CHAPTER 15
ACIDS AND BASES

Problem Categories
Biological: 15.96, 15.107, 15.135, 15.143, 15.147.
Conceptual: 15.32, 15.35, 15.36, 15.70, 15.75, 15.76, 15.77, 15.78, 15.81, 15.82, 15.95, 15.98, 15.100, 15.113, 15.127, 15.128, 15.139.
Environmental: 15.134

Difficulty Level
Easy: 15.3, 15.4, 15.5, 15.6, 15.7, 15.8, 15.15, 15.16, 15.17, 15.18, 15.19, 15.20, 15.21, 15.22, 15.23, 15.24, 15.26, 15.31, 15.33, 15.34, 15.37, 15.67, 15.68, 15.69, 15.78, 15.92, 15.94, 15.98, 15.99, 15.100, 15.102, 15.105, 15.109, 15.112, 15.129, 15.133.

15.3 Table 15.2 of the text contains a list of important Brønsted acids and bases. (a) both (why?), (b) base, (c) acid, (d) base, (e) acid, (f) base, (g) base, (h) base, (i) acid, (j) acid.

15.4 Recall that the conjugate base of a Brønsted acid is the species that remains when one proton has been removed from the acid.

(a) nitrite ion: NO2−
(b) hydrogen sulfate ion (also called bisulfate ion): HSO4−
(c) hydrogen sulfide ion (also called bisulfide ion): HS−
(d) cyanide ion: CN−
(e) formate ion: HCOO−

15.5 In general the components of the conjugate acid–base pair are on opposite sides of the reaction arrow. The base always has one fewer proton than the acid.

(a) The conjugate acid–base pairs are (1) HCN (acid) and CN− (base) and CH3COOH (acid).
(b) (1) HCO3− (acid) and CO32− (base) and (2) HCO3− (base) and H2CO3 (acid).
(c) (1) H2PO4− (acid) and HPO42− (base) and (2) NH3 (base) and NH4+ (acid).
(d) (1) HClO (acid) and ClO− (base) and (2) CH3NH2 (base) and CH3NH3+ (acid).
(e) (1) H2O (acid) and OH− (base) and (2) CO32− (base) and HCO3− (acid).

15.6 The conjugate acid of any base is just the base with a proton added.

(a) H2S (b) H2CO3 (c) HCO3− (d) H2PO4 (e) H2PO4−
(f) HPO42− (g) H2SO4 (h) HSO4− (i) HSO3−
15.7 (a) The Lewis structures are

\[
\begin{align*}
\text{O} & \text{C} \text{-} \text{C} \text{O} \text{O} \text{O}^{-} \\
\text{O} & \text{H} \text{O} \text{O}^{-}
\end{align*}
\]

and

\[
\begin{align*}
\text{O} & \text{C} \text{-} \text{C} \text{O} \text{O} \text{O}^{-} \\
\text{O} & \text{O} \text{O}^{-}
\end{align*}
\]

(b) \( \text{H}^+ \) and \( \text{H}_2\text{C}_2\text{O}_4 \) can act only as acids, \( \text{HC}_2\text{O}_4^- \) can act as both an acid and a base, and \( \text{C}_2\text{O}_4^{2-} \) can act only as a base.

15.8 The conjugate base of any acid is simply the acid minus one proton.

(a) \( \text{CH}_2\text{ClCOO}^- \)

(b) \( \text{IO}_4^- \)

(c) \( \text{H}_2\text{PO}_4^- \)

(d) \( \text{HPO}_4^{2-} \)

(e) \( \text{PO}_4^{3-} \)

(f) \( \text{HSO}_4^- \)

(g) \( \text{SO}_4^{2-} \)

(h) \( \text{IO}_3^- \)

(i) \( \text{SO}_3^{2-} \)

(j) \( \text{NH}_3 \)

(k) \( \text{HS}^- \)

(l) \( \text{S}^{2-} \)

(m) \( \text{OCl}^- \)

15.15 \([\text{H}^+] = 1.4 \times 10^{-3} \text{ M}\)

\([\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-3}} = 7.1 \times 10^{-12} \text{ M}\)

15.16 \([\text{OH}^-] = 0.62 \text{ M}\)

\([\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{0.62} = 1.6 \times 10^{-14} \text{ M}\)

15.17 (a) \( \text{HCl} \) is a strong acid, so the concentration of hydrogen ion is also \( 0.0010 \text{ M} \). (What is the concentration of chloride ion?) We use the definition of pH.

\[\text{pH} = -\log[\text{H}^+] = -\log(0.0010) = 3.00\]

(b) \( \text{KOH} \) is an ionic compound and completely dissociates into ions. We first find the concentration of hydrogen ion.

\[\frac{[\text{H}^+]}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{0.76} = 1.3 \times 10^{-14} \text{ M}\]

The pH is then found from its defining equation

\[\text{pH} = -\log[\text{H}^+] = -\log[1.3 \times 10^{-14}] = 13.89\]

15.18 (a) \( \text{Ba(OH)}_2 \) is ionic and fully ionized in water. The concentration of the hydroxide ion is \( 5.6 \times 10^{-4} \text{ M} \) (Why? What is the concentration of \( \text{Ba}^{2+} \)?) We find the hydrogen ion concentration.

\[\frac{[\text{H}^+]}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{5.6 \times 10^{-4}} = 1.8 \times 10^{-11} \text{ M}\]

The pH is then:

\[\text{pH} = -\log[\text{H}^+] = -\log(1.8 \times 10^{-11}) = 10.74\]

(b) Nitric acid is a strong acid, so the concentration of hydrogen ion is also \( 5.2 \times 10^{-4} \text{ M} \). The pH is:

\[\text{pH} = -\log[\text{H}^+] = -\log(5.2 \times 10^{-4}) = 3.28\]
15.19 Since $\text{pH} = -\log[H^+]$, we write $[H^+] = 10^{-\text{pH}}$

(a) $[H^+] = 10^{-2.42} = 3.8 \times 10^{-3} \text{ M}$(c) $[H^+] = 10^{-6.96} = 1.1 \times 10^{-7} \text{ M}$

(b) $[H^+] = 10^{-11.21} = 6.2 \times 10^{-12} \text{ M}$(d) $[H^+] = 10^{-15.00} = 1.0 \times 10^{-15} \text{ M}$

15.20 For (a) and (b) we can calculate the $H^+$ concentration using the equation representing the definition of pH.

**Strategy:** Here we are given the pH of a solution and asked to calculate $[H^+]$. Because pH is defined as $\text{pH} = -\log[H^+]$, we can solve for $[H^+]$ by taking the antilog of the pH; that is, $[H^+] = 10^{-\text{pH}}$.

**Solution:** From Equation (15.4) of the text:

(a) $\text{pH} = -\log[H^+] = 5.20$

$\log[H^+] = -5.20$

To calculate $[H^+]$, we need to take the antilog of $-5.20$.

$[H^+] = 10^{-5.20} = 6.3 \times 10^{-6} \text{ M}$

**Check:** Because the pH is between 5 and 6, we can expect $[H^+]$ to be between $1 \times 10^{-5} \text{ M}$ and $1 \times 10^{-6} \text{ M}$. Therefore, the answer is reasonable.

