and that the unshared electron pair (and negative charge) is shared equally by the two terminal carbons.

\[
\text{allyl anion} \\
\text{[H}_2\text{C}=-\text{CH}=\text{CH}_2 \quad ? \text{ ]}
\]

(c) Using the curved-arrow notation, derive a resonance structure for benzene (shown here) which shows that all carbon–carbon bonds are identical and have a bond order of 1.5.

\[
\text{[benzene]}
\]

3.4 BRøNSTED–LOWRY ACIDS AND BASES

A. Definition of Brønsted Acids and Bases

Although less general than the Lewis concept, the Brønsted–Lowry acid–base concept provides another way of thinking about acids and bases that is extremely important and useful in organic chemistry. The Brønsted–Lowry definition of acids and bases was published in 1923, the same year that Lewis formulated his ideas of acidity and basicity. A species that donates a proton in a chemical reaction is called a Brønsted acid; a species that accepts a proton in a chemical reaction is a Brønsted base.

The reaction of ammonium ion with hydroxide ion (see Eq. 3.5) is an example of a Brønsted acid–base reaction.

\[
\text{ammonium ion} \quad \text{hydroxide ion} \quad \text{ammonia} \quad \text{water} \\
\text{(a Brønsted acid)} \quad \text{(a Brønsted base)} \quad \text{(a Brønsted base)} \quad \text{(a Brønsted acid)}
\]

On the left side of this equation, the ammonium ion is acting as a Brønsted acid and the hydroxide ion is acting as a Brønsted base; looking at the equation from right to left, water is acting as a Brønsted acid, and ammonia as a Brønsted base.

The “classical” definition of a Brønsted acid–base reaction given above focuses on the movement of a proton. But in organic chemistry, we are always going to focus on the movement of electrons. As Eq. 3.9a illustrates, any Brønsted acid–base reaction can be described with the curved-arrow notation for electron-pair displacement reactions. A Brønsted acid–base reaction is nothing more than an electron-pair displacement reaction on a hydrogen. It’s the action of the electrons that causes the net transfer of a proton from the Brønsted acid to the Brønsted base. In terms of electrons, a Brønsted base, then, is merely a special case of a Lewis base: a Brønsted base is a Lewis base that donates its electron pair to a proton. A Brønsted acid is the species that provides a proton to the base.
When a Brønsted acid loses a proton, its **conjugate base** is formed; when a Brønsted base gains a proton, its **conjugate acid** is formed. When a Brønsted acid loses a proton, it becomes a Brønsted base; this acid and the resulting base constitute a **conjugate acid–base pair**. In any Brønsted acid–base reaction there are two conjugate acid–base pairs. Hence, in Eq. 3.9, $\text{NH}_4^+$ and $\text{NH}_3$ are one conjugate acid–base pair, and $\text{H}_2\text{O}$ and $\text{OH}^-$ are the other.

Notice that the conjugate acid–base relationship is **across the equilibrium arrows**. For example, $\text{NH}_4^+$ and $\text{NH}_3$ are a conjugate acid–base pair, but $\text{NH}_4^+$ and $\text{OH}^-$ are not a conjugate acid–base pair.

The identification of a compound as an acid or a base depends on how it behaves in a specific chemical reaction. Water, for example, can act as either an acid or a base. Compounds that can act as either acids or bases are called **amphoteric compounds**. Water is the archetypal example of an amphoteric compound. For example, in Eq. 3.10, water is the conjugate **acid** in the acid–base pair $\text{H}_2\text{O}^-/\text{OH}^-$; in the following reaction, water is the conjugate **base** in the acid–base pair $\text{H}_2\text{O}^+/\text{H}_2\text{O}$:

$$
\text{H}_2\text{O}^- + \text{H}_2\text{O}^+ \leftrightarrow \text{H}_2\text{O} + \text{H}_3\text{O}^+
$$

### PROBLEMS

3.5 In the following reactions, label the conjugate acid–base pairs. Then draw the curved-arrow notation for these reactions in the left-to-right direction.

