8.1 The Nature of Acids and Bases

People first recognized acids as a class of substances that taste sour. Vinegar tastes sour because it is a dilute solution of acetic acid. The sour taste of lemons is caused by citric acid. Bases, sometimes called alkalis, are characterized by their bitter taste and slippery feel. Commercial preparations for unclogging drains are highly basic. Scientists have studied acids and bases for over 200 years and have developed several theories that help explain what acids and bases are and why they behave the way they do. We will examine two acid–base theories: the Arrhenius theory and the Brønsted–Lowry theory.

The Arrhenius Theory of Acids and Bases

Figure 1 In 1903, Svante Arrhenius won a Nobel Prize in Chemistry for his proposal that ionic substances split into charged ions when they dissolve in water.

Arrhenius theory a theory stating that, in an aqueous solution, an acid is a substance that produces hydrogen ions and a base is a substance that produces hydroxide ions

The first person to recognize the essential nature of acids and bases was the Swedish chemist Svante Arrhenius (1859–1927) (**Figure 1**). Arrhenius performed experiments and explained his observations by suggesting that acids produce hydrogen ions, $H^+(aq)$, in aqueous solution. A hydrogen ion is a hydrogen atom without an electron. In essence, a hydrogen ion is a proton. Arrhenius also proposed that bases produce hydroxide ions, $OH^-(aq)$, when they dissolve. This explanation is known as the **Arrhenius theory** of acids and bases.

According to the Arrhenius theory, hydrogen chloride, $HCl(g)$, is an acid because when it dissolves in water it produces hydrogen ions, $H^+(aq)$, and chloride ions, $Cl^-(aq)$. The dissolved hydrogen ions give the solution its acidic properties (for example, its sour taste).

$$HCl(g) \xrightarrow{\text{water}} H^+(aq) + Cl^-(aq)$$

According to the Arrhenius theory, sodium hydroxide, $NaOH(s)$, is a base because when it dissolves in water it dissociates into sodium ions, $Na^+(aq)$, and hydroxide ions, $OH^-(aq)$. The hydroxide ions give the solution its basic (alkaline) properties (for example, its bitter taste and slippery feel).

$$NaOH(s) \xrightarrow{\text{water}} Na^+(aq) + OH^-(aq)$$

The Arrhenius theory was a major step forward in explaining acid–base chemistry. However, this theory is limited because it allows for only one kind of base—compounds containing the hydroxide ion—and it assumes that all acid–base reactions occur in aqueous solutions. Like all theories, Arrhenius's proposal was tentative and subject to change as further investigations produced other evidence. Indeed, later studies showed that basic solutions can also be formed by compounds, such as ammonia, $NH_3(aq)$, that do not contain the hydroxide ion. Chemists continued searching for a theory that explained this observation.

The Brønsted–Lowry Theory of Acids and Bases

Brønsted–Lowry theory a theory stating that an acid is a hydrogen ion (proton) donor and a base is a hydrogen ion (proton) acceptor

A more general explanation of acids and bases was suggested by the Danish chemist Johannes Brønsted (1879–1947) and the English chemist Thomas Lowry (1874–1936) (**Figure 2**). In the **Brønsted–Lowry theory**,

An acid is a hydrogen ion donor.
A base is a hydrogen ion acceptor.

This theory applies to all of the Arrhenius acids and bases, plus some others that are not categorized as acids and bases under the Arrhenius definition.

The Brønsted–Lowry Theory and Acidic Solutions

Hydrofluoric acid, $HF(aq)$, is typically produced by dissolving gaseous hydrogen fluoride, $HF(g)$, in water. The Arrhenius theory predicts that hydrogen ions and fluoride ions will be produced. Experimental evidence suggests, however, that the hydrogen ion is not stable on its own. Rather, the hydrogen ion appears to react with a water molecule. When hydrogen fluoride dissolves in water, therefore, each hydrogen fluoride molecule reacts with a water molecule to form a **hydronium ion**, $H_3O^+(aq)$, and a fluoride ion, $F^-(aq)$ (**Figure 3**). The oxygen atom of the water molecule pulls a hydrogen ion away from the hydrogen fluoride molecule, leaving behind a fluoride ion. Thus, in this reaction, hydrogen fluoride is an acid according to the Brønsted–Lowry theory because it "donates" the proton that bonds with the water molecule to form the hydronium ion. Water is a Brønsted–Lowry base because it "accepts" a proton from the hydrogen fluoride molecule. The water molecule acts as a Brønsted–Lowry base in this reaction because its oxygen atom has lone electron pairs. One of these electron pairs forms a coordinate covalent bond with the "donated" hydrogen ion, forming a hydronium ion.

