# Theoretical Acid–Base Definitions

People have had a practical understanding of acids and bases and their applications for centuries. As our understanding of chemistry has grown, several theories have been proposed to explain the properties of acids and bases. In 1777, Antoine Lavoisier discovered that air contained an invisible gas, which he called "vital air," that was necessary for combustion. He also observed that burning sulfur and phosphorus in air produced acidic solutions. This observation led Lavoisier to believe that "vital air" was an element that was common to all acids. He was so confident in this conclusion that he renamed this element "oxygen" from the Greek words *oxys* (sour) and *genes* (born).

The first challenge to Lavoisier's oxygen theory of acids came in 1789. This was when Claude Louis Berthollet showed that hydrocyanic acid, HCN(aq), did not contain oxygen. However, the acidic properties of HCN(aq) were so mild that chemists doubted whether it was a true acid. The oxygen theory of acids remained the dominant acid theory until the early 1800s. That was when Humphrey Davy discovered that muriatic (hydrochloric) acid did not contain oxygen. Rather, it consisted only of hydrogen and a new element that Davy named "chlorine."

## Arrhenius Theory of Acids and Bases

By the 1880s, Swedish chemist Svante Arrhenius had developed a theory about electrolytes such as sodium chloride. His theory explained why solutions of electrolytes conduct electricity. According to Arrhenius, when an electrolyte dissolves, its ions dissociate (come apart). This allows them to move freely in the solution and to conduct electricity. In the mid-1880s, Arrhenius modified his theory to include acids and bases. Since acidic and basic solutions also conduct electricity, he concluded that these solutions must also contain ions (**Figure 1**).



**Figure 1** Solutions of hydrochloric acid, sodium hydroxide, and sodium chloride are good conductors of electricity because of the ions they contain. According to Arrhenius, pure water is a poor conductor because it does not contain ions.

Arrhenius proposed that a base is an ionic compound that dissociates into cations and hydroxide ions, OH<sup>-</sup>, as it dissolves in water. Hydroxide ions give bases their characteristic properties. The dissociation of a base is similar to that of other ionic compounds discussed in Chapter 9. For example, the equation for dissociation of calcium hydroxide is

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

Arrhenius also proposed that an acid is a molecular compound that ionizes to produce hydrogen ions in water. Hydrogen ions give acids their characteristic properties. For example, the ionization equation for nitric acid is

 $HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq)$ 

## CAREER LINK

Theoretical chemists may work in any branch of chemistry, proposing and testing explanations for observations. Many years of education and laboratory experience are necessary. To learn about this career,

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Ionization and dissociation are both events in which a compound breaks apart in water, causing the presence of ions in the water. However, there are subtle differences in how these processes occur. Dissociation occurs when water molecules pull the positive and negative ions of an ionic hydroxide (or any soluble ionic compound) apart. The ions dissociate from each other. **Ionization**, however, involves the formation of ions from uncharged molecules. Previously uncharged entities become ionized. Arrhenius likely assumed that the ionization process involved water but did not explain how this occurred.

In summary, ionic compounds dissociate in water; molecular compounds ionize. The chemical equations for these two processes look the same.

#### **Neutralization Reactions**

For an acid-base theory to be useful, it should be able to explain acid-base properties. Let's see how Arrhenius applied his theory to explain the neutralization of hydrochloric acid with sodium hydroxide. Hydrochloric acid conducts electricity very well—much better than some other acids at the same concentration. Arrhenius therefore assumed that it completely ionizes in water, leaving no hydrogen chloride molecules in solution:

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

Similarly, sodium hydroxide completely dissociates into its ions:

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

When these solutions are combined, the ions move about freely and react. When we combine the two equations above and consider how the ions react, we are writing a total ionic equation for the reaction:

 $H^{+}(aq) + Cl^{-}(aq) + Na^{+}(aq) + OH^{-}(aq) \rightarrow H_{2}O(l) + Na^{+}(aq) + Cl^{-}(aq)$ 

The total ionic equation includes some spectator ions. Remember that spectator ions are ions that appear on both sides of the equation and are not involved in the reaction.

 $\mathrm{H^{+}(aq)} + \mathrm{Cl^{-}(aq)} + \mathrm{Na^{+}(aq)} + \mathrm{OH^{-}(aq)} \rightarrow \mathrm{H_{2}O(l)} + \mathrm{Na^{+}(aq)} + \mathrm{Cl^{-}(aq)}$ 

After removing the spectator ions, this equation simplifies to

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

Since acids ionize to produce hydrogen ions, and bases dissociate to release hydroxide ions, we can simplify any neutralization reaction to

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

We can test this idea with the neutralization of hydrochloric acid with aluminum hydroxide (the active ingredient in some antacid tablets).