(a) $\text{NH}_4^+ + \text{OH}^- \leftrightarrow \text{NH}_3 + \text{H}_2\text{O}$
(b) $\text{NH}_4^+ + \text{OH}^- \leftrightarrow \text{NH}_3 + \text{H}_2\text{O}$

3.6 Write a Brønsted acid–base reaction in which $\text{H}_2\text{O}^-/\text{OH}^-$ and $\text{CH}_3\text{OH}/\text{CH}_3\text{O}^-$ act as conjugate acid–base pairs.
B. Nucleophiles, Electrophiles, and Leaving Groups

The Brønsted–Lowry acid–base concept is important for organic chemistry because many reactions are Brønsted acid–base reactions, and many others have close analogy to Brønsted acid–base reactions. Let’s look at one example.

\[ \text{HO}^- + 
\begin{array}{c}
\text{H}_2\text{C} - \text{Br}^+ \\
\end{array} \rightarrow \text{HO}^- + \text{CH}_3 + \text{Br}^- \] (3.12a)

An analogous Brønsted acid–base reaction is

\[ \text{HO}^- + 
\begin{array}{c}
\text{H} - \text{Br}^+ \\
\end{array} \rightarrow \text{HO}^- + \text{H} + \text{Br}^- \] (3.12b)

These reactions are very similar: Both reactions are electron-pair displacements initiated by the Lewis base hydroxide. In Eq. 3.12a, the hydroxide base donates electrons to a carbon. In Eq. 3.12b, the hydroxide base donates electrons to a hydrogen. The process in Eq. 3.12a is a well-known organic reaction; the process in Eq. 3.12b is a well-known Brønsted acid–base reaction. The Brønsted acid–base reaction is much faster than the reaction at carbon, but, other than that difference, these processes are essentially the same. We’ll see analogies like this all the time in organic chemistry. What makes them particularly useful is that we know a lot about Brønsted acid–base reactions. We can apply what we know about these reactions to understanding the analogous organic reactions.

This analogy leads to additional widely used terminology that we have to master. As we learned in the previous section, a Lewis base (such as hydroxide on the left of Eq. 3.12b) that donates an electron pair to a proton is called a Brønsted base. A Lewis base (such as hydroxide on the left of Eq. 3.12a) that donates an electron pair to an atom other than hydrogen is called a nucleophile (from the Greek philos, loving; nucleophile = “nucleus-loving”). Thus, hydroxide is a Brønsted base in one reaction and a nucleophile in the other.

- **Electron-pair donation to hydrogen:**
  \[ \text{HO}^- + 
\begin{array}{c}
\text{H} - \text{Br}^+ \\
\end{array} \rightarrow \text{HO}^- + \text{H} + \text{Br}^- \] (3.13a)

- **Electron-pair donation to an atom other than hydrogen:**
  \[ \text{HO}^- + 
\begin{array}{c}
\text{H}_3\text{C} - \text{Br}^+ \\
\end{array} \rightarrow \text{HO}^- + \text{CH}_3 + \text{Br}^- \] (3.13b)

The atom that receives a pair of electrons from the Lewis base is called an electrophile (“electron-loving”). An electrophile is a type of Lewis acid. An electrophile can be a proton or it can be another atom. What makes it an electrophile is the same thing that makes it a Lewis acid: it receives a pair of electrons from a Lewis base, whether that base is a nucleophile or a Brønsted base.
The group that receives electrons from the breaking bond, in this case the —Br, is called a leaving group. A group becomes a leaving group when one of its atoms accepts an electron pair from a breaking bond. One of the author’s students has put it less formally, but perhaps more descriptively: a leaving group is a group that takes a pair of bonding electrons and runs.

\[
\ce{H-O-} \text{ } \ce{H-C-Br} \rightarrow \ce{H-O-} \text{ } \ce{H-C-Br} + \text{a Brønsted acid}
\]  

(3.15)

A leaving group in one direction of a reaction becomes a nucleophile in the other direction, as the following example demonstrates.

\[
\ce{H-O-} \text{ } \ce{H-C-Br} \rightleftharpoons \ce{H-O-} \text{ } \ce{H-C-Br} + \ce{CH_3} + :\text{Br}^-
\]  

(3.16)

The term leaving group can also be used in Lewis acid–base dissociation reactions. Note the absence of a nucleophile in a Lewis acid–base dissociation, and the absence of a leaving group in a Lewis acid–base association.

\[
\ce{F^-} \text{ } \ce{B-F} \rightleftharpoons \ce{F^-} \text{ } \ce{B-F} + \ce{F^-}
\]  

(3.17)

The terms you’ve learned here are important because they are used throughout the world of organic chemistry. Your instructor will use them, and we’ll use them throughout this book. To summarize:

1. A Lewis base can act as either a Brønsted base or a nucleophile. A Brønsted base is a Lewis base that donates a pair of electrons to a hydrogen and removes the hydrogen as a proton. A nucleophile is a Lewis base that donates a pair of electrons to an atom other than hydrogen.
2. An electrophile is the atom that receives an electron pair from a Lewis base.