(b) $\text{pH} = -\log[H^+] = 16.00$

$\log[H^+] = -16.00$

$[H^+] = 10^{-16.00} = 1.0 \times 10^{-16} \text{ M}$

(c) For part (c), it is probably easiest to calculate the $[H^+]$ from the ion product of water.

**Strategy:** We are given the concentration of $OH^-$ ions and asked to calculate $[H^+]$. The relationship between $[H^+]$ and $[OH^-]$ in water or an aqueous solution is given by the ion-product of water, $K_w$ [Equation (15.3) of the text].

**Solution:** The ion product of water is applicable to all aqueous solutions. At 25°C,

$K_w = 1.0 \times 10^{-14} = [H^+][OH^-]$

Rearranging the equation to solve for $[H^+]$, we write

$[H^+] = \frac{1.0 \times 10^{-14}}{[OH^-]} = \frac{1.0 \times 10^{-14}}{3.7 \times 10^{-9}} = 2.7 \times 10^{-6} \text{ M}$

**Check:** Since the $[OH^-] < 1 \times 10^{-7} \text{ M}$ we expect the $[H^+]$ to be greater than $1 \times 10^{-7} \text{ M}$.

### Table for 15.21

<table>
<thead>
<tr>
<th>pH</th>
<th>$[H^+]$</th>
<th>Solution is:</th>
</tr>
</thead>
<tbody>
<tr>
<td>$&lt;7$</td>
<td>$&gt;1.0 \times 10^{-7} \text{ M}$</td>
<td>acidic</td>
</tr>
<tr>
<td>$&gt;7$</td>
<td>$&lt;1.0 \times 10^{-7} \text{ M}$</td>
<td>basic</td>
</tr>
<tr>
<td>$=7$</td>
<td>$=1.0 \times 10^{-7} \text{ M}$</td>
<td>neutral</td>
</tr>
</tbody>
</table>

15.22 (a) acidic (b) neutral (c) basic
15.23 The pH can be found by using Equation (15.9) of the text.

\[ \text{pH} = 14.00 - \text{pOH} = 14.00 - 9.40 = 4.60 \]

The hydrogen ion concentration can be found as in Example 15.4 of the text.

\[ 4.60 = -\log[H^+] \]

Taking the antilog of both sides:

\[ [H^+] = 2.5 \times 10^{-5} \text{ M} \]

15.24 

\[ 5.50 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.360 \text{ mol}}{1 \text{ L}} = 1.98 \times 10^{-3} \text{ mol KOH} \]

KOH is a strong base and therefore ionizes completely. The \( \text{OH}^- \) concentration equals the \( \text{KOH} \) concentration, because there is a 1:1 mole ratio between \( \text{KOH} \) and \( \text{OH}^- \).

\[ [\text{OH}^-] = 0.360 \text{ M} \]

\[ \text{pOH} = -\log[\text{OH}^-] = 0.444 \]

15.25 We can calculate the \( \text{OH}^- \) concentration from the pOH.

\[ \text{pOH} = 14.00 - \text{pH} = 14.00 - 10.00 = 4.00 \]

\[ [\text{OH}^-] = 10^{-\text{pOH}} = 1.0 \times 10^{-4} \text{ M} \]

Since \( \text{NaOH} \) is a strong base, it ionizes completely. The \( \text{OH}^- \) concentration equals the initial concentration of \( \text{NaOH} \).

\[ [\text{NaOH}] = 1.0 \times 10^{-4} \text{ mol/L} \]

So, we need to prepare 546 mL of \( 1.0 \times 10^{-4} \text{ M} \) \( \text{NaOH} \).

This is a dimensional analysis problem. We need to perform the following unit conversions.

\[ \text{mol/L} \rightarrow \text{mol NaOH} \rightarrow \text{grams NaOH} \]

\[ 546 \text{ mL} = 0.546 \text{ L} \]

\[ ? \text{ g NaOH} = 546 \text{ mL} \times \frac{1.0 \times 10^{-4} \text{ mol NaOH}}{1000 \text{ mL soln}} \times \frac{40.0 \text{ g NaOH}}{1 \text{ mol NaOH}} = 2.2 \times 10^{-3} \text{ g NaOH} \]

15.26 Molarity of the HCl solution is:

\[ \frac{18.4 \text{ g HCl} \times 1 \text{ mol HCl}}{662 \times 10^{-3} \text{ L}} = 0.762 \text{ M} \]

\[ \text{pH} = -\log(0.762) = 0.118 \]

15.31 A strong acid, such as HCl, will be completely ionized, choice (b).

A weak acid will only ionize to a lesser extent compared to a strong acid, choice (c).

A very weak acid will remain almost exclusively as the acid molecule in solution. Choice (d) is the best choice.
**15.32** (1) The two steps in the ionization of a weak diprotic acid are:

\[
\begin{align*}
H_2A(aq) + H_2O(l) &\rightleftharpoons H_3O^+(aq) + HA^-(aq) \\
HA^-(aq) + H_2O(l) &\rightleftharpoons H_3O^+(aq) + A^{2-}(aq)
\end{align*}
\]

The diagram that represents a weak diprotic acid is (c). In this diagram, we only see the first step of the ionization, because HA\(^-\) is a much weaker acid than H\(_2\)A.

(2) Both (b) and (d) are chemically implausible situations. Because HA\(^-\) is a much weaker acid than H\(_2\)A, you would not see a higher concentration of A\(^{2-}\) compared to HA\(^-\).

**15.33**

(a) strong acid,  
(b) weak acid,  
(c) strong acid (first stage of ionization),  
(d) weak acid,  
(e) weak acid,  
(f) weak acid,  
(g) strong acid,  
(h) weak acid,  
(i) weak acid.

**15.34**

(a) strong base  
(b) weak base  
(c) weak base  
(d) weak base  
(e) strong base

**15.35** The maximum possible concentration of hydrogen ion in a 0.10 M solution of HA is 0.10 M. This is the case if HA is a strong acid. If HA is a weak acid, the hydrogen ion concentration is less than 0.10 M. The pH corresponding to 0.10 M [H\(^+\)] is 1.00. (Why three digits?) For a smaller [H\(^+\)] the pH is larger than 1.00 (why?).

(a) false, the pH is greater than 1.00  
(b) false, they are equal  
(c) true  
(d) false

**15.36**

(a) false, they are equal  
(b) true, find the value of log(1.00) on your calculator  
(c) true  
(d) false, if the acid is strong, [HA] = 0.00 M

**15.37** The direction should favor formation of F\(^-\)(aq) and H\(_2\)O(l). Hydroxide ion is a stronger base than fluoride ion, and hydrofluoric acid is a stronger acid than water.

**15.38** Cl\(^-\) is the conjugate base of the strong acid, HCl. It is a negligibly weak base and has no affinity for protons. Therefore, the reaction will not proceed from left to right to any measurable extent.

Another way to think about this problem is to consider the possible products of the reaction.

\[
CH_3COOH(aq) + Cl^-(aq) \rightarrow HCl(aq) + CH_3COO^- (aq)
\]

The favored reaction is the one that proceeds from right to left. HCl is a strong acid and will ionize completely, donating all its protons to the base, CH\(_3\)COO\(^-\).