Balanced chemical equation:

 $3 \text{ HCl}(aq) + \text{Al}(\text{OH})_3(aq) \rightarrow 3 \text{ H}_2\text{O}(l) + \text{AlCl}_3(aq)$ 

Total ionic equation:

3 H<sup>+</sup>(aq) + 3 Cl<sup>-</sup>(aq) +  $\Delta$ l<sup>3+</sup>(aq) + 3 OH<sup>-</sup>(aq)  $\rightarrow$  3 H<sub>2</sub>O(l) +  $\Delta$ l<sup>3+</sup>(aq) + 3 Cl<sup>-</sup>(aq) Net ionic equation:

 $3 \text{ H}^+(aq) + 3 \text{ OH}^-(aq) \rightarrow 3 \text{ H}_2\text{O}(l)$ 

which simplifies to

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

The Arrhenius theory of acids and bases provides a simple and consistent explanation of the properties of acids and bases. However, as with all scientific theories, it does have limitations. For example, some substances have basic properties and yet do not contain hydroxide ions in their chemical formula. Household ammonia cleaner,  $NH_3(aq)$ , for example, has a pH of 11 to 12 and can neutralize acids (**Figure 2**). A different theory of acids and bases explains this observation. You may study this theory in future chemistry courses.

Scientific knowledge changes over time. An essential feature of science is the existence of competing theories to explain the same phenomenon. Multiple competing **ionization** the formation of ions from uncharged molecules

#### LEARNING **TIP**

Dissociation and Ionization Both dissociation and ionization result in the presence of ions in solution. Dissociation separates ions that already exist in the neutral compound.  $M^+X^-(s) \rightarrow M^+(aq) + X^-(aq)$  $\bigoplus \bigoplus \bigoplus$ During ionization, new ions form from a neutral compound.  $HA(aq) \rightarrow H^+(aq) + A^-(aq)$ 



Figure 2 An ammonia solution is basic, with a pH of almost 12.



**Figure 3** Powdered magnesium metal reacts with (a) hydrochloric acid and with (b) ethanoic acid. The foam in test tube (a) indicates that oxygen is produced much more rapidly than in test tube (b).

**strong acid** a substance that ionizes completely in water; strong acids have strong acidic properties (e.g., low pH and vigorous reactivity)

weak acid a substance that only partially ionizes in water; weak acids have weak acidic properties (e.g., moderate pH and mild reactivity) theories do not make science invalid in any way. Rather, the existence of competing theories pushes scientists to test and refine their theories so that they explain as many examples as possible.

### Strong and Weak Acids

The concentration of ethanoic acid (acetic acid) in vinegar is similar to the concentration of the hydrochloric acid that you have used in investigations. Yet vinegar is safe to consume, while handling a comparable solution of hydrochloric acid requires special precautions. Hydrochloric acid also reacts more vigorously with metals (**Figure 3**). Why is there such a difference in the strength of these acids?

According to Arrhenius, the strength of an acid depends on the extent to which it ionizes. Hydrochloric acid is a **strong acid** because it completely ionizes in solution. All of the hydrogen chloride molecules react to form hydrogen ions and chloride ions:

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

This formation of many ions explains why hydrochloric acid is a good conductor of electricity (**Figure 4(a)**). We classify ethanoic acid as a **weak acid** because only a small fraction of its molecules ionize:

$$HC_2H_3O_2(aq) \xrightarrow{(partial ionization)} H^+(aq) + C_2H_3O_2^-(aq)$$

This explains why ethanoic acid is a weak electrolyte and does not conduct electricity as well as hydrochloric acid at the same concentration (**Figure 4(b**)).



**Figure 4** If (a) an ethanoic acid solution has the same concentration as (b) a hydrochloric acid solution, then the hydrochloric acid solution will be a better conductor of electricity.

In general, the strength of an acid, HA(aq), depends on how much it ionizes in aqueous solution:

 $HA(aq) \rightarrow H^+(aq) + A^-(aq)$ 

Strong acids ionize almost completely. Weak acids ionize only partially: about 2 % (Figure 5).



**Figure 5** (a) A strong acid, HA(aq), almost completely ionizes into  $H^+(aq)$  and  $A^-(aq)$ . Virtually no molecules of a strong acid remain in solution. (b) A weak acid, HA(aq), partially ionizes into  $H^+(aq)$  and  $A^-(aq)$ . Most molecules of a weak acid remain intact.

#### LEARNING **TIP**

#### "Strong" Is Not Necessarily "Concentrated"

Be sure that you understand the difference between "strong" (completely ionized or dissociated) and "concentrated" (having a relatively large quantity of solute in a given volume of solution). Similarly, try not to mix up "weak" (only slightly ionized or dissociated) and "dilute" (having a relatively small quantity of solute in a given volume of solution). Table 1 lists some common strong acids and weak acids.