hydronium ion a water molecule that has accepted a hydrogen ion, H_3O^+

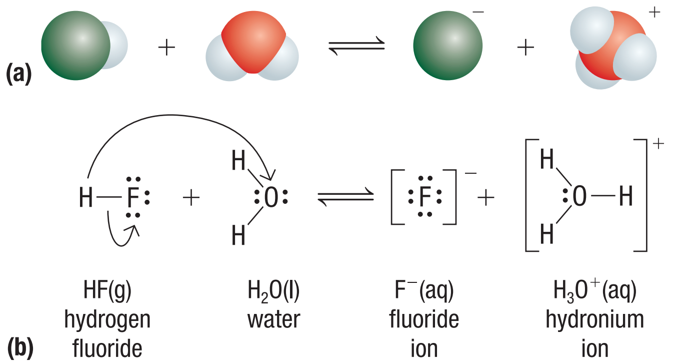

Figure 3 The Brønsted–Lowry theory explaining the reaction of hydrogen fluoride with water can be illustrated as (a) a space-fill representation or (b) Lewis structures.

As Figure 3 illustrates, the reaction of hydrogen fluoride and water is reversible and results in a dynamic equilibrium in an aqueous solution. The dissolved hydronium ions are responsible for the solution's acidic properties.

In general, Brønsted–Lowry bases contain at least one atom with one or more lone electron pairs (most often, O, N, or P).

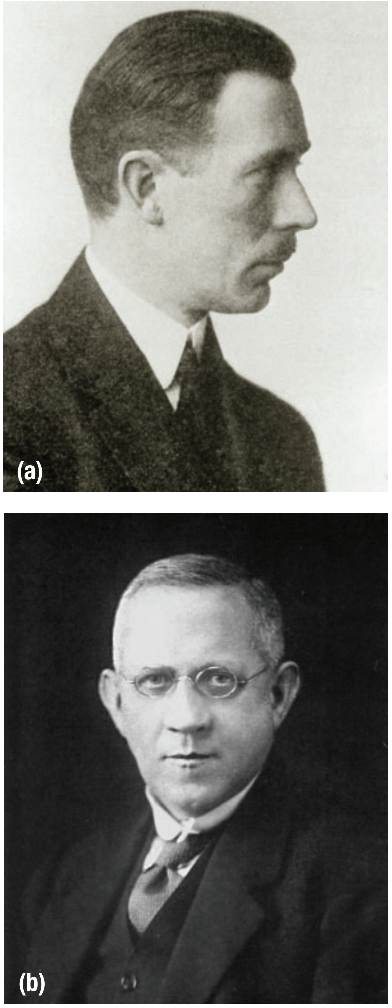

Figure 2 (a) J. Brønsted (1879–1947) and (b) T. Lowry (1874–1936) proposed new acid–base theories centred on hydrogen ion transfer.

The Brønsted–Lowry Theory and Basic Solutions

When gaseous ammonia, $NH_3(g)$, dissolves in water, ammonia molecules react with water molecules, producing a dynamic equilibrium. In this reaction, a water molecule donates a hydrogen ion to the ammonia molecule, forming an ammonium ion, $NH_4^+(aq)$, and a hydroxide ion, $OH^-(aq)$ (**Figure 4**). Thus, the water molecule acts as an acid (a proton donor) and the ammonia acts as a base (a proton acceptor) according to the Brønsted–Lowry theory. The hydroxide ions are responsible for the solution's basic properties.