**15.43** We set up a table for the dissociation.

\[
\begin{array}{ccc}
C_6H_5COOH(aq) &\rightleftharpoons & H^+(aq) + C_6H_5COO^-(aq) \\
\text{Initial (M):} & 0.10 & 0.00 & 0.00 \\
\text{Change (M):} & -x & +x & +x \\
\text{Equilibrium (M):} & (0.10 - x) & x & x \\
\end{array}
\]
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\[ K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \]

\[ 6.5 \times 10^{-5} = \frac{x^2}{(0.10 - x)} \]

\[ x^2 + (6.5 \times 10^{-5})x - (6.5 \times 10^{-6}) = 0 \]

Solving the quadratic equation:

\[ x = 2.5 \times 10^{-3} M = [H^+] \]

\[ pH = -\log(2.5 \times 10^{-3}) = 2.60 \]

This problem could be solved more easily if we could assume that \((0.10 - x) \approx 0.10\). If the assumption is mathematically valid, then it would not be necessary to solve a quadratic equation, as we did above.

Re-solve the problem above, making the assumption. Was the assumption valid? What is our criterion for deciding?

15.44 **Strategy:** Recall that a weak acid only partially ionizes in water. We are given the initial quantity of a weak acid (CH₃COOH) and asked to calculate the concentrations of H⁺, CH₃COO⁻, and CH₃COOH at equilibrium. First, we need to calculate the initial concentration of CH₃COOH. In determining the H⁺ concentration, we ignore the ionization of H₂O as a source of H⁺, so the major source of H⁺ ions is the acid. We follow the procedure outlined in Section 15.5 of the text.

**Solution:**

**Step 1:** Calculate the concentration of acetic acid before ionization.

\[
0.0560 \text{ g acetic acid} \times \frac{1 \text{ mol acetic acid}}{60.05 \text{ g acetic acid}} = 9.33 \times 10^{-4} \text{ mol acetic acid}
\]

\[
\frac{9.33 \times 10^{-4} \text{ mol}}{0.0500 \text{ L soln}} = 0.187 \text{ M acetic acid}
\]

**Step 2:** We ignore water’s contribution to [H⁺]. We consider CH₃COOH as the only source of H⁺ ions.

**Step 3:** Letting \(x\) be the equilibrium concentration of H⁺ and CH₃COO⁻ ions in mol/L, we summarize:

| Initial (M) | 0.0187 | 0 | 0 |
| Change (M)  | -x     | +x | +x |
| Equilibrium (M) | 0.0187 - x | x | x |

**Step 3:** Write the ionization constant expression in terms of the equilibrium concentrations. Knowing the value of the equilibrium constant \((K_a)\), solve for \(x\). You can look up the \(K_a\) value in Table 15.3 of the text.

\[ K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \]

\[ 1.8 \times 10^{-5} = \frac{((x)(x))}{(0.0187 - x)} \]
At this point, we can make an assumption that $x$ is very small compared to 0.0187. Hence,

$$0.0187 - x \approx 0.0187$$

$$1.8 \times 10^{-5} = \frac{(x)(0.0187)}{0.0187}$$

$$x = 5.8 \times 10^{-4} \text{ M} = [H^+] = [\text{CH}_3\text{COO}^-]$$

$$[\text{CH}_3\text{COOH}] = (0.0187 \times 5.8 \times 10^{-4}) \text{ M} = 0.0181 \text{ M}$$

**Check:** Testing the validity of the assumption,

$$\frac{5.8 \times 10^{-4}}{0.0187} \times 100\% = 3.1\% < 5\%$$

The assumption is valid.

15.45 First we find the hydrogen ion concentration.

$$[H^+] = 10^{-pH} = 10^{-6.20} = 6.3 \times 10^{-7} \text{ M}$$

If the concentration of $[H^+]$ is $6.3 \times 10^{-7} \text{ M}$, that means that $6.3 \times 10^{-7} \text{ M}$ of the weak acid, HA, ionized because of the 1:1 mole ratio between HA and $H^+$. Setting up a table:

<table>
<thead>
<tr>
<th>Initial (M)</th>
<th>Change (M)</th>
<th>Equilibrium (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA$(aq)$</td>
<td>$-6.3 \times 10^{-7}$</td>
<td>$6.3 \times 10^{-7}$</td>
</tr>
<tr>
<td>$0.010$</td>
<td>$0$</td>
<td>$6.3 \times 10^{-7}$</td>
</tr>
<tr>
<td>$0$</td>
<td>$+6.3 \times 10^{-7}$</td>
<td>$6.3 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

Substituting into the acid ionization constant expression:

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(6.3 \times 10^{-7})(6.3 \times 10^{-7})}{0.010} = 4.0 \times 10^{-11}$$

We have omitted the contribution to $[H^+]$ due to water.

15.46 A pH of 3.26 corresponds to a $[H^+]$ of $5.5 \times 10^{-4} \text{ M}$. Let the original concentration of formic acid be $I$. If the concentration of $[H^+]$ is $5.5 \times 10^{-4} \text{ M}$, that means that $5.5 \times 10^{-4} \text{ M}$ of HCOOH ionized because of the 1:1 mole ratio between HCOOH and $H^+$.

<table>
<thead>
<tr>
<th>Initial (M)</th>
<th>Change (M)</th>
<th>Equilibrium (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCOOH$(aq)$</td>
<td>$-5.5 \times 10^{-4}$</td>
<td>$5.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>$I$</td>
<td>$0$</td>
<td>$5.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>$0$</td>
<td>$+5.5 \times 10^{-4}$</td>
<td>$5.5 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Substitute $K_a$ and the equilibrium concentrations into the ionization constant expression to solve for $I$.

$$K_a = \frac{[H^+][\text{HCOO}^-]}{[\text{HCOOH}]}$$

$$1.7 \times 10^{-4} = \frac{(5.5 \times 10^{-4})^2}{x - (5.5 \times 10^{-4})}$$

$$I = [\text{HCOOH}] = 2.3 \times 10^{-3} \text{ M}$$
15.47 (a) Set up a table showing initial and equilibrium concentrations.

\[
\begin{array}{ccc}
C_6H_5COOH(aq) & \rightleftharpoons & H^+(aq) + C_6H_5COO^-(aq) \\
\text{Initial (M)}: & 0.20 & 0.00 & 0.00 \\
\text{Change (M)}: & -x & +x & +x \\
\text{Equilibrium (M)}: & (0.20 - x) & x & x \\
\end{array}
\]

Using the value of \(K_a\) from Table 15.3 of the text:

\[
K_a = \frac{[H^+][C_6H_5COO^-]}{[C_6H_5COOH]}
\]

\[
6.5 \times 10^{-5} = \frac{x^2}{(0.20 - x)}
\]

We assume that \(x\) is small so \((0.20 - x) \approx 0.20\)

\[
6.5 \times 10^{-5} = \frac{x^2}{0.20}
\]

\[
x = 3.6 \times 10^{-3} \text{ M} = [H^+] = [C_6H_5COO^-]
\]

\[
\text{Percent ionization} = \frac{3.6 \times 10^{-3} \text{ M}}{0.20 \text{ M}} \times 100\% = 1.8\%
\]