Table 1	Common	Strong	Acids	and	Weak	Acids
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Strong acids	Application	Weak acids	Application
hydrochloric acid, HCl(aq)	<ul> <li>stomach acid</li> <li>used for cleaning or "pickling" steel</li> </ul>	phosphoric acid, $H_3PO_4(aq)$	<ul> <li>rust remover</li> <li>an ingredient in pop</li> </ul>
nitric acid, HNO <sub>3</sub> (aq)	used in the production of fertilizers and rocket fuel	ethanoic acid, $HC_2H_3O_2(aq)$	<ul> <li>the acid in vinegar</li> <li>an ingredient in pickled vegetables</li> </ul>
perchloric acid, HClO <sub>4</sub> (aq)	a powerful bleaching     agent	methanoic acid (formic acid), HCO <sub>2</sub> H(aq)	produced by ants
sulfuric acid, $H_2SO_4(aq)$	<ul> <li>the acid in car batteries</li> <li>used in the production of detergents and plastics</li> </ul>	carbonic acid, $H_2CO_3(aq)$	<ul> <li>makes rain naturally acidic</li> <li>an ingredient in pop</li> </ul>

#### pH AND ACIDITY

You have already learned that the pH is a measure of how acidic or basic a solution is. The pH scale (**Figure 6**) is a numerical scale of all the possible values of pH ranging from 0 to 14. A solution with a pH less than 7 is considered acidic while a solution with a pH greater than 7 is basic. A solution with a pH of 7 is neutral: neither acidic nor basic.

Quantitatively, a change of one pH unit represents a tenfold change in how acidic or basic a solution is. For example, lemon juice, with a pH of 2, is ten times more acidic than pop with a pH of 3. Conversely, aqueous ammonia, with a pH of 11, is ten times more basic than milk of magnesia, with a pH of 10. Two steps along the pH scale represent a  $10 \times 10$  or a hundredfold change in how acidic or basic a solution is. Lemon juice, with a pH of 2, is 100 times more acidic than tomatoes, with a pH of 4. Conversely, a concentrated solution of sodium hydroxide used in drain openers, with pH 14, is  $10 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10 = 10\ 000\ 000\ times$  more basic than water (pH 7).

Living things can tolerate only small changes in pH. Most freshwater fish, for example, thrive in a pH range of 5.5 to 7.5, depending on the species. "Clean" rain can have a pH of about 5.6. Rain is naturally acidic due to the formation of some carbonic acid. Atmospheric pollution, however, can lower the pH of rain to 4.6. This means that acid precipitation is 10 times more acidic than normal rain. This change can devastate aquatic life in fragile ecosystems (**Figure 7**). In Section 5.3 you learned about some other effects of acidic conditions in the environment.



Figure 7 (a) A healthy salamander embryo and (b) a salamander embryo raised in acidic water





#### CAREER LINK

Environmental technicians collect data on many properties of soil and water, including their pH. If you are interested in this career, which generally involves fieldwork,



#### Investigation 10.2.1

Not All Acids Are Created Equal (p. 486)

In this controlled experiment you will predict and explore the reactions of three acids to compare their reactivity.



Figure 8 The cuticle of a human hair

In some cases, however, acidic environments can be beneficial. For example, the outer covering of human hair is called the cuticle and consists of tiny overlapping plates (**Figure 8**). Washing hair with a slightly acidic shampoo or a lemon rinse causes these plates of the cuticle to close tightly around the shaft of hair. This makes each hair strand smoother and less likely to tangle with its neighbours. Most shampoos are slightly acidic for this reason.

## Mini Investigation

#### pH and Dilution

Skills: Planning, Performing, Observing, Communicating

SKILLS A1, A2.4, A3

In this investigation you will observe the effect of dilution on the pH of an acidic solution.

**Equipment and Materials:** chemical safety goggles; lab apron; pH meter; 50 mL graduated cylinder; volumetric pipette; pipette pump or bulb; three 150 mL beakers; hydrochloric acid, HCl(aq) (0.1 mol/L); wash bottle of distilled water

Hydrochloric acid is an irritant. Avoid skin and eye contact. If acid spills in your eyes or on your skin, wash the affected area with plenty of cool water.

