Reactions in Aqueous Solutions I: Acids, Bases, and Salts

10

Many foods and other household items contain weak acids, weak bases, and salts.

OUTLINE

OBJECTIVES

After you have studied this chapter, you should be able to

- *Describe the Arrhenius theory of acids and bases*

- *Describe hydrated hydrogen ions*

- *Describe the Brønsted–Lowry theory of acids and bases*

- *List properties of aqueous solutions of acids*

- *List properties of aqueous solutions of bases*

- *Arrange binary acids in order of increasing strength*

- *Arrange ternary acids in order of increasing strength*

- *Describe the Lewis theory of acids and bases*

- *Complete and balance equations for acid–base reactions*

- *Define acidic and basic salts*

- *Explain amphoterism*

- *Describe methods for preparing acids*

In technological societies, acids, bases, and salts are indispensable compounds. Table 4-13 lists the 16 such compounds that were included in the top 50 chemicals produced in the United States in 1997. The production of H_2SO_4 (number 1) was more than twice as great as the production of lime (number 2). Sixty-five percent of the H_2SO_4 is used in the production of fertilizers.

Many acids, bases, and salts occur in nature and serve a wide variety of purposes. For instance, your "digestive juice" contains approximately 0.10 mole of hydrochloric acid per liter. Human blood and the aqueous components of most cells are mildly acidic. The liquid in your car battery is approximately 40% H_2SO_4 by mass. Baking soda is a salt of carbonic acid. Sodium hydroxide, a base, is used in the manufacture of soaps, paper, and many other chemicals. "Drāno" is solid NaOH that contains some aluminum chips. Sodium chloride is used to season food and as a food preservative. Calcium chloride is used to melt ice on

You will encounter many of these in your laboratory work.

Left, Many common household liquids are acidic, including soft drinks, vinegar, and fruit juices. *Right*, Most cleaning materials are basic.

highways and in the emergency treatment of cardiac arrest. Several ammonium salts are used as fertilizers. Many organic acids (carboxylic acids) and their derivatives occur in nature. Acetic acid is present in vinegar; the sting of an ant bite is due to formic acid. Amino acids are the building blocks of proteins, which are important materials in the bodies of animals, including humans. Amino acids are carboxylic acids that also contain basic groups derived from ammonia. The pleasant odors and flavors of ripe fruit are due in large part to the presence of esters (Chapter 27), which are formed from the acids in unripe fruit.

10-1 PROPERTIES OF AQUEOUS SOLUTIONS OF ACIDS AND BASES

Aqueous solutions of most **protonic acids** (those containing acidic hydrogen atoms) exhibit certain properties, which are properties of hydrated hydrogen ions in aqueous solution.

1. They have a sour taste. Pickles are usually preserved in vinegar, a 5% solution of acetic acid. Many pickled condiments contain large amounts of sugar so that the taste of acetic acid is partially masked by the sweet taste of sugar. Lemons contain citric acid, which is responsible for their characteristic sour taste.

2. They change the colors of many indicators (highly colored dyes). Acids turn blue litmus red, and cause bromthymol blue to change from blue to yellow.

3. Nonoxidizing acids react with metals above hydrogen in the activity series (Section 4-8, part 2) to liberate hydrogen gas, H_2. (HNO_3, a common oxidizing acid, reacts with metals to produce nitrogen oxides, not H_2.)

4. They react with (neutralize) metal oxides and metal hydroxides to form salts and water (Section 4-9, part 1).

5. They react with salts of weaker or more volatile acids to form the weaker or more volatile acid and a new salt.

6. Aqueous solutions of acids conduct an electric current because they are totally or partly ionized.

Caution: We should *never* try to identify a substance by taste. You have, however, probably experienced the sour taste of acetic acid in vinegar or citric acid in foods that contain citrus fruits.

The indicator bromthymol blue is yellow in acidic solution and blue in basic solution.

Aqueous solutions of most bases also exhibit certain properties, which are due to the hydrated hydroxide ions present in aqueous solutions of bases.

1. They have a bitter taste.
2. They have a slippery feeling. Soaps are common examples; they are mildly basic. A solution of household bleach feels very slippery because it is quite basic.
3. They change the colors of many indicators: litmus changes from red to blue, and bromthymol blue changes from yellow to blue, in bases.
4. They react with (neutralize) acids to form salts and, in most cases, water.
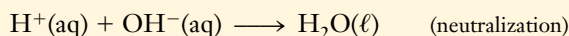5. Their aqueous solutions conduct an electric current because they are dissociated or ionized.

10-2 THE ARRHENIUS THEORY

This is an extremely important idea.

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 4.7, Acids, and Screen 4.8, Bases.

In 1680, Robert Boyle noted that acids (1) dissolve many substances, (2) change the colors of some natural dyes (indicators), and (3) lose their characteristic properties when mixed with alkalis (bases). By 1814, J. Gay-Lussac concluded that acids *neutralize* bases and that the two classes of substances should be defined in terms of their reactions with each other.

In 1884, Svante Arrhenius (1859–1927) presented his theory of electrolytic dissociation, which resulted in the Arrhenius theory of acid–base reactions. In his view,

> an **acid** is a substance that contains hydrogen and produces H^+ in aqueous solution. A **base** is a substance that contains the OH (hydroxyl) group and produces hydroxide ions, OH^-, in aqueous solution.

Neutralization is defined as the combination of H^+ ions with OH^- ions to form H_2O molecules.

We now know that all ions are hydrated in aqueous solution.

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(\ell) \qquad \text{(neutralization)}$$

Review Sections 4-2, 4-9, part 1, 6-7, and 6-8.

The Arrhenius theory of acid–base behavior satisfactorily explained reactions of *protonic acids* with metal hydroxides (hydroxy bases). It was a significant contribution to chemical thought and theory in the latter part of the nineteenth century. The Arrhenius model of acids and bases, although limited in scope, led to the development of more general theories of acid–base behavior. They will be considered in later sections.

10-3 THE HYDRONIUM ION (HYDRATED HYDROGEN ION)

The most common isotope of hydrogen, ^1_1H, has no neutrons. Thus, $^1_1H^+$ is a bare proton. In discussions of acids and bases, we use the terms "hydrogen ion," "proton," and "H^+" interchangeably.

Although Arrhenius described H^+ ions in water as bare ions (protons), we now know that they are hydrated in aqueous solution and exist as $H^+(H_2O)_n$, in which n is some small integer. This is due to the attraction of the H^+ ions, or protons, for the oxygen end ($\delta-$) of water molecules. Although we do not know the extent of hydration of H^+ in most solu-

tions, we usually represent the hydrated hydrogen ion as the **hydronium ion,** H_3O^+, or $H^+(H_2O)_n$, in which $n = 1$.

> The hydrated hydrogen ion is the species that gives aqueous solutions of acids their characteristic acidic properties.

Whether we use the designation $H^+(aq)$ or H_3O^+, we always mean the hydrated hydrogen ion.

$$H^+ + :\ddot{O}-H \longrightarrow H-\ddot{O}-H^+$$
$$\qquad\quad | \qquad\qquad\quad |$$
$$\qquad\quad H \qquad\qquad\quad H$$
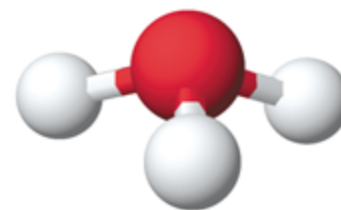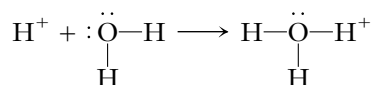
Hydronium ion, H_3O^+.
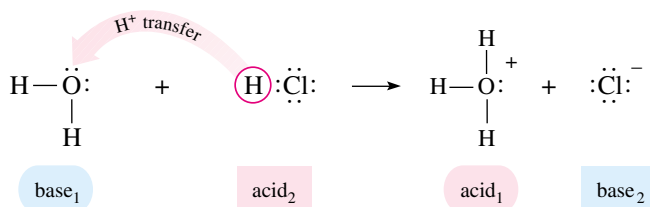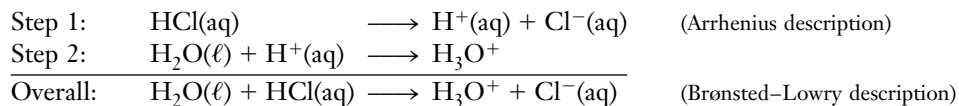
10-4 THE BRØNSTED–LOWRY THEORY

In 1923, J. N. Brønsted (1879–1947) and T. M. Lowry (1874–1936) independently presented logical extensions of the Arrhenius theory. Brønsted's contribution was more thorough than Lowry's, and the result is known as the **Brønsted theory** or the **Brønsted–Lowry theory.**

> An **acid** is defined as a *proton donor* (H^+) and a **base** is defined as a *proton acceptor*.

These definitions are sufficiently broad that any hydrogen-containing molecule or ion capable of releasing a proton, H^+, is an acid, whereas any molecule or ion that can accept a proton is a base. (In the Arrhenius theory of acids and bases, only substances that contain the OH^- group would be called bases.)

> An acid–base reaction is the transfer of a proton from an acid to a base.

Thus, the complete ionization of hydrogen chloride, HCl, a *strong* acid, in water is an acid–base reaction in which water acts as a base or proton acceptor.

Step 1:	$HCl(aq)$	$\longrightarrow$ $H^+(aq) + Cl^-(aq)$	(Arrhenius description)
Step 2:	$H_2O(\ell) + H^+(aq)$	$\longrightarrow H_3O^+$	
Overall:	$H_2O(\ell) + HCl(aq)$	$\longrightarrow H_3O^+ + Cl^-(aq)$	(Brønsted–Lowry description)

The Brønsted–Lowry theory is especially useful for reactions in aqueous solutions. It is widely used in medicine and in the biological sciences.

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 17.2, Brønsted Acids and Bases.

Remember that in this text we use red to indicate acids and blue to indicate bases.

$$H-\ddot{O}: \quad + \quad (H):\ddot{C}l: \quad \longrightarrow \quad H-\ddot{O}:^+ \quad + \quad :\ddot{C}l:^-$$

base₁ · acid₂ · acid₁ · base₂

Various measurements (electrical conductivity, freezing point depression, etc.) indicate that HF is only *slightly* ionized in water.

The ionization of hydrogen fluoride, a *weak* acid, is similar, but it occurs to only a slight extent, so we use a double arrow to indicate that it is reversible.

$$H_2O(\ell) \quad + \quad HF(aq) \quad \rightleftharpoons \quad H_3O^+ \quad + \quad F^-(aq)$$

$$\text{base}_1 \qquad\qquad \text{acid}_2 \qquad\qquad \text{acid}_1 \qquad \text{base}_2$$

The double arrow is used to indicate that the reaction occurs in both the forward and the reverse directions.

We use rectangles to indicate one conjugate acid–base pair and ovals to indicate the other pair.
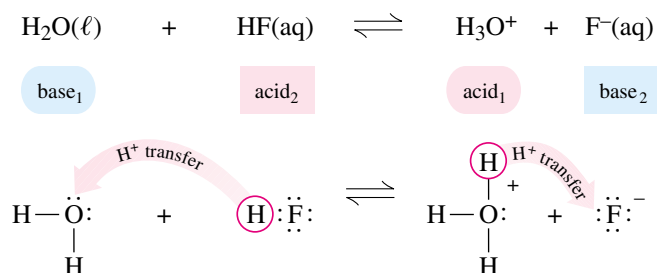
We can describe Brønsted–Lowry acid–base reactions in terms of **conjugate acid–base pairs.** These are two species that differ by a proton. In the preceding equation, HF (acid$_2$) and F$^-$ (base$_2$) are one conjugate acid–base pair, and H$_2$O (base$_1$) and H$_3$O$^+$(acid$_1$) are the other pair. The members of each conjugate pair are designated by the same numerical subscript. In the forward reaction, HF and H$_2$O act as acid and base, respectively. In the reverse reaction, H$_3$O$^+$ acts as the acid, or proton donor, and F$^-$ acts as the base, or proton acceptor.

It makes no difference which conjugate acid–base pair, HF and F$^-$ or H$_3$O$^+$ and H$_2$O, is assigned the subscripts 1 and 2.

✔ Problem-Solving Tip: *Conjugate Acid-Base Pairs*

When the *weak* acid, HF, dissolves in water, the HF molecules give up some H$^+$ ions that can be accepted by either of two bases, F$^-$ or H$_2$O. The fact that HF is only slightly ionized tells us that F$^-$ is a stronger base than H$_2$O. When the *strong* acid, HCl, dissolves in water, the HCl molecules give up H$^+$ ions that can be accepted by either of two bases, Cl$^-$ or H$_2$O. The fact that HCl is completely ionized in dilute aqueous solution tells us

F$^-$ is a stronger base than H$_2$O. H$_2$O is a stronger base than Cl$^-$. F$^-$ is therefore a stronger base than Cl$^-$.

that Cl^- is a weaker base than H_2O. Thus, the weaker acid, HF, has the stronger conjugate base, F^-. The stronger acid, HCl, has the weaker conjugate base, Cl^-. We can generalize:

The stronger the acid, the weaker is its conjugate base; the weaker the acid, the stronger is its conjugate base.