(b) Set up a table as above.

\[
\begin{array}{ccc}
C_6H_5COOH(aq) & \rightleftharpoons & H^+(aq) + C_6H_5COO^-(aq) \\
\text{Initial (M)}: & 0.00020 & 0.00000 & 0.00000 \\
\text{Change (M)}: & -x & +x & +x \\
\text{Equilibrium (M)}: & (0.00020 - x) & x & x \\
\end{array}
\]

Using the value of \(K_a\) from Table 15.3 of the text:

\[
K_a = \frac{[H^+][C_6H_5COO^-]}{[C_6H_5COOH]}
\]

\[
6.5 \times 10^{-5} = \frac{x^2}{(0.00020 - x)}
\]

In this case we cannot apply the approximation that \((0.00020 - x) \approx 0.00020\) (see the discussion in Example 15.8 of the text). We obtain the quadratic equation:

\[
x^2 + (6.5 \times 10^{-5})x - (1.3 \times 10^{-8}) = 0
\]

The positive root of the equation is \(x = 8.6 \times 10^{-5} \text{ M}\). (Is this less than 5% of the original concentration, 0.00020 M? That is, is the acid more than 5% ionized?) The percent ionization is then:

\[
\text{Percent ionization} = \frac{8.6 \times 10^{-5} \text{ M}}{0.00020 \text{ M}} \times 100\% = 43\%
\]

Note that the extent to which a weak acid ionizes depends on the initial concentration of the acid. The more dilute the solution, the greater the percent ionization (see Figure 15.4 of the text).
Percent ionization is defined as:
\[
\text{percent ionization} = \frac{\text{ionized acid concentration at equilibrium}}{\text{initial concentration of acid}} \times 100\% 
\]

For a monoprotic acid, HA, the concentration of acid that undergoes ionization is equal to the concentration of H\(^+\) ions or the concentration of A\(^-\) ions at equilibrium. Thus, we can write:
\[
\text{percent ionization} = \frac{[\text{H}^+]}{[\text{HA}]_0} \times 100\% 
\]

(a) First, recognize that hydrofluoric acid is a weak acid. It is not one of the six strong acids, so it must be a weak acid.

**Step 1:** Express the equilibrium concentrations of all species in terms of initial concentrations and a single unknown \(x\), that represents the change in concentration. Let \((-x)\) be the depletion in concentration (mol/L) of HF. From the stoichiometry of the reaction, it follows that the increase in concentration for both H\(^+\) and F\(^-\) must be \(x\). Complete a table that lists the initial concentrations, the change in concentrations, and the equilibrium concentrations.

\[
\begin{array}{cccc}
\text{Species} & \text{Initial (M)} & \text{Change (M)} & \text{Equilibrium (M)} \\
\text{HF} & 0.60 & 0 & 0.60-x \\
\text{H}^+ & 0 & +x & x \\
\text{F}^- & 0 & +x & x \\
\end{array}
\]

**Step 2:** Write the ionization constant expression in terms of the equilibrium concentrations. Knowing the value of the equilibrium constant \((K_a)\), solve for \(x\).
\[
K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} 
\]

You can look up the \(K_a\) value for hydrofluoric acid in Table 15.3 of your text.

\[
7.1 \times 10^{-4} = \frac{(x)(x)}{(0.60 - x)} 
\]

At this point, we can make an assumption that \(x\) is very small compared to 0.60. Hence,
\[
0.60 - x \approx 0.60 
\]

Oftentimes, assumptions such as these are valid if \(K\) is very small. A very small value of \(K\) means that a very small amount of reactants go to products. Hence, \(x\) is small. If we did not make this assumption, we would have to solve a quadratic equation.

\[
7.1 \times 10^{-4} = \frac{(x)(x)}{0.60} 
\]

Solving for \(x\).
\[
x = 0.021 \text{ M} = [\text{H}^+] 
\]

**Step 3:** Having solved for the [H\(^+\)], calculate the percent ionization.
\[
\text{percent ionization} = \frac{[\text{H}^+]}{[\text{HF}]_0} \times 100\% 
\]
\[
= \frac{0.021 \text{ M}}{0.60 \text{ M}} \times 100\% = 3.5\% 
\]
(b) – (c) are worked in a similar manner to part (a). However, as the initial concentration of HF becomes smaller, the assumption that \( x \) is very small compared to this concentration will no longer be valid. You must solve a quadratic equation.

\[
\begin{align*}
(b) & \quad K_a = \frac{[H^+][F^-]}{[HF]} = \frac{x^2}{(0.0046 - x)} = 7.1 \times 10^{-4} \\
& \quad x^2 + (7.1 \times 10^{-4})x - (3.3 \times 10^{-6}) = 0 \\
& \quad x = 1.5 \times 10^{-3} \text{ M} \\
\text{Percent ionization} & = \frac{1.5 \times 10^{-3} \text{ M}}{0.0046 \text{ M}} \times 100\% = 33\% \\
(c) & \quad K_a = \frac{[H^+][F^-]}{[HF]} = \frac{x^2}{(0.00028 - x)} = 7.1 \times 10^{-4} \\
& \quad x^2 + (7.1 \times 10^{-4})x - (2.0 \times 10^{-7}) = 0 \\
& \quad x = 2.2 \times 10^{-4} \text{ M} \\
\text{Percent ionization} & = \frac{2.2 \times 10^{-4} \text{ M}}{0.00028 \text{ M}} \times 100\% = 79\%
\end{align*}
\]

As the solution becomes more dilute, the percent ionization increases.

**15.49** Given 14% ionization, the concentrations must be:

\[
[H^+] = [A^-] = 0.14 \times 0.040 \text{ M} = 0.0056 \text{ M} \\
[HA] = (0.040 - 0.0056) \text{ M} = 0.034 \text{ M}
\]

The value of \( K_a \) can be found by substitution.

\[
K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(0.0056)^2}{0.034} = 9.2 \times 10^{-4}
\]

**15.50** The equilibrium is:

\[
C_9H_8O_4(aq) \rightleftharpoons H^+(aq) + C_9H_7O_4^-(aq)
\]

| Initial (M) | 0.20 | 0 | 0 |
| Change (M) | -x | +x | +x |
| Equilibrium (M) | 0.20 - x | x | x |

\[
(a) \quad K_a = \frac{[H^+][C_9H_7O_4^-]}{[C_9H_8O_4]} = 3.0 \times 10^{-4} = \frac{x^2}{(0.20 - x)}
\]

Assuming \((0.20 - x) \approx 0.20\)

\[
x = [H^+] = 7.7 \times 10^{-3} \text{ M}
\]
37.7 \times 10^{-2} = 0.20 \times 0.20

\text{Percent ionization} = \frac{x}{0.20} \times 100\% = \frac{7.7 \times 10^{-3} M}{0.20 M} \times 100\% = 3.9\%

(b) At pH 1.00 the concentration of hydrogen ion is 0.10 \text{ M} ([H^+] = 10^{-pH}). The extra hydrogen ions will tend to suppress the ionization of the weak acid (LeChâtelier's principle, Section 14.5 of the text). The position of equilibrium is shifted in the direction of the un-ionized acid. Let's set up a table of concentrations with the initial concentration of H^+ equal to 0.10 \text{ M}.