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

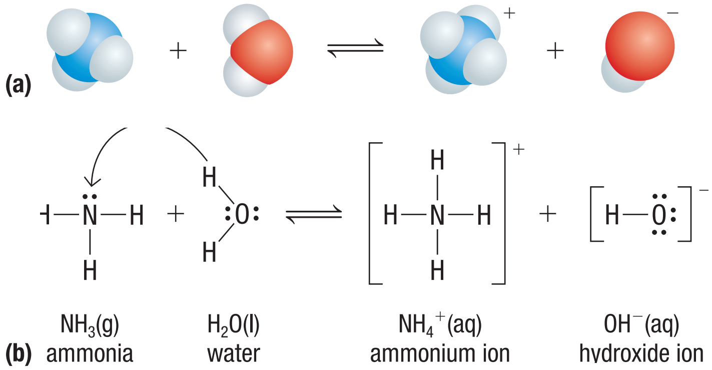

Figure 4 The Brønsted–Lowry theory explaining the reaction of ammonia with water can be illustrated as (a) a space-fill representation or (b) Lewis structures.

Conjugate Acid–Base Pairs

Since acid–base reactions are reversible, a hydrogen ion (proton) transfer may occur in the forward reaction and also in the reverse reaction. Thus, there is a Brønsted–Lowry acid (hydrogen ion donor) and a Brønsted–Lowry base (hydrogen ion acceptor) on each side of the reaction equation. Imagine the equilibrium reaction of a hypothetical acid, HA(aq), with water to form an acidic solution (**Figure 5(a)**). This reaction system is represented by the equation

$$\mathrm{HA(aq)} + \mathrm{H_2O(l)} \rightleftharpoons \mathrm{A^-(aq)} + \mathrm{H_3O^+(aq)}$$

In the forward reaction, the acid molecule donates a hydrogen ion to a water molecule, which acts as a base. This results in the formation of an anion, $A^-(aq)$, and a hydronium ion, $H_3O^+(aq)$. In the reverse reaction, the hydronium ion transfers a hydrogen ion to the $A^-(aq)$ ion. Now the hydronium ion acts as an acid (called a "conjugate acid") and the $A^-(aq)$ ion acts as a base (called a "conjugate base"). In general, a **conjugate acid** is an acid formed when a base accepts a hydrogen ion from an acid. A **conjugate base** is a base formed when an acid loses a hydrogen ion to a base.

conjugate acid the substance that forms when a base, according to the Brønsted–Lowry theory, accepts a hydrogen ion (proton)

conjugate base the substance that forms when an acid loses a hydrogen ion (proton)

Similarly, imagine the equilibrium reaction of a hypothetical base, B(aq), with water to form a basic solution (**Figure 5(b)**).

$$\mathrm{B(aq)} + \mathrm{H_2O(l)} \rightleftharpoons \mathrm{HB^+(aq)} + \mathrm{OH^-(aq)}$$

In the forward reaction, the base molecule takes a hydrogen ion from a water molecule, which acts as an acid. This results in the formation of a cation, $HB^+(aq)$ (the conjugate acid), and a hydroxide ion, $OH^-(aq)$ (the conjugate base).

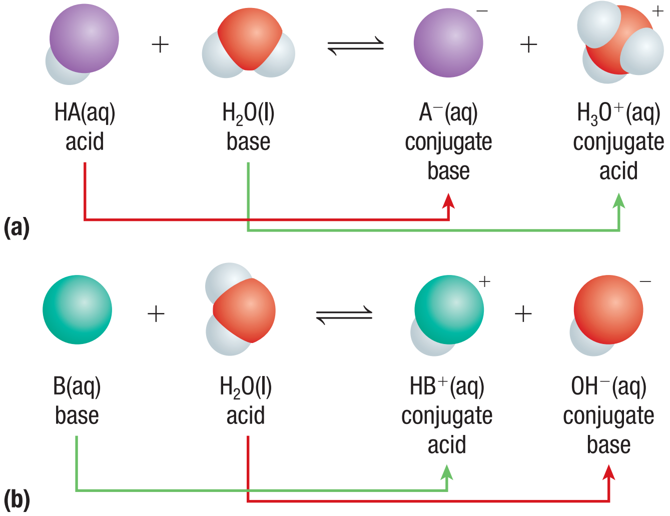

Figure 5 Note the conjugate acid–base pairs in the equations representing the reactions between (a) a hypothetical acid, HA(aq), and water and (b) a hypothetical base, B(aq), and water.