"Strong" and "weak," like many other adjectives, are used in a relative sense. We do not mean to imply that the fluoride ion, F^-, is a strong base compared with species such as the hydroxide ion, OH^-. We mean that *relative to the anions of strong acids*, which are very weak bases, F^- is a much stronger base.

Ammonia acts as a weak Brønsted–Lowry base, and water acts as an acid in the ionization of aqueous ammonia.

Be careful to avoid confusing *solubility in water* and *extent of ionization.* They are not necessarily related. Ammonia is very *soluble* in water (≈15 mol/L at 25°C). In 0.10 M solution, NH_3 is only 1.3% ionized and 98.7% nonionized.

$$NH_3(aq) \; + \; H_2O(\ell) \; \rightleftharpoons \; NH_4{}^+(aq) \; + \; OH^-(aq)$$

base$_1$ acid$_2$ acid$_1$ base$_2$
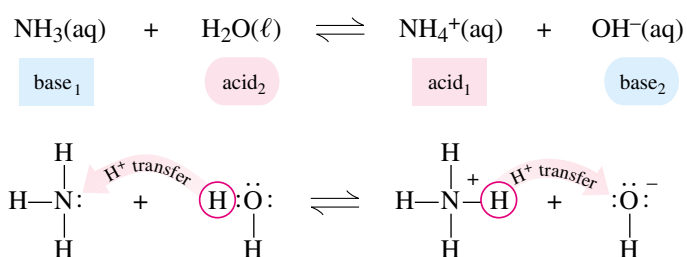
As we see in the reverse reaction, ammonium ion, $NH_4{}^+$, is the conjugate acid of NH_3. The hydroxide ion, OH^-, is the conjugate base of water. In three dimensions, the molecular structures are

Trigonal pyramidal molecule   Angular molecule   Tetrahedral ion   Linear ion
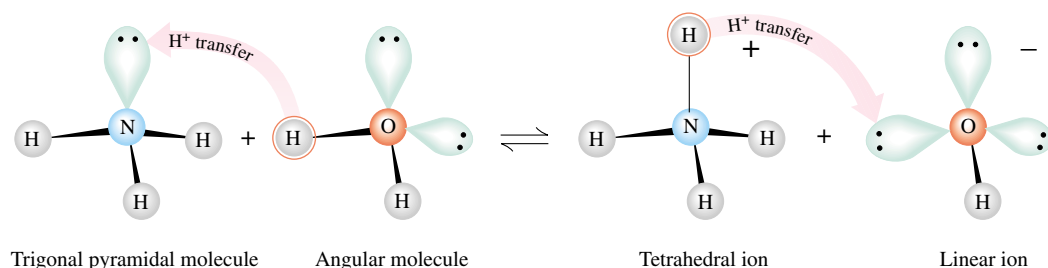
Water acts as an acid (H^+ donor) in its reaction with NH_3, whereas it acts as a base (H^+ acceptor) in its reactions with HCl and with HF.

Whether water acts as an acid or as a base depends on the other species present.
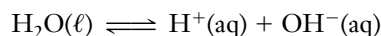
10-5   THE AUTOIONIZATION OF WATER

Careful measurements show that pure water ionizes ever so slightly to produce equal numbers of hydrated hydrogen ions and hydroxide ions.
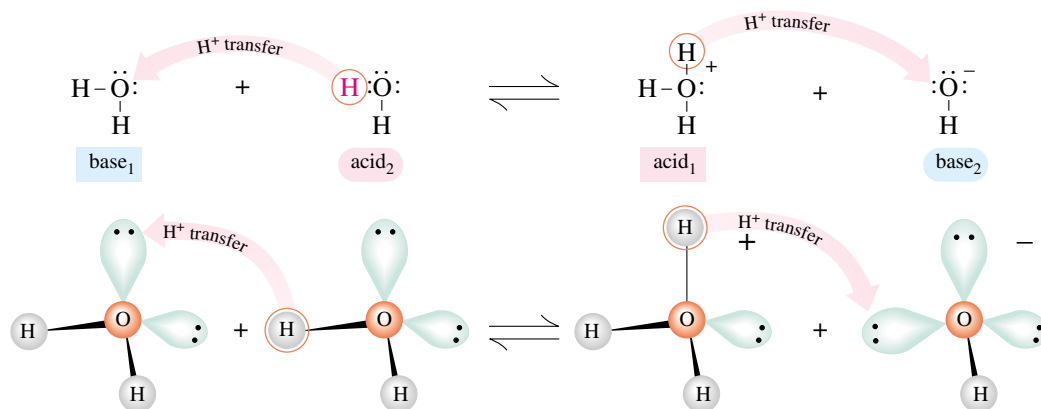
See the *Saunders Interactive General Chemistry CD-ROM,* Screen 17.3, Acid–Base Properties of Water.

In simplified notation, we represent this reaction as

$$H_2O(\ell) \rightleftharpoons H^+(aq) + OH^-(aq)$$

This **autoionization** (self-ionization) of water is an acid–base reaction according to the Brønsted–Lowry theory. One H_2O molecule (the acid) donates a proton to another H_2O molecule (the base). The H_2O molecule that donates a proton becomes an OH^- ion, the conjugate base of water. The H_2O molecule that accepts a proton becomes an H_3O^+ ion. Examination of the reverse reaction (right to left) shows that H_3O^+ (an acid) donates a proton to OH^- (a base) to form two H_2O molecules. One H_2O molecule behaves as an acid and the other acts as a base in the autoionization of water. Water is said to be **amphiprotic;** that is, H_2O molecules can both donate and accept protons.

As we saw in Section 4-9, part 1, H_3O^+ and OH^- ions combine to form nonionized water molecules when strong acids and strong soluble bases react to form soluble salts and water. The reverse reaction, the autoionization of water, occurs only slightly, as expected.

The prefix "amphi-" means "of both kinds." "Amphiprotism" refers to amphoterism by accepting and donating a proton in different reactions (see Section 10-6).

10-6   AMPHOTERISM

As we have seen, whether a particular substance behaves as an acid or as a base depends on its environment. Earlier we described the amphiprotic nature of water. **Amphoterism** is a more general term that describes the ability of a substance to react either as an acid or as a base. *Amphiprotic behavior* describes the cases in which substances exhibit amphoterism by accepting and by donating a proton, H^+. Several *insoluble* metal hydroxides are amphoteric; that is, they react with acids to form salts and water, but they also dissolve in and react with excess strong bases.

Aluminum hydroxide is a typical amphoteric metal hydroxide. Its behavior as a *base* is illustrated by its reaction with nitric acid to form a *normal salt.* The balanced formula unit, total ionic, and net ionic equations for this reaction are, respectively:

Everyday Salts of Ternary Acids

You may have encountered some salts of ternary acids without even being aware of them. For example, the iron in many of your breakfast cereals and breads may have been added in the form of iron(II) sulfate, $FeSO_4$, or iron(II) phosphate, $Fe_3(PO_4)_2$; the calcium in these foods often comes from the addition of calcium carbonate, $CaCO_3$. Fruits and vegetables keep fresh longer after an application of sodium sulfite, Na_2SO_3, and sodium hydrogen sulfite, $NaHSO_3$. Restaurants also use these two sulfites to keep their salad bars more appetizing. The red color of fresh meat is maintained for much longer by the additives sodium nitrate, $NaNO_3$, and sodium nitrite, $NaNO_2$. Sodium phosphate, Na_3PO_4, is used to prevent metal ion flavors and to control acidity in some canned goods.

Many salts of ternary acids are used in medicine. Lithium carbonate, Li_2CO_3, has been used successfully to combat severe jet lag. Lithium carbonate is also useful in the treatment of mania, depression, alcoholism, and schizophrenia. Magnesium sulfate, $MgSO_4$, sometimes helps to prevent convulsions during pregnancy and to reduce the solubility of toxic barium sulfate in internally administered preparations consumed before gastrointestinal X-ray films are taken.

Other salts of ternary acids that you may find in your home include potassium chlorate, $KClO_3$, in matches as an oxidizing agent and oxygen source; sodium hypochlorite, $NaClO$, in bleaches and mildew removers; and ammonium carbonate, $(NH_4)_2CO_3$, which is the primary ingredient in smelling salts. Limestone and marble are calcium carbonate; gypsum and plaster of Paris are primarily calcium sulfate, $CaSO_4$. Fireworks get their brilliant colors from salts such as barium
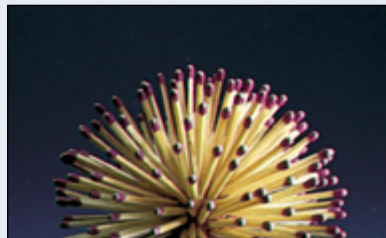
The tips of "strike anywhere" matches contain tetraphosphorus trisulfide, red phosphorus, and potassium chlorate. Friction converts kinetic energy into heat, which initiates a spontaneous reaction.
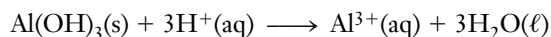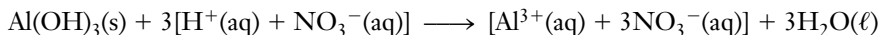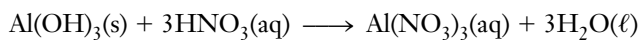
$$P_4S_3(s) + 8O_2 \longrightarrow P_4O_{10}(s) + 3SO_2(g)$$
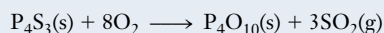
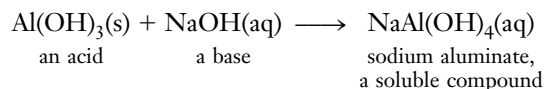*The thermal decomposition of $KClO_3$ provides additional oxygen for this reaction.*

nitrate, $Ba(NO_3)_2$, which imparts a green color; strontium carbonate, $SrCO_3$, which gives a red color; and copper(II) sulfate, $CuSO_4$, which produces a blue color. Should your fireworks get out of hand and accidentally start a fire, the ammonium phosphate, $(NH_4)_3PO_4$, sodium hydrogen carbonate, $NaHCO_3$, and potassium hydrogen carbonate, $KHCO_3$, in your ABC dry fire extinguisher will come in handy.

An unexpected place to find ternary acid salts is in your long-distance phone bills; nitrates, NO_3^-, are cheaper than day rates.
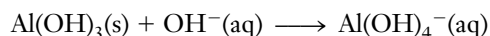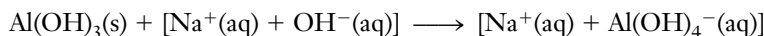
Ronald DeLorenzo
Middle Georgia College

$$Al(OH)_3(s) + 3HNO_3(aq) \longrightarrow Al(NO_3)_3(aq) + 3H_2O(\ell)$$

$$Al(OH)_3(s) + 3[H^+(aq) + NO_3^-(aq)] \longrightarrow [Al^{3+}(aq) + 3NO_3^-(aq)] + 3H_2O(\ell)$$

$$Al(OH)_3(s) + 3H^+(aq) \longrightarrow Al^{3+}(aq) + 3H_2O(\ell)$$

When an excess of a solution of any strong base, such as NaOH, is added to solid aluminum hydroxide, the $Al(OH)_3$ acts as an acid and dissolves. The equation for the reaction is usually written

All hydroxides containing small, highly charged metal ions are insoluble in water.

$$\underset{\text{an acid}}{Al(OH)_3(s)} + \underset{\text{a base}}{NaOH(aq)} \longrightarrow \underset{\substack{\text{sodium aluminate,} \\ \text{a soluble compound}}}{NaAl(OH)_4(aq)}$$

The total ionic and net ionic equations are

$$Al(OH)_3(s) + [Na^+(aq) + OH^-(aq)] \longrightarrow [Na^+(aq) + Al(OH)_4^-(aq)]$$

$$Al(OH)_3(s) + OH^-(aq) \longrightarrow Al(OH)_4^-(aq)$$

TABLE 10-1	Amphoteric Hydroxides	
Metal or Metalloid ions	**Insoluble Amphoteric Hydroxide**	**Complex Ion Formed in an Excess of a Strong Base**
Be^{2+}	$Be(OH)_2$	$[Be(OH)_4]^{2-}$
Al^{3+}	$Al(OH)_3$	$[Al(OH)_4]^-$
Cr^{3+}	$Cr(OH)_3$	$[Cr(OH)_4]^-$
Zn^{2+}	$Zn(OH)_2$	$[Zn(OH)_4]^{2-}$
Sn^{2+}	$Sn(OH)_2$	$[Sn(OH)_3]^-$
Sn^{4+}	$Sn(OH)_4$	$[Sn(OH)_6]^{2-}$
Pb^{2+}	$Pb(OH)_2$	$[Pb(OH)_4]^{2-}$
As^{3+}	$As(OH)_3$	$[As(OH)_4]^-$
Sb^{3+}	$Sb(OH)_3$	$[Sb(OH)_4]^-$
Si^{4+}	$Si(OH)_4$	SiO_4^{4-} and SiO_3^{2-}
Co^{2+}	$Co(OH)_2$	$[Co(OH)_4]^{2-}$
Cu^{2+}	$Cu(OH)_2$	$[Cu(OH)_4]^{2-}$

Generally, elements of intermediate electronegativity form amphoteric hydroxides. Those of high and low electronegativity form acidic and basic "hydroxides," respectively.