\begin{align*}
\text{C}_9\text{H}_8\text{O}_4(aq) & \rightleftharpoons \text{H}^+(aq) + \text{C}_9\text{H}_7\text{O}_4^-(aq) \\
\text{Initial (M):} & \quad 0.20 \quad 0.10 \quad 0 \\
\text{Change (M):} & \quad -x \quad +x \quad +x \\
\text{Equilibrium (M):} & \quad 0.20 - x \quad 0.10 + x \quad x
\end{align*}

\[ K_a = \frac{[\text{H}^+][\text{C}_9\text{H}_7\text{O}_4^-]}{[\text{C}_9\text{H}_8\text{O}_4]} \]

\[ 3.0 \times 10^{-4} = \frac{x(0.10 + x)}{(0.20 - x)} \]

Assuming \((0.20 - x) \approx 0.20\) and \((0.10 + x) \approx 0.10\)

\[ x = 6.0 \times 10^{-4} \text{ M} \]

\[ \text{Percent ionization} = \frac{x}{0.20} \times 100\% = \frac{6.0 \times 10^{-4} M}{0.20 M} \times 100\% = 0.30\% \]

The high acidity of the gastric juices appears to enhance the rate of absorption of unionized aspirin molecules through the stomach lining. In some cases this can irritate these tissues and cause bleeding.

15.53 (a) We construct the usual table.

\[ \text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq) \]

\begin{align*}
\text{Initial (M):} & \quad 0.10 \quad 0.00 \quad 0.00 \\
\text{Change (M):} & \quad -x \quad +x \quad +x \\
\text{Equilibrium (M):} & \quad (0.10 - x) \quad x \quad x
\end{align*}

\[ K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \]

\[ 1.8 \times 10^{-5} = \frac{x^2}{(0.10 - x)} \]

Assuming \((0.10 - x) \approx 0.10\), we have:

\[ 1.8 \times 10^{-5} = \frac{x^2}{0.10} \]

\[ x = 1.3 \times 10^{-3} \text{ M} = [\text{OH}^-] \]

\[ \text{pOH} = -\log(1.3 \times 10^{-3}) = 2.89 \]

\[ \text{pH} = 14.00 - 2.89 = 11.11 \]
By following the identical procedure, we can show: (b) \( \text{pH} = 8.96 \).

**15.54 Strategy:** Weak bases only partially ionize in water.

\[
B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)
\]

Note that the concentration of the weak base given refers to the initial concentration before ionization has started. The pH of the solution, on the other hand, refers to the situation at equilibrium. To calculate \( K_b \), we need to know the concentrations of all three species, \([B]\), \([BH^+]\), and \([OH^-]\) at equilibrium. We ignore the ionization of water as a source of \( OH^- \) ions.

**Solution:** We proceed as follows.

**Step 1:** The major species in solution are \( B, OH^- \), and the conjugate acid \( BH^+ \).

**Step 2:** First, we need to calculate the hydroxide ion concentration from the pH value. Calculate the pOH from the pH. Then, calculate the \( OH^- \) concentration from the pOH.

\[
pOH = 14.00 - \text{pH} = 14.00 - 10.66 = 3.34
\]

\[
pOH = -\log[OH^-]
\]

\[
-pOH = \log[OH^-]
\]

Taking the antilog of both sides of the equation,

\[
10^{-pOH} = [OH^-]
\]

\[
[OH^-] = 10^{-3.34} = 4.6 \times 10^{-4} \text{ M}
\]

**Step 3:** If the concentration of \( OH^- \) is \( 4.6 \times 10^{-4} \text{ M} \) at equilibrium, that must mean that \( 4.6 \times 10^{-4} \text{ M} \) of the base ionized. We summarize the changes.

<table>
<thead>
<tr>
<th>Initial (M)</th>
<th>0.30</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change (M)</td>
<td>(-4.6 \times 10^{-4})</td>
<td>(+4.6 \times 10^{-4})</td>
<td>(+4.6 \times 10^{-4})</td>
</tr>
<tr>
<td>Equilibrium (M)</td>
<td>(0.30 - (4.6 \times 10^{-4}))</td>
<td>(4.6 \times 10^{-4})</td>
<td>(4.6 \times 10^{-4})</td>
</tr>
</tbody>
</table>

**Step 4:** Substitute the equilibrium concentrations into the ionization constant expression to solve for \( K_b \).

\[
K_b = \frac{[BH^+] [OH^-]}{[B]}\]

\[
K_b = \frac{(4.6 \times 10^{-4})^2}{(0.30)} = 7.1 \times 10^{-7}
\]

**15.55** A pH of 11.22 corresponds to a \([H^+]\) of \(6.03 \times 10^{-12} \text{ M}\) and a \([OH^-]\) of \(1.66 \times 10^{-3} \text{ M}\).

Setting up a table:

<table>
<thead>
<tr>
<th>( \text{Initial (M)} )</th>
<th>( \text{NH}_3(aq) + H_2O(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial (M)</td>
<td>(1)</td>
</tr>
<tr>
<td>Change (M)</td>
<td>(-1.66 \times 10^{-3})</td>
</tr>
<tr>
<td>Equilibrium (M)</td>
<td>(1 - (1.66 \times 10^{-3}))</td>
</tr>
</tbody>
</table>
\[ K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \]

\[ 1.8 \times 10^{-5} = \frac{(1.66 \times 10^{-3})(1.66 \times 10^{-3})}{1 - (1.66 \times 10^{-3})} \]

Assuming \(1.66 \times 10^{-3}\) is small relative to \(x\), then

\[ x = 0.15 \ M = [\text{NH}_3] \]

15.56 The reaction is:

\[ \text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq) \]

<table>
<thead>
<tr>
<th>Initial (M)</th>
<th>Change (M)</th>
<th>Equilibrium (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.080</td>
<td>-x</td>
<td>0.080 - x</td>
</tr>
<tr>
<td>0</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>x</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

At equilibrium we have:

\[ K_a = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \]

\[ 1.8 \times 10^{-5} = \frac{x^2}{(0.080 - x)} \approx \frac{x^2}{0.080} \]

\[ x = 1.2 \times 10^{-3} \ M \]

Percent \(\text{NH}_3\) present as \(\text{NH}_4^+\) = \[\frac{1.2 \times 10^{-3}}{0.080} \times 100\% = 1.5\%\]

15.61 If \(K_{a1} >> K_{a2}\), we can assume that the equilibrium concentration of hydrogen ion results only from the first stage of ionization. In the second stage this always leads to an expression of the type:

\[ \frac{(c + y)(y)}{(c - y)} = K_{a2} \]

where \(c\) represents the equilibrium hydrogen ion concentration found in the first stage. If \(c >> K_{a2}\), we can assume \((c \pm y) \approx c\), and consequently \(y = K_{a2}\).

Is this conclusion also true for the second stage ionization of a triprotic acid like \(\text{H}_3\text{PO}_4\)?

