frequently corresponded with Michael Faraday during his long, distinguished career;
- the professor who supervised Arrhenius' research and who frequently discussed the experimental results with him;
- a scientist who is dissatisfied with the current theories of electricity; or
- a young scientist who wants to know how Arrhenius' ideas would explain the acid–base properties of solutions.

DECISION-MAKING SKILLS

- ○ Define the Issue
- ● Identify Alternatives
- ● Research
- ● Analyze the Issue
- ● Defend a Decision
- ○ Evaluate

Sections 8.3–8.4 Questions

Understanding Concepts

1. Distinguish between a strong and weak acid using the concept of reaction with water.
2. What class of substances are strong bases? Explain their properties.
3. What are the properties of a weak base? Explain these properties.
4. Write appropriate chemical equations to explain the acidic or basic properties of each of the following substances added to water.
   (a) hydrogen bromide (acidic)
   (b) potassium hydroxide (basic)
   (c) benzoic acid, $HC_7H_5O_{2(aq)}$ (acidic)
   (d) sodium sulfide (basic)
5. Theories in science develop over a period of time. Illustrate this development by writing theoretical definitions of an acid, using the following concepts. Begin your answer with, "According to [name of concept], acids are substances that…"
   (a) the Arrhenius concept
   (b) the revised Arrhenius concept
   (c) the Brønsted-Lowry concept
6. Repeat question 5, defining bases. Refer to both strong and weak bases in your answer.
7. According to the Brønsted-Lowry concept, what happens in an acid–base reaction?
8. Use the Brønsted-Lowry definitions to identify each of the reactants in the following equations as acids or bases.
   (a) $HCO^-_{3(aq)} + S^{2-}_{(aq)} \rightarrow HS^-_{(aq)} + CO^{2-}_{3(aq)}$
   (b) $H_2CO_{3(aq)} + OH^-_{(aq)} \rightarrow HCO^-_{3(aq)} + H_2O_{(l)}$
9. Complete the following chemical equations to predict the acid–base reaction products.
   (a) $HSO^-_{4(aq)} + PO^{3-}_{4(aq)} \rightarrow$
   (b) $H_3O^+_{(aq)} + HPO^{2-}_{4(aq)} \rightarrow$
10. Some ions can form more than one conjugate acid–base pair. List the two conjugate acid–base pairs involving a hydrogen carbonate ion.
11. Identify the two acid–base conjugate pairs in each of the following reactions.
    (a) $H_3O^+_{(aq)} + HSO^-_{3(aq)} \rightarrow H_2O_{(l)} + H_2SO_{3(aq)}$
    (b) $OH^-_{(aq)} + HSO^-_{3(aq)} \rightarrow H_2O_{(l)} + SO^{2-}_{3(aq)}$

Applying Inquiry Skills

12. Baking soda is a common chemical but its chemical properties are difficult for chemists to explain and predict. Baking soda is amphiprotic and forms a basic solution. List some of the chemical properties of baking soda and indicate why some of these properties are difficult to explain and predict.
    Follow the links for Nelson Chemistry 11, 8.4.

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Making Connections

13. Common kitchen-variety baking soda has so many uses that it has entire books written about it. Use references to gather a list of uses for baking soda. Identify the uses that involve acid–base reactions.