Other amphoteric metal hydroxides undergo similar reactions.

Table 10-1 contains lists of the common amphoteric hydroxides. Three are hydroxides of metalloids, As, Sb, and Si, which are located along the line that divides metals and nonmetals in the periodic table.

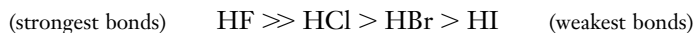## 10-7 STRENGTHS OF ACIDS

Binary Acids

The ease of ionization of binary protonic acids depends on both (1) the ease of breaking H—X bonds and (2) the stability of the resulting ions in solution. Let us consider the relative strengths of the Group VIIA hydrohalic acids. Hydrogen fluoride ionizes only slightly in dilute aqueous solutions.

A *weak* acid may be very reactive. For example, HF dissolves sand and glass. The equation for its reaction with sand is

$SiO_2(s) + 4HF(g) \longrightarrow$
$\qquad SiF_4(g) + 2H_2O(\ell)$

The reaction with glass and other silicates is similar. These reactions are *not* related to acid strength; none of the three *strong* hydrohalic acids— HCl, HBr, or HI—undergoes such a reaction.

$$HF(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + F^-(aq)$$
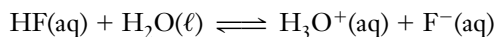
HCl, HBr, and HI, however, ionize completely or nearly completely in dilute aqueous solutions because the H—X bonds are much weaker.
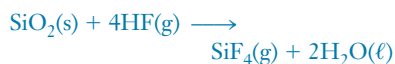
$$HX(aq) + H_2O(\ell) \longrightarrow H_3O^+(aq) + X^-(aq) \qquad X = Cl, Br, I$$
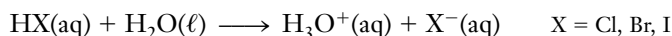
The order of *bond strengths* for the hydrogen halides is

(strongest bonds) $HF \gg HCl > HBr > HI$ (weakest bonds)

To understand why HF is so much weaker an acid than the other hydrogen halides, let us consider the following factors.

1. In HF the electronegativity difference is 1.9, compared with 0.9 in HCl, 0.7 in HBr, and 0.4 in HI (Section 7-8). We might expect the very polar H—F bond in HF to ionize easily. The fact that HF is the *weakest* of these acids suggests that this effect must be of minor importance.

2. The bond strength is considerably greater in HF than in the other three molecules. This tells us that the H—F bond is harder to break than the H—Cl, H—Br, and H—I bonds.

3. The small, highly charged F^- ion, formed when HF ionizes, causes increased ordering of the water molecules. This increase is unfavorable to the process of ionization.

Bond strength is shown by the bond energies introduced in Chapter 7 and tabulated in Section 15-9. The strength of the H—F bond is due largely to the very small size of the F atom.

The net result of all factors is that HF is a much weaker acid than the other hydrohalic acids: HCl, HBr, and HI.

In dilute aqueous solutions, hydrochloric, hydrobromic, and hydroiodic acids are completely ionized, and all show the same apparent acid strength. Water is sufficiently basic that it does not distinguish among the acid strengths of HCl, HBr, and HI, and therefore it is referred to as a **leveling solvent** for these acids. It is not possible to determine the order of the strengths of these three acids in water because they are so nearly completely ionized.

When these compounds dissolve in anhydrous acetic acid or other solvents less basic than water, however, they exhibit significant differences in their acid strengths. The observed order of acid strengths is:

$$HCl < HBr < HI$$

We observe that

the hydronium ion is the strongest acid that can exist in aqueous solution. All acids stronger than $H_3O^+(aq)$ react completely with water to produce $H_3O^+(aq)$ and their conjugate bases.

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 17.10, Acid–Base Properties of Salts.

This is called the **leveling effect** of water. For example $HClO_4$ (Table 10-2) reacts completely with H_2O to form $H^+(aq)$ and $ClO_4^-(aq)$.

$$HClO_4(aq) + H_2O(\ell) \longrightarrow H_3O^+(aq) + ClO_4^-(aq)$$
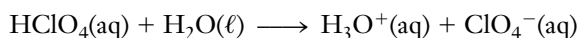
Similar observations have been made for aqueous solutions of strong bases such as NaOH and KOH. Both are completely dissociated in dilute aqueous solutions.
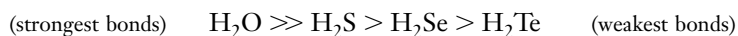
$$NaOH(s) \xrightarrow{H_2O} Na^+(aq) + OH^-(aq)$$
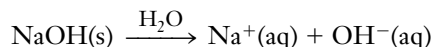
The hydroxide ion is the strongest base that can exist in aqueous solution. Bases stronger than OH^- react completely with H_2O to produce OH^- and their conjugate acids.

When metal amides such as sodium amide, $NaNH_2$, are placed in H_2O, the amide ion, NH_2^-, reacts with H_2O completely.

The amide ion, NH_2^-, is a stronger base than OH^-.

$$NH_2^-(aq) + H_2O(\ell) \longrightarrow NH_3(aq) + OH^-(aq)$$
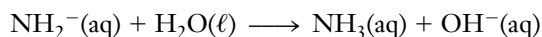
Thus, we see that H_2O is a leveling solvent for all bases stronger than OH^-.

Acid strengths for other *vertical* series of binary acids vary in the same way as those of the VIIA elements. The order of bond strengths for the VIA hydrides is

(strongest bonds) $H_2O \gg H_2S > H_2Se > H_2Te$ (weakest bonds)

TABLE 10-2	*Relative Strengths of Conjugate Acid–Base Pairs*

<div style="margin-left:2em">

The trends in binary acid strengths *across* a period (e.g., $CH_4 < NH_3 < H_2O < HF$) are *not* those predicted from trends in bond energies and electronegativity differences. The correlations used for *vertical* trends cannot be used for *horizontal* trends. This is because a "horizontal" series of compounds has different stoichiometries and different numbers of unshared pairs of electrons on the central atoms.

</div>

H—O bonds are much stronger than the bonds in the other Group VI hydrides. As we might expect, the order of acid strengths for these hydrides is just the reverse of the order of bond strengths.
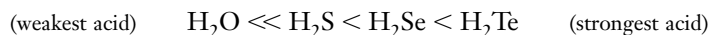
$$\text{(weakest acid)} \qquad H_2O \ll H_2S < H_2Se < H_2Te \qquad \text{(strongest acid)}$$

Table 10-2 displays relative acid and base strengths of a number of conjugate acid–base pairs.

Ternary Acids

Most ternary acids are *hydroxyl compounds of nonmetals* (oxoacids) that ionize to produce $H^+(aq)$. The formula for nitric acid is commonly written HNO_3 to emphasize the presence of an acidic hydrogen atom, but it could also be written as $HONO_2$, as its structure shows (see margin).

In most ternary acids the hydroxyl oxygen is bonded to a fairly electronegative nonmetal. In nitric acid the nitrogen draws the electrons of the N—O (hydroxyl) bond closer to itself than would a less electronegative element such as sodium. The oxygen pulls the electrons of the O—H bond close enough so that the hydrogen atom ionizes as H^+, leaving NO_3^-.

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

<div style="margin-left:2em">

Bond that breaks to form H^+ and NO_3^-

Hydroxyl group

</div>

Let us consider the hydroxyl compounds of metals. We call these compounds "hydroxides" because they can produce hydroxide ions in water to give basic solutions. Oxygen is much more electronegative than most metals, such as sodium. It draws the electrons of the sodium–oxygen bond in NaOH (a strong base) so close to itself that the bonding is
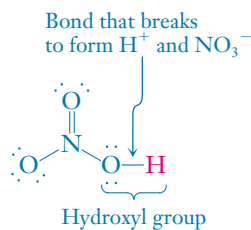
ionic. NaOH therefore exists as Na^+ and OH^- ions, even in the solid state, and dissociates into Na^+ and OH^- ions when it dissolves in H_2O.

$$NaOH(s) \xrightarrow{H_2O} Na^+(aq) + OH^-(aq)$$
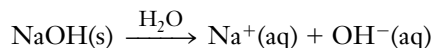
Returning to our consideration of ternary acids, we usually write the formula for sulfuric acid as H_2SO_4 to emphasize that it is a polyprotic acid. The formula can also be written as $(HO)_2SO_2$, however, because the structure of sulfuric acid (see margin) shows clearly that H_2SO_4 contains two O—H groups bound to a sulfur atom. Because the O—H bonds are easier to break than the S—O bonds, sulfuric acid ionizes as an acid.

Step 1: $H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq)$

Step 2: $HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$
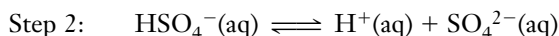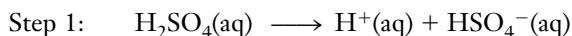
The first step in the ionization of H_2SO_4 is complete in dilute aqueous solution. The second step is nearly complete in very dilute aqueous solutions. The first step in the ionization of a polyprotic acid always occurs to a greater extent than the second step, because it is easier to remove a proton from a neutral acid molecule than from a negatively charged anion.

Sulfurous acid, H_2SO_3, is a polyprotic acid that contains the same elements as H_2SO_4. H_2SO_3 is a weak acid, however, which tells us that the H—O bonds in H_2SO_3 are stronger than those in H_2SO_4.

Comparison of the acid strengths of nitric acid, HNO_3, and nitrous acid, HNO_2, shows that HNO_3 is a much stronger acid than HNO_2.
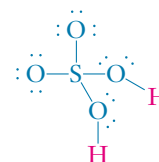
Sulfuric acid is called a polyprotic acid because it has more than one ionizable hydrogen atom per molecule. It is the only *common* polyprotic acid that is also a strong acid.

Nitrous acid, HNO_2.

> Acid strengths of most ternary acids containing the same central element increase with increasing oxidation state of the central element and with increasing numbers of oxygen atoms.

The following orders of increasing acid strength are typical.

$H_2SO_3 < H_2SO_4$
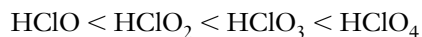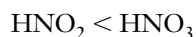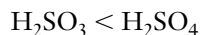
$HNO_2 < HNO_3$ (strongest acids are on the right side)

$HClO < HClO_2 < HClO_3 < HClO_4$
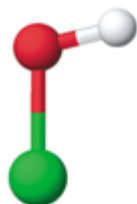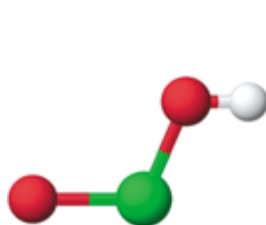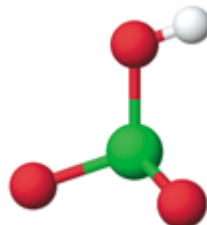
HOCl (or HClO) $HClO_2$ $HClO_3$ $HClO_4$

> For most ternary acids containing different elements in the same oxidation state from the same group in the periodic table, acid strengths increase with increasing electronegativity of the central element.

$$H_2SeO_4 < H_2SO_4 \qquad H_2SeO_3 < H_2SO_3$$
$$H_3PO_4 < HNO_3$$
$$HBrO_4 < HClO_4 \qquad HBrO_3 < HClO_3$$

Contrary to what we might expect, H_3PO_3 is a stronger acid than HNO_2. Care must be exercised to compare acids that have *similar structures*. For example, H_3PO_2, which has two H atoms bonded to the P atom, is a stronger acid than H_3PO_3, which has one H atom bonded to the P atom. H_3PO_3 is a stronger acid than H_3PO_4, which has no H atoms bonded to the P atom.

In *most* ternary inorganic acids, all H atoms are bonded to O.

Common Strong Acids	
Binary	**Ternary**
HCl	$HClO_4$
HBr	$HClO_3$
HI	HNO_3
	H_2SO_4

Strong Bases	
LiOH	
NaOH	
KOH	$Ca(OH)_2$
RbOH	$Sr(OH)_2$
CsOH	$Ba(OH)_2$

See *Saunders Interactive General Chemistry CD-ROM,* Screen 18.2, Acid–Base Reactions (I).