15.62 The pH of a 0.040 \(M\) \(\text{HCl}\) solution (strong acid) is: \(\text{pH} = -\log(0.040) = 1.40\).

**Strategy:** Determining the pH of a diprotic acid in aqueous solution is more involved than for a monoprotic acid. The first stage of ionization for \(\text{H}_2\text{SO}_4\) goes to completion. We follow the procedure for determining the pH of a strong acid for this stage. The conjugate base produced in the first ionization (\(\text{HSO}_4^-\)) is a weak acid. We follow the procedure for determining the pH of a weak acid for this stage.

**Solution:** We proceed according to the following steps.

**Step 1:** \(\text{H}_2\text{SO}_4\) is a strong acid. The first ionization stage goes to completion. The ionization of \(\text{H}_2\text{SO}_4\) is

\[ \text{H}_2\text{SO}_4(aq) \rightarrow \text{H}^+(aq) + \text{HSO}_4^-(aq) \]
The concentrations of all the species (H$_2$SO$_4$, H$^+$, and HSO$_4^-$) before and after ionization can be represented as follows.

\[
\begin{align*}
H_2SO_4(aq) & \rightarrow H^+(aq) + HSO_4^-(aq) \\
\text{Initial (M)}: & \quad 0.040 \quad 0 \quad 0 \\
\text{Change (M)}: & \quad -0.040 \quad +0.040 \quad +0.040 \\
\text{Final (M)}: & \quad 0 \quad 0.040 \quad 0.040
\end{align*}
\]

**Step 2:** Now, consider the second stage of ionization. HSO$_4^-$ is a weak acid. Set up a table showing the concentrations for the second ionization stage. Let $x$ be the change in concentration. Note that the initial concentration of H$^+$ is 0.040 M from the first ionization.

\[
\begin{align*}
\text{Initial (M)}: & \quad 0.040 \quad 0.040 \quad 0 \\
\text{Change (M)}: & \quad -x \quad +x \quad +x \\
\text{Equilibrium (M)}: & \quad 0.040 - x \quad 0.040 + x \quad x
\end{align*}
\]

Write the ionization constant expression for $K_a$. Then, solve for $x$. You can find the $K_a$ value in Table 15.5 of the text.

\[
K_a = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]}
\]

\[
1.3 \times 10^{-2} = \frac{(0.040 + x)(x)}{(0.040 - x)}
\]

Since $K_a$ is quite large, we cannot make the assumptions that 

\[
0.040 - x \approx 0.040 \quad \text{and} \quad 0.040 + x \approx 0.040
\]

Therefore, we must solve a quadratic equation.

\[
x^2 + 0.053x - (5.2 \times 10^{-4}) = 0
\]

\[
x = \frac{-0.053 \pm \sqrt{(0.053)^2 - 4(1)(-5.2 \times 10^{-4})}}{2(1)}
\]

\[
x = \frac{-0.053 \pm 0.070}{2}
\]

\[
x = 8.5 \times 10^{-3} \quad \text{M} \quad \text{or} \quad x = -0.062 \quad \text{M}
\]

The second solution is physically impossible because you cannot have a negative concentration. The first solution is the correct answer.

**Step 3:** Having solved for $x$, we can calculate the H$^+$ concentration at equilibrium. We can then calculate the pH from the H$^+$ concentration.

\[
[H^+] = 0.040 \ M + x = [0.040 + (8.5 \times 10^{-3})]M = 0.049 \ M
\]

\[
\text{pH} = -\log(0.049) = 1.31
\]

Without doing any calculations, could you have known that the pH of the sulfuric acid would be lower (more acidic) than that of the hydrochloric acid?
15.63 There is no \( \text{H}_2\text{SO}_4 \) in the solution because \( \text{HSO}_4^- \) has no tendency to accept a proton to produce \( \text{H}_2\text{SO}_4 \). (Why?) We are only concerned with the ionization:

\[
\text{HSO}_4^- (aq) \rightleftharpoons \text{H}^+ (aq) + \text{SO}_4^{2-} (aq)
\]

<table>
<thead>
<tr>
<th>Initial (M)</th>
<th>0.20</th>
<th>0.00</th>
<th>0.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change (M)</td>
<td>(-x)</td>
<td>(+x)</td>
<td>(+x)</td>
</tr>
<tr>
<td>Equilibrium (M)</td>
<td>((0.20 - x))</td>
<td>(+x)</td>
<td>(+x)</td>
</tr>
</tbody>
</table>

\[
K_a = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]}
\]

\[
1.3 \times 10^{-2} = \frac{(x)(x)}{(0.20 - x)}
\]

Solving the quadratic equation:

\[
x = [\text{H}^+] = [\text{SO}_4^{2-}] = 0.045 \text{ M}
\]

\[
[\text{HSO}_4^-] = (0.20 - 0.045) \text{ M} = 0.16 \text{ M}
\]

15.64 For the first stage of ionization:

\[
\text{H}_2\text{CO}_3(aq) \rightleftharpoons \text{H}^+ (aq) + \text{HCO}_3^- (aq)
\]

<table>
<thead>
<tr>
<th>Initial (M)</th>
<th>0.025</th>
<th>0.00</th>
<th>0.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change (M)</td>
<td>(-x)</td>
<td>(+x)</td>
<td>(+x)</td>
</tr>
<tr>
<td>Equilibrium (M)</td>
<td>((0.025 - x))</td>
<td>(x)</td>
<td>(x)</td>
</tr>
</tbody>
</table>

\[
K_{a_1} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}
\]

\[
4.2 \times 10^{-7} = \frac{x^2}{(0.025 - x)} \approx \frac{x^2}{0.025}
\]

\[
x = 1.0 \times 10^{-4} \text{ M}
\]

For the second ionization,

\[
\text{HCO}_3^- (aq) \rightleftharpoons \text{H}^+ (aq) + \text{CO}_3^{2-} (aq)
\]

<table>
<thead>
<tr>
<th>Initial (M)</th>
<th>(1.0 \times 10^{-4})</th>
<th>(1.0 \times 10^{-4})</th>
<th>0.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change (M)</td>
<td>(-x)</td>
<td>(+x)</td>
<td>(+x)</td>
</tr>
<tr>
<td>Equilibrium (M)</td>
<td>((1.0 \times 10^{-4}) - x)</td>
<td>((1.0 \times 10^{-4}) + x)</td>
<td>(x)</td>
</tr>
</tbody>
</table>

\[
K_{a_2} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}
\]

\[
4.8 \times 10^{-11} = \frac{[(1.0 \times 10^{-4}) + x](x)}{(1.0 \times 10^{-4}) - x} \approx \frac{(1.0 \times 10^{-4})(x)}{(1.0 \times 10^{-4})}
\]

\[
x = 4.8 \times 10^{-11} \text{ M}
\]

Since \( \text{HCO}_3^- \) is a very weak acid, there is little ionization at this stage. Therefore we have:

\[
[\text{H}^+] = [\text{HCO}_3^-] = 1.0 \times 10^{-4} \text{ M} \text{ and } [\text{CO}_3^{2-}] = x = 4.8 \times 10^{-11} \text{ M}
\]
15.67 The strength of the H–X bond is the dominant factor in determining the strengths of binary acids. As with the hydrogen halides (see Section 15.9 of the text), the H–X bond strength decreases going down the column in Group 6A. The compound with the weakest H–X bond will be the strongest binary acid: \( \text{H}_2\text{Se} > \text{H}_2\text{S} > \text{H}_2\text{O} \).