3. A leaving group is a group containing an atom that accepts an electron pair from one of its bonds, which is broken as a result.

This section is about analyzing the roles of the various species in reactions. The definitions developed here describe these roles. You will find that most of the reactions you will study can be analyzed in terms of these roles, and hence an understanding of this section will prove to be crucial in helping you to understand and even predict reactions. The first step in this understanding is to apply these definitions in the analysis of reactions. Study Problem 3.5 points you in this direction.

### Study Problem 3.5

Following is a series of acid–base reactions that represent the individual steps in a known organic transformation, the replacement of \(-\text{Br}\) by \(-\text{OH}\) at a carbon bearing three alkyl groups. Considering only the forward direction, classify each reaction as a Brønsted acid–base reaction or a Lewis acid–base association/dissociation. Classify each labeled species (or a group within each species) with one or more of the following terms: Brønsted base, Brønsted acid, Lewis base, Lewis acid, nucleophile, electrophile, and/or leaving group.

\[
\begin{align*}
\text{H}_3\text{C}\text{C}^-\text{Br}^- & \quad \text{H}_3\text{C}\text{C}^+\text{Br}^- \\
\text{CH}_3 & \quad \text{CH}_3 \\
A & \quad B \\
\text{H}_3\text{C}\text{C}^+\text{O}^-\text{H} & \quad \text{H}_3\text{C}\text{C}^-\text{O}^+\text{H} \\
\text{CH}_3 & \quad \text{CH}_3 \\
B & \quad E \\
\text{H}_3\text{C}\text{C}^-\text{O}^-\text{H} & \quad \text{H}_3\text{C}\text{C}^+\text{O}^-\text{H} + \text{H}^\text{+}\text{O}^-\text{H}_2 \\
\text{CH}_3 & \quad \text{CH}_3 \\
E & \quad F & \quad G & \quad H \\
\end{align*}
\]

**Solution**

Classify each reaction first, and then analyze the role of each species. Reaction 3.18a is a Lewis acid–base dissociation. (Notice that a single curved arrow describes the dissociation.) In compound A, Br is the leaving group.

Reaction 3.18b is a Lewis acid–base association reaction. Cation B (specifically, its electron-deficient carbon) is a Lewis acid and an electrophile. Water molecule D is a Lewis base and a nucleophile.

Reaction 3.18c is a Brønsted acid–base reaction. Ion E and compound G constitute a conjugate Brønsted acid–base pair, and compound F and compound H are a conjugate Brønsted base–acid pair. The water molecule F is both a Lewis base and a Brønsted base. The proton of E that receives an electron pair from water is a Lewis acid and is also an electrophile. The part of E that becomes G is a leaving group.
Another aspect of acid–base chemistry that can be widely applied to understanding organic reactions is the strengths of Brønsted acids and bases. The strength of a Brønsted acid is determined by how well it transfers a proton to a standard Brønsted base. The standard base traditionally used for comparison is water. The transfer of a proton from a general acid, HA, to water is indicated by the following equilibrium:

\[
\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{A}^- + \text{H}_3\text{O}^+ \tag{3.19}
\]

The equilibrium constant for this reaction is given by

\[
K_{\text{eq}} = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}][\text{H}_2\text{O}]} \tag{3.20}
\]

(The quantities in brackets are molar concentrations at equilibrium.) Because water is the solvent, and its concentration remains effectively constant, regardless of the concentrations of the other species in the equilibrium, we multiply Eq. 3.20 through by [H\textsubscript{2}O] and thus define another constant \(K_a\), called the dissociation constant:

\[
K_a = K_{\text{eq}}[\text{H}_2\text{O}] = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]} \tag{3.21}
\]
Each acid has its own unique dissociation constant. The larger the dissociation constant of an acid, the more \( H_3O^+ \) ions are formed when the acid is dissolved in water at a given concentration. Thus, the strength of a Brønsted acid is measured by the magnitude of its dissociation constant.