For any acid–base reaction, there will always be one **conjugate acid–base pair** made up of an acid and its conjugate base and another conjugate acid–base pair made up of a base and its conjugate acid. Within each pair, the formulas differ only by a hydrogen ion.

conjugate acid–base pair two substances related to each other by the donating and accepting of a single hydrogen ion

The Brønsted–Lowry Theory and Non-aqueous Reactions

The Arrhenius theory assumes that acid–base reactions occur in aqueous solutions. The Brønsted–Lowry theory is not limited to aqueous solutions because it can be extended to reactions in other states. For example, consider the reaction between gaseous hydrogen chloride and gaseous ammonia:

$$\mathrm{HCl(g)} + \mathrm{NH_3(g)} \rightleftharpoons \mathrm{NH_4Cl(s)}$$

In this reaction, the hydrogen chloride molecule donates a hydrogen ion to the ammonia molecule (**Figure 6**). An ammonium ion and a chloride ion are produced.

These ions form ammonium chloride crystals (**Figure 7**). According to the Arrhenius concept this is not considered an acid–base reaction because neither hydrogen ions nor hydroxide ions are produced. However, according to the Brønsted–Lowry theory it *is* an acid–base reaction: hydrogen chloride is an acid, ammonia is a base, NH_4^+ is a conjugate acid, and Cl^- is a conjugate base.

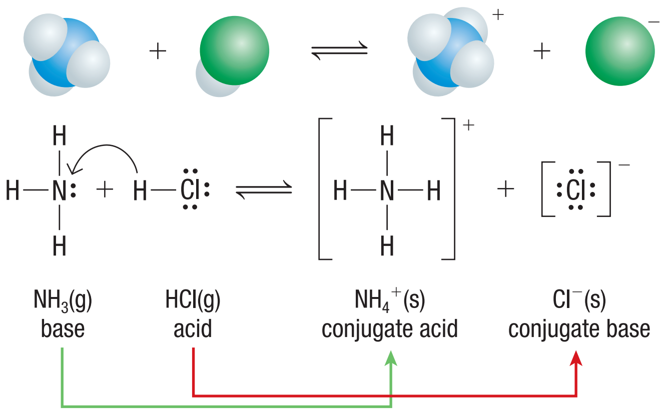

Figure 6 Ammonia reacts with hydrochloric acid to form ammonium ions and chloride ions.

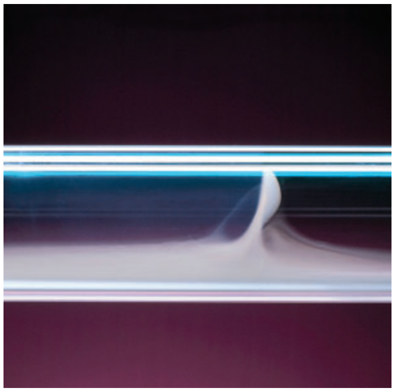

Figure 7 When gaseous hydrogen chloride and ammonia meet in a tube, a white disc of ammonium chloride crystals, $NH_4Cl(s)$, forms.

Amphiprotic (Amphoteric) Substances

Note that a substance can be classified as an acid or base, according to the Brønsted–Lowry theory, only for a specific reaction. A substance may act as an acid in one reaction and a base in another reaction. For example, in the reaction of hydrogen fluoride with water (Figure 3), water acts as a base, but in the reaction of ammonia with water (Figure 4), water acts as an acid. A substance that may act as a Brønsted–Lowry acid in some reactions and as a Brønsted–Lowry base in others is called **amphiprotic** (or **amphoteric**). Both water and the hydrogen carbonate ion, $HCO_3^-(aq)$, are amphiprotic:

$$\underset{\text{base}}{HCO_3^-(aq)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons \underset{\substack{\text{conjugate}\\\text{acid}}}{H_2CO_3(aq)} + \underset{\substack{\text{conjugate}\\\text{base}}}{OH^-(aq)}$$

$$\underset{\text{acid}}{HCO_3^-(aq)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons \underset{\substack{\text{conjugate}\\\text{base}}}{CO_3^{2-}(aq)} + \underset{\substack{\text{conjugate}\\\text{acid}}}{H_3O^+(aq)}$$

amphiprotic (amphoteric) able to donate or accept a hydrogen ion (proton) and thus act as both a Brønsted–Lowry acid and a Brønsted–Lowry base

Tutorial 1 Acid–Base Pairs and Amphiprotic Entities

In this tutorial, you will identify conjugate acid–base pairs and amphiprotic entities in acid–base reactions.