15.68 All the listed pairs are oxoacids that contain different central atoms whose elements are in the same group of the periodic table and have the same oxidation number. In this situation the acid with the most electronegative central atom will be the strongest.

(a) \( \text{H}_2\text{SO}_4 > \text{H}_2\text{SeO}_4 \).
(b) \( \text{H}_3\text{PO}_4 > \text{H}_3\text{AsO}_4 \)

15.69 The \( \text{CHCl}_2\text{COOH} \) is a stronger acid than \( \text{CH}_2\text{ClCOOH} \). Having two electronegative chlorine atoms compared to one, will draw more electron density toward itself, making the O–H bond more polar. The hydrogen atom in \( \text{CHCl}_2\text{COOH} \) is more easily ionized compared to the hydrogen atom in \( \text{CH}_2\text{ClCOOH} \).

15.70 The conjugate bases are \( \text{C}_6\text{H}_5\text{O}^- \) from phenol and \( \text{CH}_3\text{O}^- \) from methanol. The \( \text{C}_6\text{H}_5\text{O}^- \) is stabilized by resonance:

The \( \text{CH}_3\text{O}^- \) ion has no such resonance stabilization. A more stable conjugate base means an increase in the strength of the acid.

15.75 (a) The \( \text{K}^+ \) cation does not hydrolyze. The \( \text{Br}^- \) anion is the conjugate base of the strong acid HBr. Therefore, \( \text{Br}^- \) will not hydrolyze either, and the solution is neutral, \( \text{pH} \approx 7 \).
(b) \( \text{Al}^{3+} \) is a small metal cation with a high charge, which hydrolyzes to produce \( \text{H}^+ \) ions. The \( \text{NO}_3^- \) anion does not hydrolyze. It is the conjugate base of the strong acid, HNO₃. The solution will be acidic, \( \text{pH} < 7 \).
(c) The \( \text{Ba}^{2+} \) cation does not hydrolyze. The \( \text{Cl}^- \) anion is the conjugate base of the strong acid HCl. Therefore, \( \text{Cl}^- \) will not hydrolyze either, and the solution is neutral, \( \text{pH} \approx 7 \).
(d) \( \text{Br}^{3+} \) is a small metal cation with a high charge, which hydrolyzes to produce \( \text{H}^+ \) ions. The \( \text{NO}_3^- \) anion does not hydrolyze. It is the conjugate base of the strong acid, HNO₃. The solution will be acidic, \( \text{pH} < 7 \).

15.76 **Strategy:** In deciding whether a salt will undergo hydrolysis, ask yourself the following questions: Is the cation a highly charged metal ion or an ammonium ion? Is the anion the conjugate base of a weak acid? If yes to either question, then hydrolysis will occur. In cases where both the cation and the anion react with water, the pH of the solution will depend on the relative magnitudes of \( K_a \) for the cation and \( K_b \) for the anion (see Table 15.7 of the text).

**Solution:** We first break up the salt into its cation and anion components and then examine the possible reaction of each ion with water.

(a) The \( \text{Na}^+ \) cation does not hydrolyze. The \( \text{Br}^- \) anion is the conjugate base of the strong acid HBr. Therefore, \( \text{Br}^- \) will not hydrolyze either, and the solution is **neutral**.
(b) The K\(^+\) cation does not hydrolyze. The SO\(_3^{2-}\) anion is the conjugate base of the weak acid HSO\(_3^-\) and will hydrolyze to give HSO\(_3^-\) and OH\(^-\). The solution will be basic.

(c) Both the NH\(_4^+\) and NO\(_2^-\) ions will hydrolyze. NH\(_4^+\) is the conjugate acid of the weak base NH\(_3\), and NO\(_2^-\) is the conjugate base of the weak acid HNO\(_2\). From Tables 15.3 and 15.4 of the text, we see that the \(K_a\) of NH\(_4^+\) (5.6 \times 10\(^{-10}\)) is greater than the \(K_b\) of NO\(_2^-\) (2.2 \times 10\(^{-11}\)). Therefore, the solution will be acidic.

(d) Cr\(_{3+}\) is a small metal cation with a high charge, which hydrolyzes to produce H\(^+\) ions. The NO\(_3^-\) anion does not hydrolyze. It is the conjugate base of the strong acid, HNO\(_3\). The solution will be acidic.

15.77 There are two possibilities: (i) MX is the salt of a strong acid and a strong base so that neither the cation nor the anion react with water to alter the pH and (ii) MX is the salt of a weak acid and a weak base with \(K_a\) for the acid equal to \(K_b\) for the base. The hydrolysis of one would be exactly offset by the hydrolysis of the other.

15.78 There is an inverse relationship between acid strength and conjugate base strength. As acid strength decreases, the proton accepting power of the conjugate base increases. In general the weaker the acid, the stronger the conjugate base. All three of the potassium salts ionize completely to form the conjugate base of the respective acid. The greater the pH, the stronger the conjugate base, and therefore, the weaker the acid. The order of increasing acid strength is HZ < HY < HX.

15.79 The salt, sodium acetate, completely dissociates upon dissolution, producing 0.36 \(M\) [Na\(^+\)] and 0.36 \(M\) [CH\(_3\)COO\(^-\)] ions. The [CH\(_3\)COO\(^-\)] ions will undergo hydrolysis because they are a weak base.

\[
\begin{align*}
\text{CH}_3\text{COO}^- (aq) + \text{H}_2\text{O}(l) & \rightleftharpoons \text{CH}_3\text{COOH}(aq) + \text{OH}^- (aq) \\
\text{Initial (M):} & \quad 0.36 \quad 0.00 \quad 0.00 \\
\text{Change (M):} & \quad -x \quad +x \quad +x \\
\text{Equilibrium (M):} & \quad (0.36 - x) \quad +x \quad +x \\

K_b &= \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \\
5.6 \times 10^{-10} &= \frac{x^2}{(0.36 - x)}
\end{align*}
\]

Assuming \((0.36 - x) \approx 0.36\), then

\[
x = [\text{OH}^-] = 1.4 \times 10^{-5}
\]

\[
\text{pOH} = -\log(1.4 \times 10^{-5}) = 4.85
\]

\[
\text{pH} = 14.00 - 4.85 = 9.15
\]

15.80 The salt ammonium chloride completely ionizes upon dissolution, producing 0.42 \(M\) [NH\(_4^+\)] and 0.42 \(M\) [Cl\(^-\)] ions. NH\(_4^+\) will undergo hydrolysis because it is a weak acid (NH\(_4^+\) is the conjugate acid of the weak base, NH\(_3\)).