10-8 ACID–BASE REACTIONS IN AQUEOUS SOLUTIONS

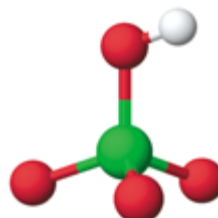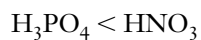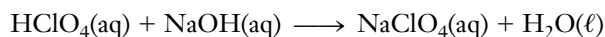In Section 4-9 we introduced classical acid–base reactions. We defined neutralization as the reaction of an acid with a base to form a salt and (in most cases) water. Most *salts* are ionic compounds that contain a cation other than H^+ and an anion other than OH^- or O^{2-}. The common *strong acids* and common *strong bases* are listed in the margin. All other common acids may be assumed to be weak. The other common metal hydroxides (bases) are insoluble in water.
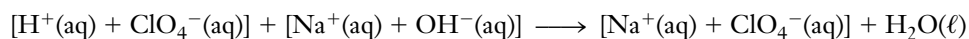
Arrhenius and Brønsted–Lowry acid–base neutralization reactions all have one thing in common. They involve the reaction of an acid with a base to form a salt that contains the cation characteristic of the base and the anion characteristic of the acid. Water is also usually formed. This is indicated in the formula unit equation. The general form of the net ionic equation, however, is different for different acid–base reactions. The net ionic equations depend on the solubility and extent of ionization or dissociation of each reactant and product.

In writing ionic equations, we always write the formulas of the predominant forms of the compounds in, or in contact with, aqueous solution. Writing ionic equations from formula unit equations requires a knowledge of the lists of strong acids and strong bases, as well as of the generalizations on solubilities of inorganic compounds. Please review carefully all of Sections 4-2 and 4-3. Study Tables 4-8 and 4-9 carefully because they summarize much information that you are about to use again.

In Section 4-2 we examined some reactions of strong acids with strong bases to form soluble salts. Let us illustrate one additional example. Perchloric acid, $HClO_4$, reacts with sodium hydroxide to produce sodium perchlorate, $NaClO_4$, a soluble ionic salt.

$$HClO_4(aq) + NaOH(aq) \longrightarrow NaClO_4(aq) + H_2O(\ell)$$

The total ionic equation for this reaction is

$$[H^+(aq) + ClO_4^-(aq)] + [Na^+(aq) + OH^-(aq)] \longrightarrow [Na^+(aq) + ClO_4^-(aq)] + H_2O(\ell)$$

Eliminating the spectator ions, Na^+ and ClO_4^-, gives the net ionic equation
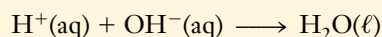
This is considered to be the same as

$$H_3O^+ + OH^- \rightarrow 2H_2O$$

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(\ell)$$

This is the net ionic equation for the reaction of all strong acids with strong bases to form soluble salts and water.

Many weak acids react with strong bases to form soluble salts and water. For example, acetic acid, CH_3COOH, reacts with sodium hydroxide, NaOH, to produce sodium acetate, $NaCH_3COO$.

$$CH_3COOH(aq) + NaOH(aq) \longrightarrow NaCH_3COO(aq) + H_2O(\ell)$$

The total ionic equation for this reaction is

$$CH_3COOH(aq) + [Na^+(aq) + OH^-(aq)] \longrightarrow [Na^+(aq) + CH_3COO^-(aq)] + H_2O(\ell)$$

Elimination of Na^+ from both sides gives the net ionic equation

$$CH_3COOH(aq) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + H_2O(\ell)$$

In general terms, the reaction of a *weak monoprotic acid* with a *strong base* to form a *soluble salt* may be represented as

$$HA(aq) + OH^-(aq) \longrightarrow A^-(aq) + H_2O(\ell) \qquad \text{(net ionic equation)}$$

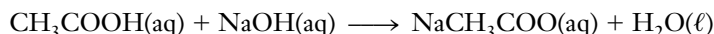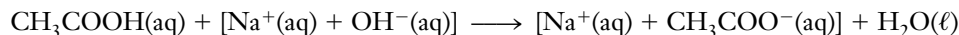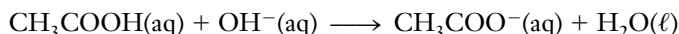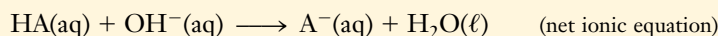Monoprotic acids contain one, diprotic acids contain two, and triprotic acids contain three acidic (ionizable) hydrogen atoms per formula unit. Polyprotic acids (those that contain more than one ionizable hydrogen atom) are discussed in detail in Chapter 18.

EXAMPLE 10-1 *Equations for Acid–Base Reactions*

Write (a) formula unit, (b) total ionic, and (c) net ionic equations for the complete neutralization of phosphoric acid, H_3PO_4, with potassium hydroxide, KOH.

When all the H^+ from the acid and all the OH^- of the base have reacted, we say that there has been complete neutralization.

Plan

(a) The salt produced in the reaction contains the cation of the base, K^+, and the PO_4^{3-} anion of the acid. The salt is K_3PO_4.

(b) H_3PO_4 is a weak acid—it is not written in ionic form. KOH is a strong base, and so it is written in ionic form. K_3PO_4 is a *soluble salt*, and so it is written in ionic form.

(c) The spectator ions are canceled to give the net ionic equation.

Solution

(a) $H_3PO_4(aq) + 3KOH(aq) \longrightarrow K_3PO_4(aq) + 3H_2O(\ell)$
(b) $H_3PO_4(aq) + 3[K^+(aq) + OH^-(aq)] \longrightarrow [3K^+(aq) + PO_4^{3-}(aq)] + 3H_2O(\ell)$
(c) $H_3PO_4(aq) + 3OH^-(aq) \longrightarrow PO_4^{3-}(aq) + 3H_2O(\ell)$

You should now work Exercise 58.

EXAMPLE 10-2 *Equations for Acid–Base Reactions*

Write (a) formula unit, (b) total ionic, and (c) net ionic equations for the neutralization of aqueous ammonia with nitric acid.

Neutralization reactions of ammonia, NH_3, form salts but do not form water.

Plan

(a) The salt produced in the reaction contains the cation of the base, NH_4^+, and the anion of the acid, NO_3^-. The salt is NH_4NO_3.

(b) HNO_3 is a strong acid—we write it in ionic form. Ammonia is a weak base. NH_4NO_3 is a soluble salt that is completely dissociated—we write it in ionic form.

(c) We cancel the spectator ions, NO_3^-, and obtain the net ionic equation.

Solution

(a) $HNO_3(aq) + NH_3(aq) \longrightarrow NH_4NO_3(aq)$
(b) $[H^+(aq) + NO_3^-(aq)] + NH_3(aq) \longrightarrow [NH_4^+(aq) + NO_3^-(aq)]$
(c) $H^+(aq) + NH_3(aq) \longrightarrow NH_4^+(aq)$

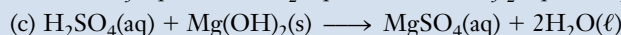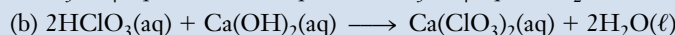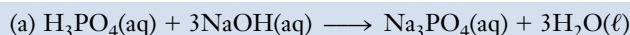*You should now work Exercise 60.*

EXAMPLE 10-3 *Preparation of Salts*

Write the formula unit equation for the reaction of an acid and a base that will produce each of the following salts: (a) Na_3PO_4, (b) $Ca(ClO_3)_2$, (c) $MgSO_4$.

Plan

(a) The salt contains the ions, Na^+ and PO_4^{3-}. Na^+ is the cation in the strong base, NaOH. PO_4^{3-} is the anion in the weak acid, H_3PO_4. The reaction of NaOH with H_3PO_4 should therefore produce the desired salt plus water.

(b) The cation, Ca^{2+}, is from the strong base, $Ca(OH)_2$. The anion, ClO_3^-, is from the strong acid, $HClO_3$. The reaction of $Ca(OH)_2$ with $HClO_3$ will produce water and the desired salt.

(c) $MgSO_4$ is the salt produced in the reaction of $Mg(OH)_2(s)$ and $H_2SO_4(aq)$.

Solution

(a) $H_3PO_4(aq) + 3NaOH(aq) \longrightarrow Na_3PO_4(aq) + 3H_2O(\ell)$
(b) $2HClO_3(aq) + Ca(OH)_2(aq) \longrightarrow Ca(ClO_3)_2(aq) + 2H_2O(\ell)$
(c) $H_2SO_4(aq) + Mg(OH)_2(s) \longrightarrow MgSO_4(aq) + 2H_2O(\ell)$

You should now work Exercise 62.

10-9 ACIDIC SALTS AND BASIC SALTS

To this point we have examined acid–base reactions in which stoichiometric amounts of Arrhenius acids and bases were mixed. Those reactions form *normal salts*. As the name implies, **normal salts** contain no ionizable H atoms or OH groups. The *complete* neutralization of phosphoric acid, H_3PO_4, with sodium hydroxide, NaOH, produces the normal salt, Na_3PO_4. The equation for this complete neutralization is

$$H_3PO_4(aq) + 3NaOH(aq) \longrightarrow Na_3PO_4(aq) + 3H_2O(\ell)$$
$$\text{1 mole} \qquad \text{3 moles} \qquad \text{sodium phosphate,}$$
$$\text{a normal salt}$$
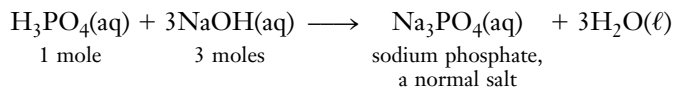
If less than stoichiometric amounts of bases react with *polyprotic* acids, the resulting salts are known as **acidic salts** because they are still capable of neutralizing bases.

$$H_3PO_4(aq) + NaOH(aq) \longrightarrow NaH_2PO_4(aq) + H_2O(\ell)$$
$$\text{1 mole} \qquad \text{1 mole} \qquad \text{sodium dihydrogen phosphate,}$$
$$\text{an acidic salt}$$

$$H_3PO_4(aq) + 2NaOH(aq) \longrightarrow Na_2HPO_4(aq) + 2H_2O(\ell)$$
$$\text{1 mole} \qquad \text{2 moles} \qquad \text{sodium hydrogen phosphate,}$$
$$\text{an acidic salt}$$
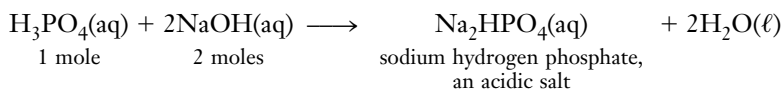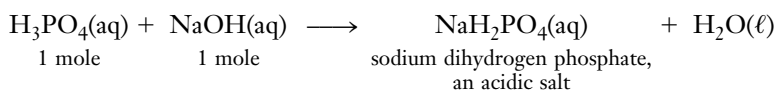
The reaction of phosphoric acid, H_3PO_4, a weak acid, with strong bases can produce the three salts shown in the three preceding equations, depending on the relative amounts of acid and base used. The acidic salts, NaH_2PO_4 and Na_2HPO_4, can react further with bases such as NaOH.

$$NaH_2PO_4(aq) + 2NaOH(aq) \longrightarrow Na_3PO_4(aq) + 2H_2O(\ell)$$
$$Na_2HPO_4(aq) + NaOH(aq) \longrightarrow Na_3PO_4(aq) + H_2O(\ell)$$
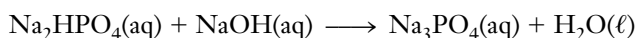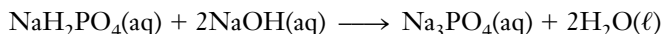
Sodium hydrogen carbonate, baking soda, is the most familiar example of an acidic salt. It can neutralize strong bases, but its aqueous solutions are slightly basic, as the blue color of the indicator bromthymol blue shows.

There are many additional examples of acidic salts. Sodium hydrogen carbonate, $NaHCO_3$, commonly called sodium bicarbonate, is classified as an acidic salt. It is, however, the acidic salt of an extremely weak acid—carbonic acid, H_2CO_3—and solutions of sodium bicarbonate are slightly basic, as are solutions of salts of other extremely weak acids.