Sample Problem 1: Identifying Conjugate Acid–Base Pairs

Use the Brønsted–Lowry theory to identify the acid, the base, the conjugate acid, and the conjugate base in the reaction represented by the following equation:

$$HC_2H_3O_2(aq) + H_2O(l) \rightarrow H_3O^+(aq) + C_2H_3O_2^-(aq)$$

Solution

Remember that, according to the Brønsted–Lowry theory, an acid donates hydrogen ions and a base accepts them. $HC_2H_3O_2(aq)$ donates a hydrogen ion. Therefore, $HC_2H_3O_2(aq)$ is the acid in this reaction. Its conjugate base is $C_2H_3O_2^-(aq)$. $H_2O(l)$ accepts the hydrogen ion, so $H_2O(l)$ is the base in this reaction. Its conjugate acid is $H_3O^+(aq)$.

$$\underset{\text{acid}}{HC_2H_3O_2(aq)} + \underset{\text{base}}{H_2O(l)} \rightarrow \underset{\substack{\text{conjugate}\\\text{acid}}}{H_3O^+(aq)} + \underset{\substack{\text{conjugate}\\\text{base}}}{C_2H_3O_2^-(aq)}$$

Sample Problem 2: Explaining Amphiprotic Entities

Explain why the hydrogen carbonate ion, $HCO_3^-(aq)$, is amphiprotic, but the fluoride ion, $F^-(aq)$, is not.

Solution

The hydrogen carbonate ion, $HCO_3^-(aq)$, may gain a proton, $H^+(aq)$, to become carbonic acid, $H_2CO_3(aq)$. Alternatively, the hydrogen carbonate ion may lose a proton to become the carbonate ion, $CO_3^{2-}(aq)$. The fluoride ion, $F^-(aq)$, may accept a proton to become a hydrofluoric acid, HF(aq). However, the fluoride ion, $F^-(aq)$, cannot lose a proton since it does not have a proton to lose.

Practice

1. Identify the acid, the base, the conjugate acid, and the conjugate base in the equilibrium reactions represented by the following equations: K/U
   (a) $HCHO_2(aq) + H_2O(l) \rightleftharpoons CHO_2^-(aq) + H_3O^+(aq)$
   (b) $C_6H_5NH_3^+(aq) + H_2O(l) \rightleftharpoons C_6H_5NH_2(aq) + H_3O^+(aq)$
   (c) $H_2CO_3(aq) + OH^-(aq) \rightleftharpoons HCO_3^-(aq) + H_2O(l)$
   (d) $HSO_4^-(aq) + HPO_4^{2-}(aq) \rightleftharpoons H_2PO_4^-(aq) + SO_4^{2-}(aq)$
   (e) $HSO_4^-(aq) + HCl(aq) \rightleftharpoons Cl^-(aq) + H_2SO_4(aq)$
2. Explain why the hydrogen sulfate ion, $HSO_4^-(aq)$, is amphiprotic. K/U

LEARNING **TIP**

Standard Conditions

Unless stated otherwise, conditions in problems in this chapter are SATP: 25 °C and 100 kPa.