- 1. Plan a procedure to prepare 20 mL of a 0.01 mol/L solution of hydrochloric acid, using the equipment and materials listed. Ask your teacher to approve your procedure.
- 2. Put on your chemical safety goggles and lab apron.
- 3. Add 20 mL of 0.1 mol/L hydrochloric acid to a clean, dry beaker.
- 4. Measure the pH of the solution using a pH meter. Record your observations.
- 5. Rinse the electrode of the pH meter with distilled water.
- 6. Proceed with procedure, planned in Step 1, once it is approved by your teacher.
- 7. Measure and record the pH of your solution.
- 8. Use the same procedure to prepare 20 mL of 0.001 mol/L and 20 mL of 0.0001 mol/L hydrochloric acid. Measure and record the pH of each solution.
- 9. Dispose of the solutions as directed by your teacher.
- A. By what factor was acid solution diluted each time?
- B. What effect did each dilution have on the measured pH value?
- C. Based on your observations, predict the pH of a 1.0 imes 10<sup>5</sup> mol/L HCl(aq) solution.  $\blacksquare$

## 10.2 Summary

- According to the Arrhenius theory, acids ionize in water to produce hydrogen ions and bases dissociate in water, resulting in hydroxide ions. Neutralization reactions are reactions of hydrogen ions with hydroxide ions.
- The strength of an acid depends on how much it ionizes. Strong acids ionize completely. Weak acids ionize partially.
- pH is used to communicate the acidity of a solution. As the hydrogen ion concentration increases, the pH of the solution decreases.
- Each step along the pH scale corresponds to a tenfold change in acidity (for example, pH 2 is 10 000 times more acidic than pH 6).

## 10.2 Questions

- 1. Classify these substances as either Arrhenius acids or bases. Justify your choice.
  - (a) HF(aq)
  - (b)  $Ba(OH)_2(aq)$
  - (c)  $H_2SO_4(aq)$
  - (d) NH<sub>4</sub>OH(aq)
- 2. Why are theories often described as being "valid" rather than "correct"? Use the Lavoisier oxygen theory as an example.
- Figure 9 represents acids and related entities at the molecular level. The white spheres represent hydrogen atoms or ions. The coloured spheres represent the other part of the acid. Which diagram best represents each of the following substances? Explain why in each case. KOU TOT (a) hydrochloric acid
  - (b) ethanoic acid
  - (D) Elitation actu
  - (c) hydrogen chloride gas



#### Figure 9

- 4. Explain how an acid can be both weak and concentrated. Use an example to illustrate.
- 6. Write the total ionic and net ionic equations for each of the following reactions: **KU TA C** 
  - (a) hydrobromic acid with potassium hydroxide
  - (b) nitric acid with barium hydroxide
- Imagine that you have two solutions of exactly the same concentration. One is a strong acid and the other is a weak acid. Compare the pH of the two solutions. Why is there a difference? KCU
- 8. (a) Stomach acid has a pH around 2, and orange juice has a pH around 4. How much more acidic is stomach acid than orange juice?
  - (b) Assuming that your stomach is healthy, why is the acidity of orange juice not a health risk?
- 9. What safety precautions should you use when working with strong acids and bases in the laboratory?
- 10. According to the data in Figure 6, approximately how much more acidic is
  - (a) lemon juice than black coffee?
  - (b) black coffee than milk of magnesia?
  - (c) battery acid than pure water at 25 °C?
  - (d) tomatoes than aqueous ammonia 💴

- 11. According to the data in Figure 6, approximately how much more basic is
  - (a) aqueous ammonia than pure water?
  - (b) 1 mol/L NaOH(aq) than milk of magnesia?
  - (c) tomatoes than lemon juice?
  - (d) milk of magnesia than black coffee?
- 12. Figure 10(a) shows the conductivity test for sulfuric acid. A similar result is observed for barium hydroxide.
  - (a) How would Arrhenius explain these observations?
  - (b) Write the chemical equation for the neutralization of sulfuric acid by barium hydroxide. Consult the solubility table (Section 4.6) to determine the state of the ionic product.
  - (c) Figure 10(b) shows the final mixture produced when sulfuric acid is completely neutralized by barium hydroxide. Why is there a difference in conductivity? What would be observed if sodium hydroxide were used instead? Why?



**Figure 10** (a) Sulfuric acid alone is an excellent conductor of electricity, as the lit bulb shows. (b) When sulfuric acid is completely neutralized with barium hydroxide, the resulting mixture does not conduct electricity and the bulb no longer lights up.

- 13. It took several years before Arrhenius's theory of acids and bases became widely accepted. Arrhenius first presented his theory in 1884 while completing his Ph.D. studies in chemistry at the University of Uppsala, Sweden. Initially, his professors were not impressed. In fact, they found his theory so controversial that they gave him the lowest possible passing mark.
  - (a) Research the impact of this rejection on Arrhenius.
  - (b) How did the scientific community finally recognize Arrhenius for his contributions to chemistry?