Polyhydroxy bases (bases that contain more than one OH per formula unit) react with stoichiometric amounts of acids to form normal salts.

$$Al(OH)_3(s) + 3HCl(aq) \longrightarrow AlCl_3(aq) + 3H_2O(\ell)$$

  1 mole 3 moles   aluminum chloride,
             a normal salt

The reaction of polyhydroxy bases with less than stoichiometric amounts of acids forms **basic salts,** that is, salts that contain unreacted OH groups. For example, the reaction of aluminum hydroxide with hydrochloric acid can produce two different basic salts:
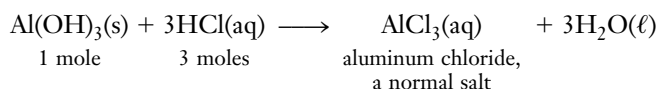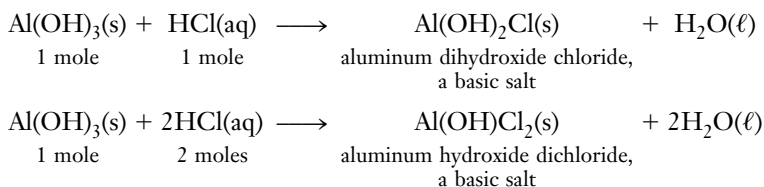
$$Al(OH)_3(s) + HCl(aq) \longrightarrow Al(OH)_2Cl(s) + H_2O(\ell)$$

  1 mole 1 mole aluminum dihydroxide chloride,
           a basic salt

$$Al(OH)_3(s) + 2HCl(aq) \longrightarrow Al(OH)Cl_2(s) + 2H_2O(\ell)$$

  1 mole 2 moles aluminum hydroxide dichloride,
           a basic salt

These basic aluminum salts are called "aluminum chlorohydrate." They are components of some deodorants.

Aqueous solutions of basic salts are not necessarily basic, but they can neutralize acids, such as,

$$Al(OH)_2Cl + 2HCl \longrightarrow AlCl_3 + 2H_2O$$
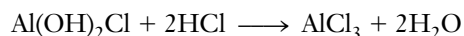
Most basic salts are rather insoluble in water.

10-10 THE LEWIS THEORY

In 1923, Professor G. N. Lewis (1875–1946) presented the most comprehensive of the classic acid–base theories. The Lewis definitions follow.

This is the same Lewis who made many contributions to our understanding of chemical bonding.

  An **acid** is any species that can accept a share in an electron pair. A **base** is any species that can make available, or "donate," a share in an electron pair.

See the Saunders Interactive General Chemistry CD-ROM, Screen 17.11, Lewis Acids and Bases, and Screen 17.12, Cationic Lewis Acids.

These definitions do *not* specify that an electron pair must be transferred from one atom to another—only that an electron pair, residing originally on one atom, must be shared between two atoms. *Neutralization* is defined as **coordinate covalent bond formation.** This results in a covalent bond in which both electrons were furnished by one atom or ion.

The reaction of boron trichloride with ammonia is a typical Lewis acid–base reaction.
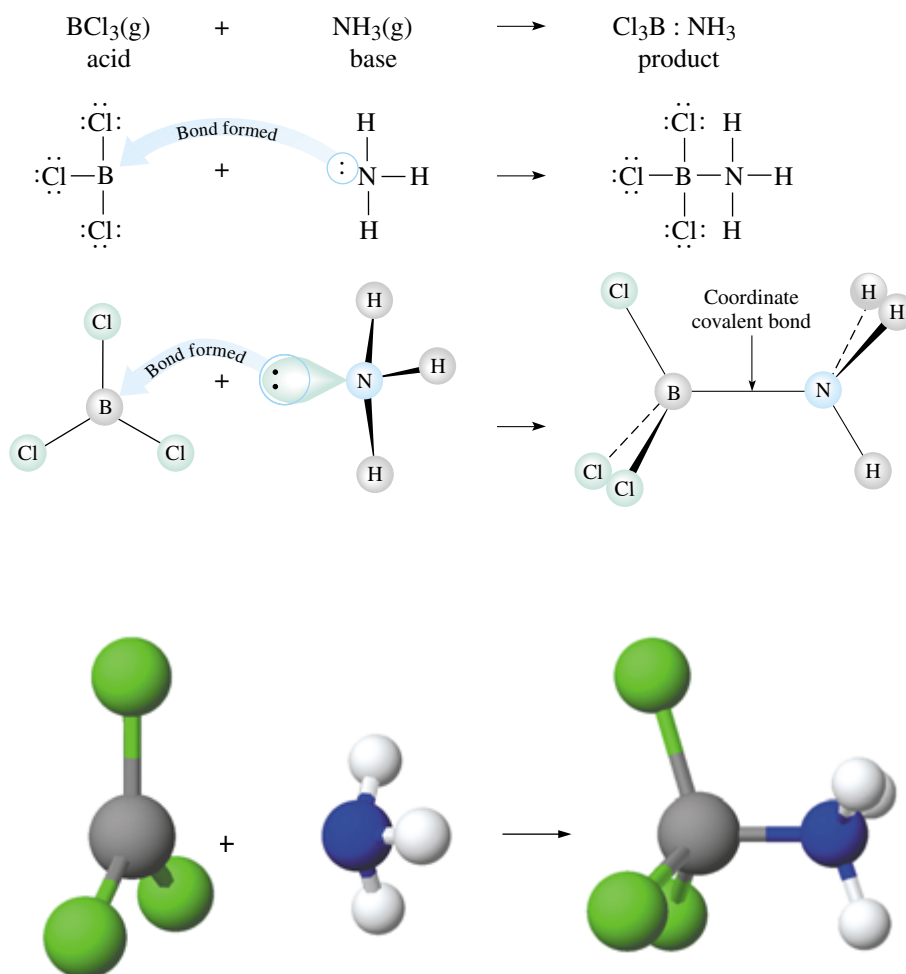
The Lewis theory is sufficiently general that it covers *all* acid–base reactions that the other theories include, plus many additional reactions such as complex formation (Chapter 25).

The autoionization of water (Section 10-5) was described in terms of Brønsted–Lowry theory. In Lewis theory terminology, this is also an acid–base reaction. The acceptance of a proton, H^+, by a base involves the formation of a coordinate covalent bond.
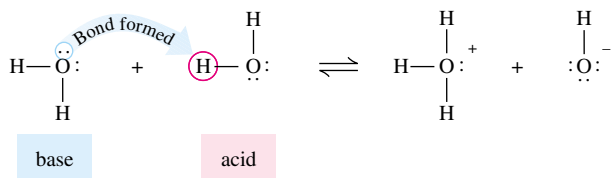
Theoretically, any species that contains an unshared electron pair could act as a base. In fact, most ions and molecules that contain unshared electron pairs undergo some reactions by sharing their electron pairs. Conversely, many Lewis acids contain only six electrons in the highest occupied energy level of the central element. They react by accepting a share in an additional pair of electrons. These species are said to have an **open sextet.** Many compounds of the Group IIIA elements are Lewis acids, as illustrated by the reaction of boron trichloride with ammonia, presented earlier.

Anhydrous aluminum chloride, $AlCl_3$, is a common Lewis acid that is used to catalyze many organic reactions. $AlCl_3$ acts as a Lewis acid when it dissolves in hydrochloric acid to give a solution that contains $AlCl_4^-$ ions.
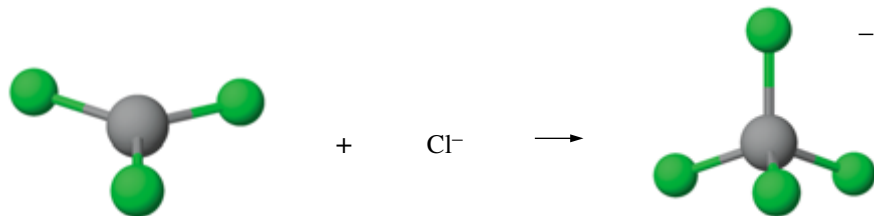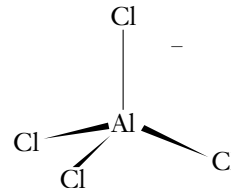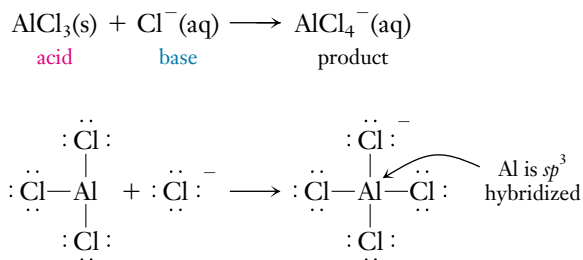
Other ions and molecules behave as Lewis acids by expansion of the valence shell of the central element. Anhydrous tin(IV) chloride is a colorless liquid that also is frequently used as a Lewis acid catalyst. The tin atom (Group IVA) can expand its valence shell by utilizing vacant d orbitals. It can accept shares in two additional electron pairs, as its reaction with hydrochloric acid illustrates.

$$SnCl_4(\ell) + 2Cl^-(aq) \longrightarrow SnCl_6{}^{2-}(aq)$$

<p align="center">acid   base</p>

Sn is sp^3 hybridized
(tetrahedral)

Sn is sp^3d^2 hybridized
(octahedral)
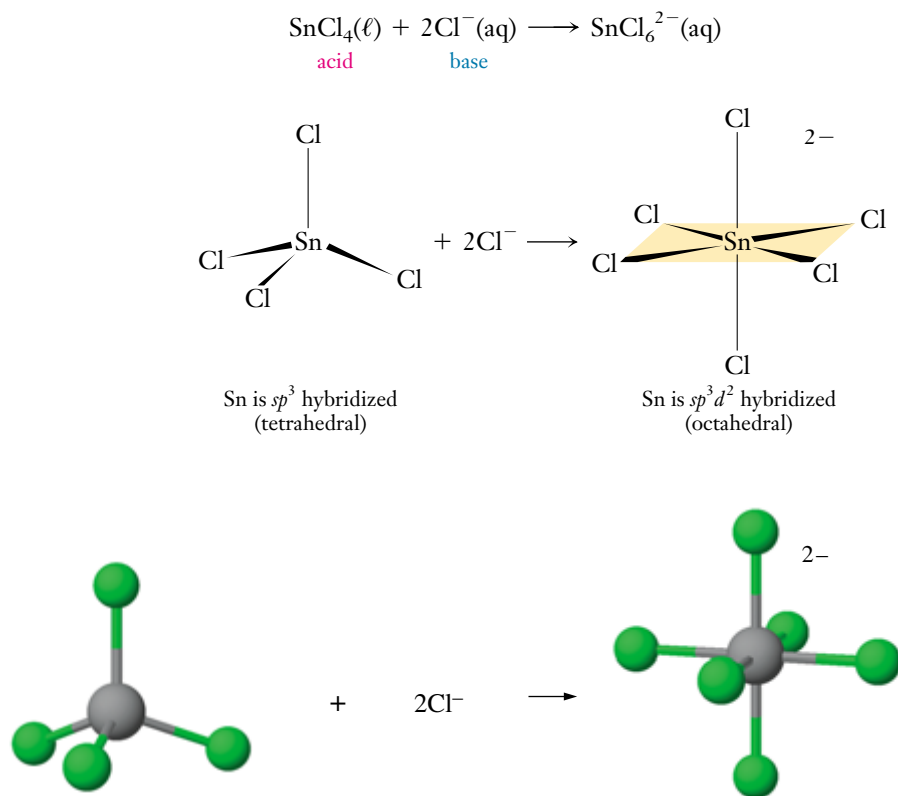
Many organic and biological reactions are acid–base reactions that do not fit within the Arrhenius or Brønsted–Lowry theories. Experienced chemists find the Lewis theory to be very useful because so many other chemical reactions are covered by it. The less experienced sometimes find the theory less useful, but as their knowledge expands so does its utility.

✔ **Problem-Solving Tip:** *Which Acid–Base Theory Should You Use?*

Remember the following:

1. Arrhenius acids and bases are also Brønsted–Lowry acids and bases; the reverse is not true.

2. Brønsted–Lowry acids and bases are also Lewis acids and bases; the reverse is not true.

3. We usually prefer the Arrhenius or the Brønsted–Lowry theory when water or another protonic solvent is present.

4. Although the Lewis theory can be used to explain the acidic or basic property of some species in protonic solvents, the most important use of the Lewis theory is for acid-base reactions in many nonaqueous solvents.

10-11 THE PREPARATION OF ACIDS

Binary acids may be prepared by combination of appropriate elements with hydrogen (Section 6-7, part 2).