The Acid Ionization Constant, K_a

The reaction of a weak acid, HA, with water forms a dynamic equilibrium involving H_3O^+ and a conjugate base, A^-:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq).$$

We may write an equilibrium law equation for this reaction. The equilibrium constant, K_a, is called the **acid ionization constant**. K_a is used for reactions in which an acid, HA(aq), reacts with water to form a conjugate base, $A^-(aq)$.

acid ionization constant (K_a) the equilibrium constant for the ionization of an acid; also called the acid dissociation constant

$$K_a = \frac{[H_3O^+(aq)][A^-(aq)]}{[H_2O(l)][HA(aq)]}$$

We can simplify this equation in two ways:

First, we know that water plays an important role in causing the acid to ionize. As you read earlier, hydrogen ions, $H^+(aq)$, do not exist as individual ions in aqueous solution; rather, every hydrogen ion is bound to a water molecule as a hydronium ion, $H_3O^+(aq)$. However, for convenience, we can write the reaction equation as though the acid, HA(aq), simply separates into $H^+(aq)$ and $A^-(aq)$ ions:

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

Second, in Chapter 7 you learned that if the concentration of a chemical substance remains constant during a reaction, that substance is omitted from the equilibrium law equation. In a dilute solution, we can assume that the concentration of liquid water remains essentially constant when an acid is dissolved. Thus, $H_2O(l)$ is omitted from the equilibrium law equation.

The equilibrium law equation, with these modifications included, is called the acid ionization constant equation and is written as follows:

$$K_a = \frac{[H^+(aq)][A^-(aq)]}{[HA(aq)]} \text{ where } [H^+(aq)] \text{ is equivalent to } [H_3O^+(aq)]$$

Table 1 shows acid ionization constants (K_a values) for several acids.

Table 1 Some Acid Ionization Constants

Acid	**Acid ionization constant, K_a**
hydrocyanic, HCN(aq)	6.2×10^{-10}
benzoic, $HC_6H_5CO_2(aq)$	6.3×10^{-5}
propanoic, $HC_3H_5O_2(aq)$	1.3×10^{-5}
ethanoic (acetic), $HC_2H_3O_2(aq)$	1.8×10^{-5}
hydrofluoric, HF(aq)	6.6×10^{-4}
nitrous, $HNO_2(aq)$	4.6×10^{-4}
methanoic (formic), $HCHO_2(aq)$	1.8×10^{-4}

Tutorial 2 / Writing Acid Ionization Constant Equations

In this tutorial, you will write acid ionization constant equations for different reactions.

Sample Problem 1: Writing K_a Equations

(a) Write the acid ionization constant equation for the equilibrium reaction of nitrous acid, $HNO_2(aq)$, with water.

(b) Write the acid ionization constant equation for the equilibrium reaction of ethanoic acid and water:

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

Solution

(a) First write the equilibrium reaction equation for the ionization of nitrous acid in water. You may write the equation with H1(aq) or H3O1(aq). Both reaction equations with their corresponding ionization constant equations are shown below. Both are correct. Remember not to include the concentration of H20(l) in acid ionization constant equations.

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$$

$$K_a = \frac{[H_3O^+(aq)][NO_2^-(aq)]}{[HNO_2(aq)]}$$

or

$$HNO_2(aq) \rightleftharpoons H^+(aq) + NO_2^-(aq)$$

$$K_a = \frac{[H^+(aq)][NO_2^-(aq)]}{[HNO_2(aq)]}$$

(b) $$K_a = \frac{[H^+(aq)][C_2H_3O_2^-(aq)]}{[HC_2H_3O_2(aq)]}$$

Practice

1. Write acid ionization constant equations for the following acids at equilibrium: K/U
   (a) hydrocyanic acid, HCN(aq)
   (b) nitrous acid, $HNO_2(aq)$
   (c) $HSO_4^-(aq)$

A Competition for Protons

Recall that, in the general equation for the reaction of an acid with water, there are always two bases:

$$\underset{\text{acid}}{HA(aq)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons \underset{\substack{\text{conjugate}\\\text{acid}}}{H_3O^+(aq)} + \underset{\substack{\text{conjugate}\\\text{base}}}{A^-(aq)}$$

It is important to note that these two bases, $H_2O(l)$ and $A^-(aq)$, compete for the hydrogen ion. If H_2O has a much greater affinity for H^+ than does A^- (if it is a stronger base), the equilibrium position will be far to the right. Most of the dissolved acid will be in the ionized form, $A^-(aq)$. Conversely, if A^- is a much stronger base than H_2O, then the equilibrium position will lie far to the left. As a result, most of the dissolved acid will be present at equilibrium as HA(aq) molecules.