Because the dissociation constants of different Brønsted acids cover a range of many powers of 10, it is useful to express acid strength in a logarithmic manner. Using \( p \) as an abbreviation for negative logarithm, we can write the following definitions:

\[
pK_a = -\log K_a \quad (3.22a)
\]
\[
pH = -\log [H_3O^+] \quad (3.22b)
\]

Some \( pK_a \) values of several Brønsted acids are given in Table 3.1 in order of decreasing \( pK_a \). Because stronger acids have larger \( K_a \) values, it follows from Eq. 3.22a that stronger acids have smaller \( pK_a \) values. Thus, HCN (\( pK_a = 9.4 \)) is a stronger acid than water (\( pK_a = 15.7 \)). In other words, the strengths of acids in the first column of Table 3.1 increase from the top to the bottom of the table.

It is important to understand the difference between \( pH \) and \( pK_a \). The \( pH \) is a measure of proton concentration and is an experimentally alterable property of a solution. The \( pK_a \) is a fixed property of a Brønsted acid. If this difference isn’t secure in your mind, be sure to consult Study Guide Link 3.4 for further help.

Three points about the \( pK_a \) values in Table 3.1 are worth special emphasis. The first has to do with the \( pK_a \) values for very strong and very weak acids. The direct \( pK_a \) determination of an acid in aqueous solution is limited to acids that are less acidic than \( H_3O^+ \) and more acidic than \( H_2O \). The reason is that \( H_3O^+ \) is the strongest acid that can exist in water. If we dissolve a stronger acid in water, it immediately ionizes to \( H_3O^+ \). Similarly, \( _{OH} \) is the strongest base that can exist in water, and stronger bases react instantly with water to form \( _{OH} \). However, \( pK_a \) values for very strong and very weak acids can be measured in other solvents, and through various methods these \( pK_a \) values can in many cases be used to estimate aqueous \( pK_a \) values. This is the basis for the estimates of the acidities of strong acids such as HCl and very weak acids such as \( NH_3 \) in Table 3.1. These approximate \( pK_a \) values will suffice for many of our applications.

The second point is that much important organic chemistry is carried out in nonaqueous solvents. In nonaqueous solvents, \( pK_a \) values typically differ substantially from \( pK_a \) values of the same acids determined in water. However, in some of these solvents, the relative \( pK_a \) values are roughly the same as they are in water. In other nonaqueous solvents, though, even the relative order of \( pK_a \) values is different. (We’ll learn about solvent effects in Chapter 8.) Despite these differences, aqueous \( pK_a \) values such as those in Table 3.1 are the most readily available and comprehensive data on which to base a discussion of acidity and basicity.

The last point has to do with the \( K_a \) of water, which is \( 10^{-15.7} \), from which we obtain \( pK_a = 15.7 \). Don’t confuse this with the ion-product constant of water, which is defined by the
**Relative Strengths of Some Acids and Bases**