Small quantities of the hydrogen halides (their solutions are called hydrohalic acids) and other *volatile acids* are usually prepared by adding concentrated nonvolatile acids to the appropriate salts. (Sulfuric and phosphoric acids are classified as *nonvolatile acids* because they have much higher boiling points than other common acids.) The reactions of concentrated sulfuric acid with solid sodium fluoride and sodium chloride produce gaseous hydrogen fluoride and hydrogen chloride, respectively.

$$H_2SO_4(\ell) + NaF(s) \longrightarrow NaHSO_4(s) + HF(g)$$

sulfuric acid   sodium fluoride   sodium hydrogen   hydrogen fluoride
bp = 336°C   sulfate   bp = 19.6°C

$$H_2SO_4(\ell) + NaCl(s) \longrightarrow NaHSO_4(s) + HCl(g)$$

sodium chloride   hydrogen chloride
bp = −84.9°C
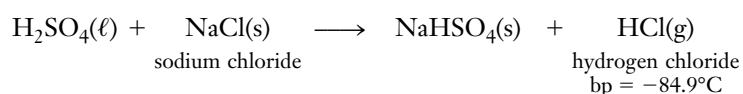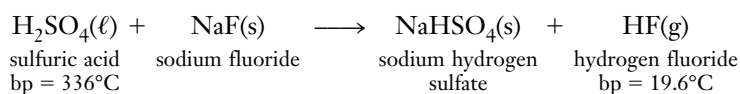
Because concentrated sulfuric acid is a fairly strong oxidizing agent, it cannot be used to prepare hydrogen bromide or hydrogen iodide; instead, the free halogens are produced. Phosphoric acid, a nonoxidizing acid, is dropped onto solid sodium bromide or sodium iodide to produce hydrogen bromide or hydrogen iodide, as the following equations show:

$$H_3PO_4(\ell) + NaBr(s) \xrightarrow{\text{heat}} NaH_2PO_4(s) + HBr(g)$$

phosphoric acid   sodium bromide   sodium dihydrogen   hydrogen bromide
bp = 213°C   phosphate   bp = −67.0°C

$$H_3PO_4(\ell) + NaI(s) \xrightarrow{\text{heat}} NaH_2PO_4(s) + HI(g)$$

sodium iodide   hydrogen iodide
bp = −35°C

This kind of reaction may be generalized as

$$\text{nonvolatile acid} + \text{salt of volatile acid} \longrightarrow \text{salt of nonvolatile acid} + \text{volatile acid}$$

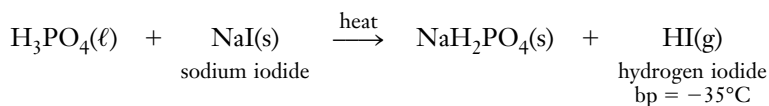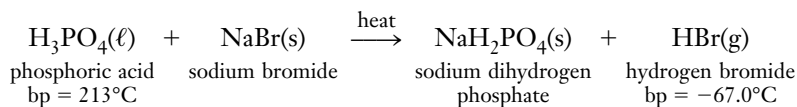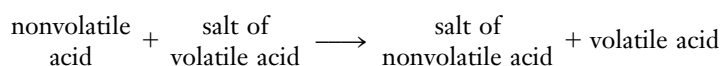Dissolving each of the gaseous hydrogen halides in water gives the corresponding hydrohalic acid.

In Section 6-8, part 2 we saw that many nonmetal oxides, called acid anhydrides, react with water to form *ternary acids* with no changes in oxidation numbers. For example, dichlorine heptoxide, Cl_2O_7, forms perchloric acid when it dissolves in water.

$$\overset{+7}{Cl_2}O_7(\ell) + H_2O(\ell) \longrightarrow 2[H^+(aq) + \overset{+7}{Cl}O_4^-(aq)]$$
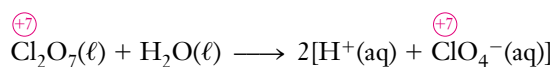
Some *high oxidation state transition metal oxides* are acidic oxides; that is, they dissolve in water to give solutions of ternary acids. Manganese(VII) oxide, Mn_2O_7, and chromium(VI) oxide, CrO_3, are the most common examples.

The volatile acid HCl can be made by dropping concentrated H_2SO_4 onto solid NaCl. Gaseous HCl is liberated. HCl(g) dissolves in the water on a piece of filter paper. The indicator methyl red on the paper turns red, its color in acidic solution.

A solution of dichromic acid, $H_2Cr_2O_7$, is deep red.

$$\overset{+7}{Mn_2O_7}(\ell) \;+\; H_2O(\ell) \longrightarrow 2[H^+(aq) + \overset{+7}{Mn}O_4^-(aq)]$$

manganese(VII) oxide   permanganic acid

$$2\overset{+6}{Cr}O_3(s) \;+\; H_2O(\ell) \longrightarrow [2H^+(aq) + \overset{+6}{Cr_2}O_7^{2-}(aq)]$$

chromium(VI) oxide   dichromic acid

Neither permanganic acid nor dichromic acid has been isolated in pure form. Many stable salts of both are well known.

The halides and oxyhalides of some nonmetals hydrolyze (react with water) to produce two acids: a (binary) hydrohalic acid and a (ternary) oxyacid of the nonmetal. Phosphorus trihalides react with water to produce the corresponding hydrohalic acids and phosphorous acid, a weak diprotic acid, whereas phosphorus pentahalides give phosphoric acid and the corresponding hydrohalic acid.

$$\overset{+3}{P}X_3 + 3H_2O(\ell) \longrightarrow \overset{+3}{H_3}PO_3(aq) + 3HX(aq)$$

$$\overset{+5}{P}X_5 + 4H_2O(\ell) \longrightarrow \overset{+5}{H_3}PO_4(aq) + 5HX(aq)$$

There are no changes in oxidation numbers in these reactions. Examples include the reactions of PCl_3 and PCl_5 with H_2O.

$$\overset{+3}{P}Cl_3(\ell) \;+\; 3H_2O(\ell) \longrightarrow \overset{+3}{H_3}PO_3(aq) \;+\; 3[H^+(aq) + Cl^-(aq)]$$

phosphorus trichloride   phosphorous acid

$$\overset{+5}{P}Cl_5(s) \;+\; 4H_2O(\ell) \longrightarrow \overset{+5}{H_3}PO_4(aq) \;+\; 5[H^+(aq) + Cl^-(aq)]$$

phosphorus pentachloride   phosphoric acid
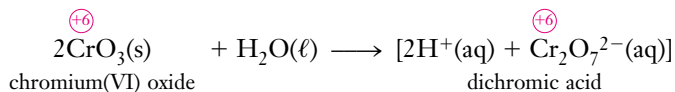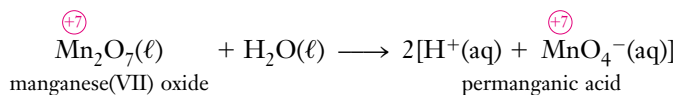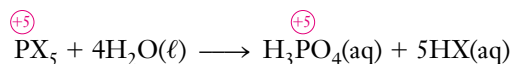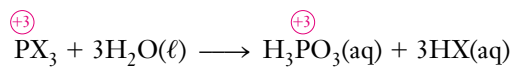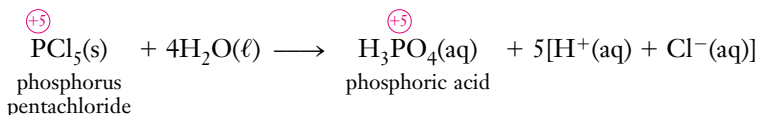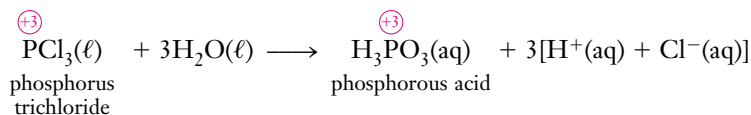
A drop of PCl_3 is added to water that contains the indicator methyl orange. As PCl_3 reacts with water to form HCl and H_3PO_3, the indicator turns red, its color in acidic solution.

Key Terms

Acid (Arrhenius or Brønsted–Lowry) A substance that produces $H^+(aq)$ ions in aqueous solution. Strong acids ionize completely or almost completely in dilute aqueous solution; weak acids ionize only slightly.

Acid anhydride The oxide of a nonmetal that reacts with water to form an acid.

Acidic salt A salt that contains an ionizable hydrogen atom; does not necessarily produce acidic solutions.

Amphiprotism The ability of a substance to exhibit amphoterism by accepting or donating protons.

Amphoterism Ability of a substance to act as either an acid or a base.

Anhydrous Without water.

Autoionization An ionization reaction between identical molecules.

Base (Arrhenius) A substance that produces $OH^-(aq)$ ions in aqueous solution. Strong bases are soluble in water and are completely *dissociated*. Weak bases ionize only slightly.

Basic anhydride The oxide of a metal that reacts with water to form a base.

Basic salt A salt containing a basic OH group.

Brønsted–Lowry acid A proton donor.

Brønsted–Lowry base A proton acceptor.

Conjugate acid–base pair In Brønsted–Lowry terminology, a reactant and product that differ by a proton, H^+.

Coordinate covalent bond A covalent bond in which both shared electrons are furnished by the same species; the bond between a Lewis acid and a Lewis base.

Dissociation In aqueous solution, the process in which a *solid ionic compound* separates into its ions.

Electrolyte A substance whose aqueous solutions conduct electricity.

Formula unit equation A chemical equation in which all compounds are represented by complete formulas.

Hydration The process by which water molecules bind to ions or molecules in the solid state or in solution.

Hydride A binary compound of hydrogen.

Hydrolysis Reaction of a substance with water.

Hydronium ion H_3O^+, the usual representation of the hydrated hydrogen ion.

Ionization In aqueous solution, the process in which a *molecular* compound reacts with water to form ions.

Leveling effect The effect by which all acids stronger than the acid that is characteristic of the solvent react with the solvent to produce that acid; a similar statement applies to bases. The strongest acid (base) that can exist in a given solvent is the acid (base) characteristic of that solvent.

Lewis acid Any species that can accept a share in an electron pair to form a coordinate covalent bond.

Lewis base Any species that can make available a share in an electron pair to form a coordinate covalent bond.

Net ionic equation The equation that results from canceling spectator ions and eliminating brackets from a total ionic equation.

Neutralization The reaction of an acid with a base to form a salt and (usually) water; usually, the reaction of hydrogen ions with hydroxide ions to form water molecules.

Nonelectrolyte A substance whose aqueous solutions do not conduct electricity.

Normal oxide A metal oxide containing the oxide ion, O^{2-} (oxygen in the -2 oxidation state).

Normal salt A salt containing no ionizable H atoms or OH groups.

Open sextet Refers to species that have only six electrons in the highest energy level of the central element (many Lewis acids).

Polyprotic acid An acid that contains more than one ionizable hydrogen atom per formula unit.

Protonic acid An Arrhenius acid, or a Brønsted–Lowry acid.

Salt A compound that contains a cation other than H^+ and an anion other than OH^- or O^{2-}.

Spectator ions Ions in solution that do not participate in a chemical reaction.

Strong electrolyte A substance that conducts electricity well in dilute aqueous solution.

Ternary acid An acid that contains three elements—usually H, O, and another nonmetal.

Ternary compound A compound that contains three different elements.

Total ionic equation The equation for a chemical reaction written to show the predominant form of all species in aqueous solution or in contact with water.

Weak electrolyte A substance that conducts electricity poorly in dilute aqueous solution.

Exercises

Basic Ideas

1. Which properties of acids did Robert Boyle observe?
2. Gay-Lussac reached an important conclusion about acids and bases. What was it?
3. Define the following terms. You may wish to refer to Chapter 4 to check the definitions. (a) acid; (b) neutralization; (c) ionization; (d) dissociation; (e) salt.

The Arrhenius Theory

4. Outline Arrhenius' ideas about acids and bases. (a) How did he define the following terms: acid, base, neutralization? (b) Give an example that illustrates each term.
5. Define and illustrate the following terms clearly and concisely. Give an example of each. (a) strong electrolyte; (b) weak electrolyte; (c) nonelectrolyte; (d) strong acid; (e) strong base; (f) weak acid; (g) weak base; (h) insoluble base.
6. Distinguish between the following pairs of terms, and provide a specific example of each. (a) strong acid and weak acid; (b) strong base and weak base; (c) strong base and insoluble base.
7. Write formulas and names for (a) the common strong acids; (b) three weak acids; (c) the common strong bases; (d) the most common weak base; (e) four soluble ionic salts; (f) four insoluble salts.
8. Describe an experiment for classifying compounds as strong electrolytes, weak electrolytes, or nonelectrolytes. Tell what would be observed for each of the following compounds and classify each. Na_2SO_4; HCN; C_2H_5COOH; CH_3CH_2OH; HF; $HClO_4$; HCOOH; NH_3.
9. Summarize the electrical properties of strong electrolytes, weak electrolytes, and nonelectrolytes.

The Hydrated Hydrogen Ion

10. Write the formula of a hydrated hydrogen ion that contains only one water of hydration. Give another name for the hydrated hydrogen ion.
11. Why is the hydrated hydrogen ion important?
12. Criticize the following statement: "The hydrated hydrogen ion should always be represented as H_3O^+."