Note that, since these equations represent equilibrium reaction systems, calling the entities on the left of the arrow "acid" and "base" and the entities on the right "conjugate acid" and "conjugate base" is arbitrary. It is equally correct to call the entities on the right of the arrow "base" and "acid" and the entities on the left "conjugate base" and "conjugate acid."

8.1 Review

Summary

- According to the Arrhenius theory, in aqueous solution an acid produces hydrogen ions, H^+, and a base produces hydroxide ions, OH^-.
- According to the Brønsted–Lowry theory, an acid is a hydrogen ion (proton) donor and a base is a hydrogen ion acceptor.
- When an acid, HA, reacts with water, the water acts as a base and forms a conjugate acid, H_3O^+. The acid forms a conjugate base, A^-, according to the equation

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

- The acid equilibrium constant, K_a, is represented by

$$K_a = \frac{[H_3O^+(aq)][A^-(aq)]}{[HA(aq)]}, \text{ which may be simplified as } K_a = \frac{[H^+(aq)][A^-(aq)]}{[HA(aq)]}$$

UNIT TASK BOOKMARK

In the Unit Task outlined on page 582 you will investigate a consumer product that is acidic or basic. You may use the information on the nature of acids and bases in this section as you work on the Unit Task.

Questions

1. Define or illustrate the meaning of the following terms: K/U
   (a) K_a
   (b) amphiprotic
   (c) hydronium ion
   (d) hydroxide ion
   (e) conjugate acid
   (f) conjugate base
2. How does the hydrogen ion concentration compare with the hydroxide ion concentration if a solution is
   (a) neutral?
   (b) acidic?
   (c) basic? K/U
3. Differentiate between the following: K/U
   (a) an Arrhenius acid and an Arrhenius base
   (b) a Brønsted–Lowry acid and a Brønsted–Lowry base
4. Write the equilibrium equation for the reaction of each of the following substances in water. Include hydronium ions in your equations. K/U
   (a) HF
   (b) HNO_2
   (c) HCO_3^-
   (d) HCN
5. Create a table with the following column headings: Substance, Arrhenius theory, and Brønsted–Lowry theory. Complete the table with each of the substances listed, stating whether each is an acid, a base, or both under the two acid–base theories. Explain your answers. K/U C
   (a) $NH_4^+(aq)$
   (b) $NH_3(aq)$
   (c) $H_2O(l)$
   (d) $C_2H_3O_2^-(aq)$
   (e) $H_3PO_4(aq)$
   (f) $Ca(OH)_2(aq)$
   (g) $HCl(aq)$
   (h) $H_3O^+(aq)$
   (i) $HC_2H_3O_2(aq)$
   (j) $H_2PO_4^-(aq)$
6. Identify the acid, its conjugate base, the base, and its conjugate acid in the equilibrium reaction systems represented by the following equations: K/U
   (a) $HNO_2(aq) + H_2O(l) \rightleftharpoons NO_2^-(aq) + H_3O^+(aq)$
   (b) $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
7. Complete each equilibrium equation and then identify the acid, base, conjugate acid, conjugate base, and all amphiprotic entities. K/U C
   (a) $H_3PO_4(aq) + NH_3(aq) \rightleftharpoons$
   (b) $HCO_2H(aq) + CN^-(aq) \rightleftharpoons$
8. Write acid equilibrium constant equations for each of the following acids: K/U
   (a) $HF(aq)$
   (b) $HCO_3^-(aq)$
   (c) $HC_4H_7O_2(aq)$
9. For each of the following naturally occurring acids and bases, write the Brønsted–Lowry equation for the reaction with water and identify the acids and bases: K/U A
   (a) methanoic acid (formic acid), $HCHO_2(l)$, produced by ants
   (b) atropine, $C_{17}H_{23}NO_3(aq)$, produced by the belladonna plant
   (c) sodium hydrogen carbonate, $NaHCO_3(s)$, a mineral found in some types of rock
10. A student in your class made the following statement: "All substances that are acids based on the Arrhenius theory are also acidic using the Brønsted–Lowry theory." Do you agree or disagree with this statement? Explain. K/U