<table>
<thead>
<tr>
<th>Conjugate acid</th>
<th>( pK_a )</th>
<th>Conjugate base</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NH}_3 ) (ammonia)</td>
<td>( -35 )†</td>
<td>( \text{N}_3 ) (amide)</td>
</tr>
<tr>
<td>( \text{RO}^- ) (alcohol)</td>
<td>15–19*</td>
<td>( \text{RO}^- ) (alkoxide)</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} ) (water)</td>
<td>15.7</td>
<td>( \text{HO}^- ) (hydroxide)</td>
</tr>
<tr>
<td>( \text{RS}^- ) (thiol)</td>
<td>10–12*</td>
<td>( \text{RS}^- ) (thiolate)</td>
</tr>
<tr>
<td>( \text{RN}^+ ) (trialkylammonium ion)</td>
<td>9–11*</td>
<td>( \text{RN}^+ ) (trialkylamine)</td>
</tr>
<tr>
<td>( \text{NH}_4^+ ) (ammonium ion)</td>
<td>9.25</td>
<td>( \text{NH}_3 ) (ammonia)</td>
</tr>
<tr>
<td>( \text{HCN} ) (hydrocyanic acid)</td>
<td>9.40</td>
<td>( \text{CN}^- ) (cyanide)</td>
</tr>
<tr>
<td>( \text{H}_3\text{SO}_4^- ) (hydrsulfuric acid)</td>
<td>7.0</td>
<td>( \text{HSO}_4^- ) (hydrsulfide)</td>
</tr>
<tr>
<td>( \text{RO}^- ) (carboxylic acid)</td>
<td>4–5*</td>
<td>( \text{RO}^- ) (carboxylate)</td>
</tr>
<tr>
<td>( \text{HF}^- ) (hydrofluoric acid)</td>
<td>3.2</td>
<td>( \text{F}^- ) (fluoride)</td>
</tr>
<tr>
<td>( \text{CH}_3\text{C}=-\text{SO}_3^- ) (p-toluene-sulfonic acid)</td>
<td>( -1 )</td>
<td>( \text{CH}_3\text{C}=-\text{SO}_3^- ) (p-toluene-sulfonate, or “tosylate”)</td>
</tr>
<tr>
<td>( \text{H}_2\text{O}^- ) (hydronium ion)</td>
<td>( -1.7 )</td>
<td>( \text{H}_2\text{O}^- ) (water)</td>
</tr>
<tr>
<td>( \text{H}_2\text{SO}_4^- ) (sulfuric acid)</td>
<td>( -3 )†</td>
<td>( \text{HSO}_4^- ) (bisulfate)</td>
</tr>
<tr>
<td>( \text{HCl}^- ) (hydrochloric acid)</td>
<td>( -6 ) to ( -7 )†</td>
<td>( \text{Cl}^- ) (chloride)</td>
</tr>
<tr>
<td>( \text{HBr}^- ) (hydrobromic acid)</td>
<td>( -8 ) to ( -9.5 )†</td>
<td>( \text{Br}^- ) (bromide)</td>
</tr>
<tr>
<td>( \text{HI}^- ) (hydroiodic acid)</td>
<td>( -9.5 ) to ( -10 )†</td>
<td>( \text{I}^- ) (iodide)</td>
</tr>
<tr>
<td>( \text{HClO}_4^- ) (perchloric acid)</td>
<td>( -10 ) (?)†</td>
<td>( \text{ClO}_4^- ) (perchlorate)</td>
</tr>
</tbody>
</table>

*Precise value varies with the structure of \( R \).
†Estimates; exact measurement is not possible.

expression \( K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 10^{-14} \text{ M}^2 \), or \(- \log K_w = 14\). The ionization constant of water is defined by the expression

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = \frac{K_w}{[\text{H}_2\text{O}]} = \frac{10^{-14}}{55.5 \text{ M}} = 10^{-15.7} \text{ M}
\]

This expression has the concentration of water itself in the denominator, and thus differs from the ion-product constant of water by a factor of \( 1/55.5 \). The logarithm of this factor, \(-1.7 \), accounts for the difference between \( pK_a \) and \( pK_w \):

\[
pK_a \text{ of } \text{H}_2\text{O} = -\log K_w - \log \left( \frac{1}{55.5} \right) = 15.7
\]

**D. Strengths of Bronsted Bases**

The strength of a Brønsted base is directly related to the \( pK_a \) of its conjugate acid. Thus, the base strength of fluoride ion is indicated by the \( pK_a \) of its conjugate acid, HF; the base strength of ammonia is indicated by the \( pK_a \) of its conjugate acid, the ammonium ion, \( \text{NH}_4^+ \). That is, when we say that a base is weak, we are also saying that its conjugate acid is strong; or, if a
base is strong, its conjugate acid is weak. Thus, it is easy to tell which of two bases is stronger by looking at the pK_a values of their conjugate acids: the stronger base has the conjugate acid with the greater (or less negative) pK_a. For example, \( \cdot \text{CN} \), the conjugate base of HCN, is a weaker base than \( \cdot \text{OH} \), the conjugate base of water, because the pK_a of HCN is less than that of water. Thus, the strengths of the bases in the third column of Table 3.1 increase from the bottom to the top of the table.

### E. Equilibria in Acid–Base Reactions

When a Brønsted acid and base react, we can tell immediately whether the equilibrium lies to the right or left by comparing the pK_a values of the two acids involved. The equilibrium in the reaction of an acid and a base always favors the side with the weaker acid and weaker base.