Brønsted–Lowry Theory

13. State the basic ideas of the Brønsted–Lowry theory.

14. Use Brønsted–Lowry terminology to define the following terms. Illustrate each with a specific example. (a) acid; (b) conjugate base; (c) base; (d) conjugate acid; (e) conjugate acid–base pair.

15. Write balanced equations that describe the ionization of the following acids in dilute aqueous solution. Use a single arrow ($\rightarrow$) to represent complete, or nearly complete, ionization and a double arrow ($\rightleftharpoons$) to represent a small extent of ionization. (a) HCl; (b) CH_3COOH; (c) H_2S; (d) HCN; (e) HF; (f) $HClO_4$.

16. Use words and equations to describe how ammonia can act as a base in (a) aqueous solution and (b) the pure state, that is, as gaseous ammonia molecules when it reacts with gaseous hydrogen chloride or a similar anhydrous acid.

17. What does autoionization mean? How can the autoionization of water be described as an acid–base reaction? What structural features must a compound have to be able to undergo autoionization?

18. Illustrate, with appropriate equations, the fact that these species are bases in water: NH_3; HS^-; CH_3COO^-; O^{2-}.

19. In terms of Brønsted–Lowry theory, state the differences between (a) a strong and a weak base and (b) a strong and a weak acid.

20. Give the products in the following acid–base reactions. Identify the conjugate acid–base pairs.
(a) $NH_4^+ + CN^-$
(b) $HS^- + H_2SO_4$
(c) $HClO_4 + [H_2NNH_3]^+$
(d) $NH_2^- + H_2O$

21. Give the conjugate acids of H_2O, OH^-, I^-, AsO_4^{3-}, NH_2^-, HPO_4^{2-}, and NO_2^-.

22. Give the conjugate bases of H_2O, HS^-, HCl, PH_4^+, and $HOCH_3$.

23. Identify the Brønsted–Lowry acids and bases in these reactions and group them into conjugate acid–base pairs.
(a) $NH_3 + HBr \rightleftharpoons NH_4^+ + Br^-$
(b) $NH_4^+ + HS^- \rightleftharpoons NH_3 + H_2S$
(c) $H_3O^+ + PO_4^{3-} \rightleftharpoons HPO_4^{2-} + H_2O$
(d) $HSO_3^- + CN^- \rightleftharpoons HCN + SO_3^{2-}$

24. Identify each species in the following reactions as either an acid or a base, in the Brønsted–Lowry sense.
(a) $CN^- + H_2O \rightleftharpoons HCN + OH^-$
(b) $HCO_3^- + H_2SO_4 \rightleftharpoons HSO_4^- + H_2CO_3$
(c) $CH_3COOH + NO_2^- \rightleftharpoons HNO_2 + CH_3COO^-$

25. Identify each species in the following reactions as either an acid or a base, in the Brønsted–Lowry sense.
(a) $NH_4^+ + HSO_3^- \rightleftharpoons NH_3 + H_2SO_3$
(b) $NH_2^- + H_2O \rightleftharpoons NH_3 + OH^-$
(c) $O^{2-} + H_2O \rightleftharpoons OH^- + OH^-$

26. Arrange the species in the reactions of Exercise 24 as Brønsted–Lowry conjugate pairs.

27. Arrange the species in the reactions of Exercise 25 as Brønsted–Lowry conjugate pairs.

28. Identify each reactant and product in the following chemical reactions as a Brønsted–Lowry acid, a Brønsted–Lowry base, or neither. Arrange the species in each reaction as conjugate acid–base pairs.
(a) $H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$
(b) $HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$
(c) $H_3PO_4 + CN^- \rightleftharpoons HCN + H_2PO_4^-$
(d) $HS^- + OH^- \rightleftharpoons H_2O + S^{2-}$

29. Identify each reactant and product in the following chemical reactions as a Brønsted–Lowry acid, a Brønsted–Lowry base, or neither. Arrange the species in each reaction as conjugate acid–base pairs.
(a) $H_2SeO_4 + H_2O \rightleftharpoons H_3O^+ + HSeO_4^-$
(b) $HPO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-}$
(c) $NH_3 + H^- \rightleftharpoons H_2 + NH_2^-$
(d) $HCl + NH_3 \rightleftharpoons NH_4Cl$

Properties of Aqueous Solutions of Acids and Bases

30. Write equations and designate conjugate pairs for the stepwise reactions in water of (a) H_2SO_4 and (b) H_2SO_3.

31. List six properties of aqueous solutions of protonic acids.

32. List five properties of bases in aqueous solution. Does aqueous ammonia exhibit these properties? Why?

33. We say that strong acids, weak acids, and weak bases *ionize* in water, but strong bases *dissociate* in water. What is the difference between ionization and dissociation?

34. Distinguish between solubility in water and extent of ionization in water. Provide specific examples that illustrate the meanings of both terms.

35. Write three general statements that describe the extents to which acids, bases, and salts are ionized in dilute aqueous solutions.

Amphoterism

36. Use chemical equations to illustrate the hydroxides of beryllium, zinc, arsenic, and antimony reacting (a) as acids; (b) as bases.

37. Draw the Lewis formula of aluminum hydroxide, and explain the features that enable it to possess amphoteric properties.

38. What do we mean when we say that water is amphiprotic? (a) Can we also describe water as amphoteric? Why? (b) Illustrate the amphiprotic nature of water by writing two equations for reactions in which water exhibits this property.

Strengths of Acids

39. What property is characteristic of all strong acids and strong bases but not weak acids and weak bases?

40. What does "base strength" mean? What does "acid strength" mean?

41. Classify each of the following substances as (a) a strong base, (b) an insoluble base, (c) a strong acid, or (d) a weak acid: LiOH; HCl; $Ba(OH)_2$; $Cu(OH)_2$; H_2S; H_2CO_3; H_2SO_4; $Zn(OH)_2$.

42. (a) What are binary protonic acids? (b) Write names and formulas for four binary protonic acids.

43. (a) How can the order of increasing acid strength in a series of similar binary protonic acids be explained? (b) Illustrate your answer for the series HF, HCl, HBr, and HI. (c) What is the order of increasing base strength of the conjugate bases of the acids in (b)? Why? (d) Is your explanation applicable to the series H_2O, H_2S, H_2Se, and H_2Te? Why?

44. Classify each of the hydrides NaH, BeH_2, BH_3, CH_4, NH_3, H_2O, and HF as a Brønsted–Lowry base, a Brønsted–Lowry acid, or neither.

45. (a) Which is the stronger acid of each pair? (1) NH_4^+, NH_3; (2) H_2O, H_3O^+; (3) HS^-, H_2S; (4) HSO_3^-, H_2SO_3. (b) How are acidity and charge related?

46. Arrange the members of each group in order of decreasing acidity: (a) H_2O, H_2Se, H_2S; (b) HI, HCl, HF, HBr; (c) H_2S, S^{2-}, HS^-.

47. Illustrate the leveling effect of water by writing equations for the reactions of HCl and HNO_3 with water.

Ternary Acids

48. In what sense can we describe nitric and sulfuric acids as hydroxyl compounds of nonmetals?

49. What are ternary acids? Write names and formulas for four of them.

50. Write proton-transfer autoionization equations for the following amphiprotic solvents. (a) NH_3, (b) NH_2OH, (c) H_2SO_4.

51. Explain the order of increasing acid strength for the following groups of acids and the order of increasing base strength for their conjugate bases. (a) H_2SO_3, H_2SO_4; (b) HNO_2, HNO_3; (c) H_3PO_3, H_3PO_4; (d) HClO, $HClO_2$, $HClO_3$, $HClO_4$.

52. (a) Write a generalization that describes the order of acid strengths for a series of ternary acids that contain different elements in the same oxidation state from the same group in the periodic table. (b) Indicate the order of acid strengths for the following: (1) HNO_3, H_3PO_4; (2) H_3PO_4, H_3AsO_4; (3) $HClO_3$, H_2SeO_4; (4) $HClO_3$, $HBrO_3$, HIO_3.

*53. List the following acids in order of increasing strength: (a) sulfuric, phosphoric, and perchloric; (b) HIO_3, HIO_2, HIO, and HIO_4; (c) selenous, sulfurous, and tellurous acids; (d) hydrosulfuric, hydroselenic, and hydrotelluric acids; (e) H_2CrO_4, H_2CrO_2, $HCrO_3$, and H_3CrO_4.

Reactions of Acids and Bases

54. Why are acid–base reactions described as neutralization reactions?

55. Distinguish among (a) formula unit equations, (b) total ionic equations, and (c) net ionic equations. What are the advantages and limitations of each?

56. Classify each substance as either an electrolyte or a non-electrolyte: NH_4Cl; HI; C_6H_6; RaF_2; $Zn(CH_3COO)_2$; $Cu(NO_3)_2$; CH_3COOH; $C_{12}H_{22}O_{11}$ (table sugar); LiOH; $KHCO_3$; $NaClO_4$; $La_2(SO_4)_3$; I_2.

57. Classify each substance as either a strong or a weak electrolyte, and then list (a) the strong acids, (b) the strong bases, (c) the weak acids, and (d) the weak bases. NaCl; $MgSO_4$; HCl; CH_3COOH; $Ba(NO_3)_2$; H_3PO_4; $Sr(OH)_2$; HNO_3; HI; $Ba(OH)_2$; LiOH; C_3H_5COOH; NH_3; CH_3NH_2; KOH; HCN; $HClO_4$.

For Exercises 58–60, write balanced (1) formula unit, (2) total ionic, and (3) net ionic equations for reactions between the acid–base pairs. Name all compounds except water. Assume complete neutralization.

58. (a) $HNO_2 + KOH \rightarrow$
(b) $H_2SO_4 + NaOH \rightarrow$
(c) $HCl + Ca(OH)_2 \rightarrow$
(d) $CH_3COOH + KOH \rightarrow$
(e) $HI + NaOH \rightarrow$

59. (a) $H_2CO_3 + Sr(OH)_2 \rightarrow$
(b) $H_2SO_4 + Ca(OH)_2 \rightarrow$
(c) $H_3PO_4 + Ba(OH)_2 \rightarrow$
(d) $HBr + KOH \rightarrow$
(e) $H_3AsO_4 + KOH \rightarrow$

60. (a) $HClO_4 + Ba(OH)_2 \rightarrow$
(b) $HBr + NH_3 \rightarrow$
(c) $HNO_3 + NH_3 \rightarrow$
(d) $H_2SO_4 + Fe(OH)_3 \rightarrow$
(e) $H_2SO_4 + Ba(OH)_2 \rightarrow$

61. Complete these equations by writing the formulas of the omitted compounds.
(a) $Ba(OH)_2 + ? \rightarrow BaSO_4(s) + 2H_2O$
(b) $FeO(s) + ? \rightarrow Fe(NO_3)_2(aq) + H_2O$
(c) $HCl(aq) + ? \rightarrow AgCl(s) + ?$
(d) $Na_2O + ? \rightarrow 2NaOH(aq)$
(e) $NaOH + ? \rightarrow Na_2HPO_4(aq) + ?$
(two possible answers)

62. Although many salts may be formed by a variety of reactions, salts are usually thought of as being derived from the reaction of an acid with a base. For each of the salts listed here, choose the acid and base that would react with each other to form the salt. Write the (i) formula unit, (ii) total ionic, and (iii) net ionic equations for the formation of each salt. (a) $Pb(NO_3)_2$; (b) $AlCl_3$; (c) $(NH_4)_2CO_3$; (d) $Ca(ClO_4)_2$; (e) $Al_2(SO_4)_3$.

63. (a) Which of the following compounds are salts? $CaCO_3$; Na_2O; $U(NO_3)_5$; $AgNO_3$; $Sr(CH_3COO)_2$.
(b) Write an acid–base equation that accounts for the formation of those identified as being salts.

64. Repeat Exercise 63 for: $KMnO_4$; $NiSO_3$; P_4O_{10}; SnF_2; K_3PO_4.

Acidic and Basic Salts

65. What are polyprotic acids? Write names and formulas for five polyprotic acids.
66. What are acidic salts? Write balanced equations to show how the following acidic salts can be prepared from the appropriate acid and base: $NaHSO_3$; $KHCO_3$; NaH_2PO_4; Na_2HPO_4; NaHS.
67. Indicate the mole ratio of acid and base required in each case in Exercise 66.
68. The following salts are components of fertilizers. They are made by reacting gaseous NH_3 with concentrated solutions of acids. The heat produced by the reactions evaporates most of the water. Write balanced formula unit equations that show the formation of each. (a) NH_4NO_3; (b) $NH_4H_2PO_4$; (c) $(NH_4)_2HPO_4$; (d) $(NH_4)_3PO_4$; (e) $(NH_4)_2SO_4$.
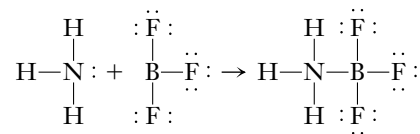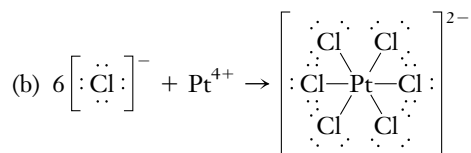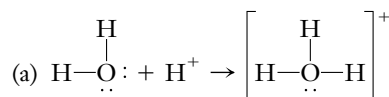

Common lawn fertilizer.

69. What are polyhydroxy bases? Write names and formulas for five polyhydroxy bases.
70. What are basic salts? (a) Write balanced equations to show how each of the following basic salts can be prepared from the appropriate acid and base: $Ca(OH)Cl$; $Al(OH)_2Cl$; $Al(OH)Cl_2$. (b) Indicate the mole ratio of acid and base required in each case.
71. What are amphoteric metal hydroxides? (a) Are they bases? (b) Write the names and formulas for four amphoteric metal hydroxides.
72. Chromium(III) hydroxide and lead(II) hydroxide are typical amphoteric hydroxides. (a) Write the formula unit, total ionic, and net ionic equations for the complete reaction of each hydroxide with nitric acid. (b) Write the same kinds of equations for the reaction of each hydroxide with an excess of potassium hydroxide solution. Reference to Table 10-1 may be helpful.
73. Write the chemical equations for the stepwise ionization of oxalic acid, $(COOH)_2$, a diprotic acid.
74. Write the chemical equations for the stepwise ionization of citric acid, $C_3H_5O(COOH)_3$, a triprotic acid.
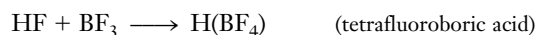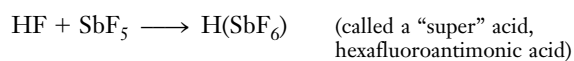
The Lewis Theory

75. Define and illustrate the following terms clearly and concisely. Write an equation to illustrate the meaning of each term. (a) Lewis acid; (b) Lewis base; (c) neutralization according to Lewis theory.
76. What are the advantages and limitations of the Brønsted–Lowry theory?
77. Explain the differences between the Brønsted–Lowry and the Lewis acid–base theories, using the formation of the ammonium ion from ammonia and water to illustrate your points.
78. Write a Lewis formula for each species in the following equations. Label the acids and bases using Lewis theory terminology.
    (a) $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$
    (b) $HCl(g) + H_2O \rightarrow H_3O^+ + Cl^-$
    (c) $NH_3(g) + H_2O \rightleftharpoons NH_4^+ + OH^-$
    (d) $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$
79. What is the term for a single covalent bond in which both electrons in the shared pair come from the same atom? Identify the Lewis acid and base and the donor and acceptor atoms in the following reaction.

$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{N}}: + \ \ \overset{:\ddot{F}:}{\underset{:\ddot{F}:}{B}}-\ddot{F}: \rightarrow H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{N}}-\underset{:\ddot{F}:}{\overset{:\ddot{F}:}{B}}-\ddot{F}:$$

80. Identify the Lewis acid and base and the donor and acceptor atoms in each of the following reactions.

(a) $H-\underset{..}{\overset{\overset{H}{|}}{O}}: + H^+ \rightarrow \left[H-\underset{..}{\overset{\overset{H}{|}}{O}}-H \right]^+$

(b) $6\left[:\ddot{Cl}: \right]^- + Pt^{4+} \rightarrow \left[\begin{array}{c} :\ddot{Cl} \ \ \ :\ddot{Cl}: \\ | \ \ \ \ \ \ | \\ :Cl-Pt-Cl: \\ | \ \ \ \ \ \ | \\ :\ddot{Cl} \ \ \ :\ddot{Cl}: \end{array} \right]^{2-}$

81. Iodine, I_2, is much more soluble in a water solution of potassium iodide, KI, than it is in H_2O. The anion found in the solution is I_3^-. Write an equation for the reaction that forms I_3^-, indicating the Lewis acid and the Lewis base.
82. A group of very strong acids are the fluoroacids, H_mXF_n. Two such acids are formed by Lewis acid–base reactions. (a) Identify the Lewis acid and the Lewis base.

$HF + SbF_5 \longrightarrow H(SbF_6)$ (called a "super" acid, hexafluoroantimonic acid)

$HF + BF_3 \longrightarrow H(BF_4)$ (tetrafluoroboric acid)

(b) To which atom is the H of the product bonded? How is the H bonded?

Preparation of Acids

83. A volatile acid such as nitric acid, HNO_3, can be prepared by adding concentrated H_2SO_4 to a salt of the acid. (a) Write the chemical equation for the reaction of H_2SO_4 with sodium nitrate (called Chile saltpeter). (b) A dilute aqueous solution of H_2SO_4 cannot be used. Why?
84. Outline a method of preparing each of the following acids and write appropriate balanced equations for each preparation: (a) H_2S; (b) HBr; (c) CH_3COOH.
85. Repeat Exercise 84 for (a) carbonic acid, (b) perchloric acid, (c) permanganic acid, and (d) phosphoric acid (two methods).

Mixed Exercises

86. Give the formula for an example chosen from the representative elements for (a) an acidic oxide, (b) an amphoteric oxide, and (c) a basic oxide.
87. Identify each of the following as (i) acidic, (ii) basic, or (iii) amphoteric. Assume all oxides are dissolved in or are in contact with water. Do not be intimidated by the way in which the formula of the compound is written. (a) Cs_2O; (b) Cl_2O_5; (c) HCl; (d) $SO_2(OH)_2$; (e) HNO_2, (f) Al_2O_3; (g) BaO; (h) H_2O; (i) CO_2; (j) SO_2.
88. Indicate which of the following substances—(a) H_2S; (b) $PO(OH)_3$; (c) H_2CaO_2; (d) $ClO_3(OH)$; (e) $Sb(OH)_3$— can act as (i) an acid, (ii) a base, or (iii) both according to the Arrhenius (classical) theory or the Brønsted–Lowry theory. Do not be confused by the way in which the formulas are written.
89. (a) Write equations for the reactions of HCO_3^- with H_3O^+ and HCO_3^- with OH^-, and indicate the conjugate acid–base pairs in each case. (b) A substance such as HCO_3^- that reacts with both H_3O^+ and OH^- is said to be _____. (Fill in the missing word.)
90. (a) List the conjugate bases of H_3PO_4, NH_4^+, and OH^- and the conjugate acids of HSO_4^-, PH_3, and PO_4^{3-}. (b) Given that NO_2^- is a stronger base than NO_3^-, which is the stronger acid—nitric acid, HNO_3, or nitrous acid, HNO_2?
*91. A 0.1 M solution of copper(II) chloride, $CuCl_2$, causes the light bulb in Figure 4-2 to glow brightly. When hydrogen sulfide, H_2S, a very weak acid, is added to the solution, a black precipitate of copper(II) sulfide, CuS, forms, and the bulb still glows brightly. The experiment is repeated with a 0.1 M solution of copper(II) acetate, $Cu(CH_3COO)_2$, which also causes the bulb to glow brightly. Again, CuS forms, but this time the bulb glows dimly. With the aid of

ionic equations, explain the difference in behavior between the $CuCl_2$ and $Cu(CH_3COO)_2$ solutions.
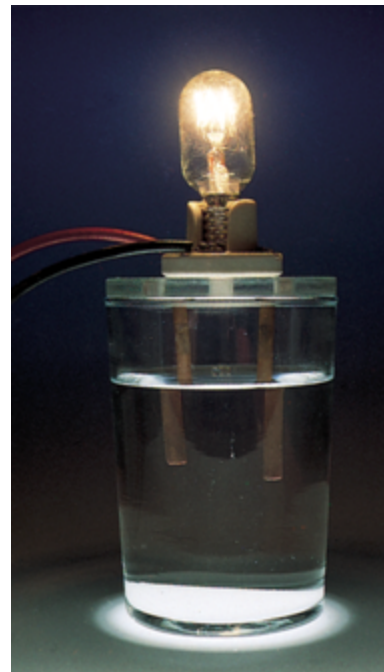
Conductivity experiment.

92. Referring again to Figure 4-2, explain the following results of a conductivity experiment (use ionic equations). (a) Individual solutions of NaOH and HCl cause the bulb to glow brightly. When the solutions are mixed, the bulb still glows brightly but not as brightly as before. (b) Individual solutions of NH_3 and CH_3COOH cause the bulb to glow dimly. When the solutions are mixed, the bulb glows brightly.
93. Which statements are true? Rewrite any false statement so that it is correct. (a) Strong acids and bases are virtually 100% ionized or dissociated in dilute aqueous solutions. (b) The leveling effect is the seemingly identical strengths of all acids and bases in aqueous solutions. (c) A conjugate acid is a molecule or ion formed by the addition of a proton to a base. (d) Amphoterism and amphiprotism are the same in aqueous solution.

CONCEPTUAL EXERCISES

94. The following diagrams are nanoscale representations of different acids in aqueous solution; the water molecules are not shown. The small, dark circles are hydrogen atoms

(a)   **(b)**   **(c)**   **(d)**
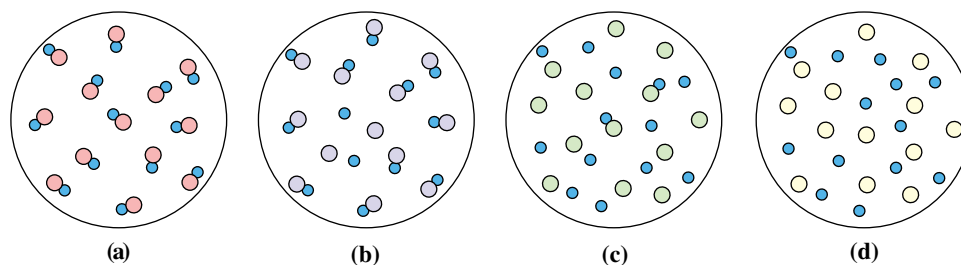
or ions. The larger, lighter circles represent the anions.
(a) Which diagram best represents hydrochloric acid?
(b) Which diagram best represents acetic acid?

95. When a 0.1 M aqueous ammonia solution is tested with a conductivity apparatus (Figure 4.2), the bulb glows dimly. When a 0.1 M hydrochloric acid solution is tested, the bulb glows brightly. Would you expect the bulb to glow more brightly, stop glowing, or stay the same as water is added to each of the solutions? Explain your reasoning.

96. On the planet Baseacidopolous, the major solvent is liquid ammonia, not water. Ammonia autoionizes much like water ($2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$). If instead of water, ammonia is used as a solvent: (a) What is the formula of the cation that would indicate that a compound is an acid? (b) What is the formula of the anion produced if a compound is a base? (c) Look at the way that NaCl is formed from an acid–base reaction on earth and determine if NaCl can be a salt on Baseacidopolous.
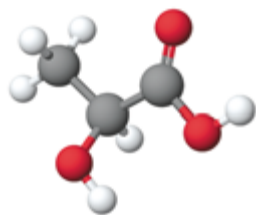
BUILDING YOUR KNOWLEDGE

97. One of the chemical products of muscle contraction is lactic acid ($CH_3CH(OH)CO_2H$), a monoprotic acid whose structure is

Prolonged exercise can temporarily overload the body's capacity for elimination of this substance, and the resulting increase in lactic acid concentration in the muscles causes pain and stiffness. (a) Lactic acid has six H atoms, yet it acts as a monoprotic acid in an aqueous environment. Which of the H atoms is ionizable? (b) Draw the structural formula of the conjugate base. (c) Write a net ionic equation that illustrates the ionization of lactic acid

in water. (d) Describe the geometry around each of the carbon atoms in lactic acid.

Runners risk suffering from lactic acid buildup.

98. Autoionization can occur when an ion other than an H^+ is transferred, as exemplified by the transfer of a Cl^- ion from one PCl_5 molecule to another. Write the equation for this reaction. What are the shapes of the two ions that are formed?

99. Limestone, $CaCO_3$, is a water-insoluble material, whereas $Ca(HCO_3)_2$ is soluble. Caves are formed when rainwater containing dissolved CO_2 passes over limestone for long periods of time. Write a chemical equation for the acid–base reaction.

100. Acids react with metal carbonates and hydrogen carbonates to form carbon dioxide and water. (a) Write the balanced equation for the reaction that occurs when baking soda, $NaHCO_3$, and vinegar, 5% acetic acid, are mixed. What causes the "fizz"? (b) Lactic acid, $CH_3CH(OH)COOH$, is found in sour milk and in buttermilk. Many of its reactions are very similar to those of acetic acid. Write the balanced equation for the reaction of baking soda, $NaHCO_3$, with lactic acid. Explain why bread "rises" during the baking process.

101. Some of the acid formed in tissues is excreted through the kidneys. One of the bases removing the acid is HPO_4^{2-}. Write the equation for the reaction. Could Cl^- serve this function?