For example, in the following acid–base reaction, the equilibrium lies well to the right, because H_2O is the weaker acid and \( \cdot \text{CN} \) is the weaker base.

\[
\begin{align*}
\text{HCN} + \text{OH}^- &\rightleftharpoons \cdot \text{CN} + \text{H}_2\text{O} \\
pK_a &= 9.4 \quad \text{(stronger base)} & pK_a &= 15.7 \quad \text{(weaker base)}
\end{align*}
\]

(3.23)

We’ll frequently find it useful to estimate the equilibrium constants of acid–base reactions. The equilibrium constant for an acid–base reaction can be calculated in a straightforward way from the pK_a values of the two acids involved. To do this calculation, subtract the pK_a of the acid on the left side of the equation from the pK_a of the acid on the right and take the antilog of the resulting number. That is, for an acid–base reaction

\[
\text{AH} + \text{B}^- \rightleftharpoons \text{A}^- + \text{BH}
\]

(3.24)

in which the pK_a of AH is pK_{AH} and the pK_a of BH is pK_{BH}, the equilibrium constant can be calculated by

\[
\log K_{eq} = pK_{BH} - pK_{AH}
\]

(3.25a)

or

\[
K_{eq} = 10^{(pK_{BH} - pK_{AH})}
\]

(3.25b)

This procedure is illustrated for the reaction in Eq. 3.23 in Study Problem 3.6, and is justified in Problem 3.46 at the end of the chapter.

**Study Problem 3.6**

Calculate the equilibrium constant for the reaction of HCN with hydroxide ion (see Eq. 3.22).

**Solution** First identify the acids on each side of the equation. The acid on the left is HCN because it loses a proton to give cyanide (\( \cdot \text{CN} \)), and the acid on the right is H_2O because it loses a proton to give hydroxide (\( \cdot \text{OH} \)). Before doing any calculation, ask whether the equilibrium should lie to the left or right. Remember that the stronger acid and stronger base are always on one side of the equation, and the weaker acid and weaker base are on the other side. The equilibrium always favors the weaker acid and weaker base. This means that the right side of Eq. 3.23 is favored and, therefore, that the equilibrium constant in the left-to-right direction is > 1. This provides a quick check on whether your calculation is reasonable. Next, apply Eq. 3.25a. Subtracting
the \( pK_a \) of the acid on the left of Eq. 3.23 (HCN) from the one on the right (H\(_2\)O) gives the logarithm of the desired equilibrium constant \( K_{eq} \). (The relevant \( pK_a \) values come from Table 3.1.)

\[
\log K_{eq} = 15.7 - 9.4 = 6.3
\]

The equilibrium constant for this reaction is the antilog of this number:

\[
K_{eq} = 10^{6.3} = 2 \times 10^6
\]

This large number means that the equilibrium of Eq. 3.23 lies far to the right. That is, if we dissolve HCN in an equimolar solution of NaOH, a reaction occurs to give a solution in which there is much more \( \text{CN}^- \) than either \( \text{OH}^- \) or HCN. Exactly how much of each species is present could be determined by a detailed calculation using the equilibrium-constant expression, but in a case like this, such a calculation is unnecessary. The equilibrium constant is so large that, even with water in large excess as the solvent, the reaction lies far to the right. This also means that if we dissolve NaCN in water, only a minuscule amount of \( \text{CN}^- \) reacts with the H\(_2\)O to give \( \text{OH}^- \) and HCN.

**PROBLEM 3.14** Using the \( pK_a \) values in Table 3.1, calculate the equilibrium constant for each of the following reactions.

(a) \( \text{NH}_3 \) acting as a base toward the acid HCN
(b) \( \text{F}^- \) acting as a base toward the acid HCN

Sometimes students confuse acid strength and base strength when they encounter an amphoteric compound (see p. 97). Water presents this sort of problem. According to the definitions just developed, the base strength of water is indicated by the \( pK_a \) of its conjugate acid, H\(_3\)O\(^+\), whereas the acid strength of water (or the base strength of its conjugate base hydroxide) is indicated by the \( pK_a \) of H\(_2\)O itself. These two quantities refer to very different reactions of water:

**Water acting as a base:**

\[
\text{H}_2\text{O} + \text{AH} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^- \\
pK_a = -1.7
\]  

(3.26a)

**Water acting as an acid:**

\[
\text{B}^- + \text{H}_2\text{O} \rightleftharpoons \text{BH} + \text{OH}^- \\
pK_a = 15.7
\]  

(3.26b)

**PROBLEM 3.15** Write an equation for each of the following equilibria, and use Table 3.1 to identify the \( pK_a \) value associated with the acidic species in each equilibrium.

(a) ammonia acting as a base toward the acid water
(b) ammonia acting as an acid toward the base water

Which of these reactions has the larger \( K_{eq} \) and therefore is more important in an aqueous solution of ammonia?