**Step 1:** Express the equilibrium concentrations of all species in terms of initial concentrations and a single unknown \(x\), that represents the change in concentration. Let \((-x\)) be the depletion in concentration (mol/L) of NH\(_4^+\). From the stoichiometry of the reaction, it follows that the increase in concentration for both H\(_3\)O\(^+\) and NH\(_3\) must be \(x\). Complete a table that lists the initial concentrations, the change in concentrations, and the equilibrium concentrations.
\[
\begin{align*}
\text{NH}_4^+(aq) + \text{H}_2\text{O}(l) & \rightleftharpoons \text{NH}_3(aq) + \text{H}_3\text{O}^+(aq) \\
\text{Initial (M):} & \quad 0.42 \quad 0.00 \quad 0.00 \\
\text{Change (M):} & \quad -x \quad +x \quad +x \\
\text{Equilibrium (M):} & \quad (0.42 - x) \quad x \quad x
\end{align*}
\]

**Step 2:** You can calculate the \( K_a \) value for \( \text{NH}_4^+ \) from the \( K_b \) value of \( \text{NH}_3 \). The relationship is

\[
K_a \times K_b = K_w
\]

or

\[
K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}
\]

**Step 3:** Write the ionization constant expression in terms of the equilibrium concentrations. Knowing the value of the equilibrium constant \( (K_a) \), solve for \( x \).

\[
K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{x^2}{0.42 - x} \approx \frac{x^2}{0.42}
\]

\[
x = [\text{H}^+] = 1.5 \times 10^{-5} \text{ M}
\]

\[
\text{pH} = -\log(1.5 \times 10^{-5}) = 4.82
\]

Since \( \text{NH}_4\text{Cl} \) is the salt of a weak base (aqueous ammonia) and a strong acid (HCl), we expect the solution to be slightly acidic, which is confirmed by the calculation.

15.81 \( \text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} \quad K_a = 4.8 \times 10^{-11} \)

\( \text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 + \text{OH}^- \quad K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.2 \times 10^{-7}} = 2.4 \times 10^{-8} \)

\( \text{HCO}_3^- \) has a greater tendency to hydrolyze than to ionize \( (K_b > K_a) \). The solution will be basic \( (\text{pH} > 7) \).

15.82 The acid and base reactions are:

- **acid:** \( \text{HPO}_4^{2-}(aq) \rightleftharpoons \text{H}^+(aq) + \text{PO}_4^{3-}(aq) \)
- **base:** \( \text{HPO}_4^{2-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{PO}_4^{-}(aq) + \text{OH}^-(aq) \)

\( K_a \) for \( \text{HPO}_4^{2-} \) is \( 4.8 \times 10^{-13} \). Note that \( \text{HPO}_4^{2-} \) is the conjugate base of \( \text{H}_2\text{PO}_4^- \), so \( K_b \) is \( 1.6 \times 10^{-7} \).

Comparing the two \( K \)'s, we conclude that the monohydrogen phosphate ion is a much stronger proton acceptor (base) than a proton donor (acid). The solution will be **basic**.

15.85 Metal ions with high oxidation numbers are unstable. Consequently, these metals tend to form covalent bonds (rather than ionic bonds) with oxygen. Covalent metal oxides are acidic while ionic metal oxides are basic. The latter oxides contain the \( \text{O}^{2-} \) ion which reacts with water as follows:

\[
\text{O}^{2-} + \text{H}_2\text{O} \rightarrow 2\text{OH}^-
\]
15.86 The most basic oxides occur with metal ions having the lowest positive charges (or lowest oxidation numbers).

(a) $\text{Al}_2\text{O}_3 < \text{BaO} < \text{K}_2\text{O}$

(b) $\text{CrO}_3 < \text{Cr}_2\text{O}_3 < \text{CrO}$

15.87 (a) $2\text{HCl}(aq) + \text{Zn(OH)}_2(s) \rightarrow \text{ZnCl}_2(aq) + 2\text{H}_2\text{O}(l)$

(b) $2\text{OH}^-(aq) + \text{Zn(OH)}_2(s) \rightarrow \text{Zn(OH)}_4^{2-}(aq)$

15.88 $\text{Al(OH)}_3$ is an amphoteric hydroxide. The reaction is:

$\text{Al(OH)}_3(s) + \text{OH}^-(aq) \rightarrow \text{Al(OH)}_4^-(aq)$

This is a Lewis acid-base reaction. Can you identify the acid and base?

15.91 (a) Lewis acid; see the reaction with water shown in Section 15.12 of the text.

(b) Lewis base; water combines with $\text{H}^+$ to form $\text{H}_3\text{O}^+$.

(c) Lewis base.

(d) Lewis acid; $\text{SO}_2$ reacts with water to form $\text{H}_2\text{SO}_3$. Compare to $\text{CO}_2$ above. Actually, $\text{SO}_2$ can also act as a Lewis base under some circumstances.

(e) Lewis base; see the reaction with $\text{H}^+$ to form ammonium ion.

(f) Lewis base; see the reaction with $\text{H}^+$ to form water.

(g) Lewis acid; does $\text{H}^+$ have any electron pairs to donate?

(h) Lewis acid; compare to the example of $\text{NH}_3$ reacting with $\text{BF}_3$.

15.92 $\text{AlCl}_3$ is a Lewis acid with an incomplete octet of electrons and $\text{Cl}^-$ is the Lewis base donating a pair of electrons.

$\begin{align*}
\text{Cl} & \text{Cl} \\
\text{Al} & \\
\text{Cl} & \text{Cl}
\end{align*}$

15.93 (a) Both molecules have the same acceptor atom (boron) and both have exactly the same structure (trigonal planar). Fluorine is more electronegative than chlorine so we would predict based on electronegativity arguments that boron trifluoride would have a greater affinity for unshared electron pairs than boron trichloride.

(b) Since it has the larger positive charge, iron(III) should be a stronger Lewis acid than iron(II).

15.94 By definition Brønsted acids are proton donors, therefore such compounds must contain at least one hydrogen atom. In Problem 15.91, Lewis acids that do not contain hydrogen, and therefore are not Brønsted acids, are $\text{CO}_2$, $\text{SO}_2$, and $\text{BCl}_3$. Can you name others?

15.95 (a) The greater the percent ionization at a given solution concentration, the stronger the acid and the larger the $K_a$ value. The amount of ionization can easily be determined by the number of hydronium ions, $\text{H}_3\text{O}^+$, produced. The acids arranged in order of increasing $K_a$ are: $\text{HY} < \text{HZ} < \text{HX}$.
(b) The stronger the acid, the weaker its conjugate base. The conjugate bases arranged in order of increasing $K_b$ are: $X^-$ < $Z^-$ < $Y^-$. 

(c) In each diagram, there were 8 acid molecules present before ionization. The percent ionization is calculated by taking the number of hydronium ions, $H_3O^+$, produced divided by the initial number of acid molecules present and then multiplying by 100 to convert to a percentage.

\[
\text{% ionization} = \frac{\text{number of } H_3O^+ \text{ ions produced}}{\text{initial number of acid molecules}} \times 100\%
\]

- $\text{% ionization of } HX = \frac{6}{8} \times 100\% = 75\%$
- $\text{% ionization of } HY = \frac{2}{8} \times 100\% = 25\%$
- $\text{% ionization of } HZ = \frac{4}{8} \times 100\% = 50\%$

(d) These salts contain the conjugate bases of the acids shown in the diagrams. As mentioned in part (b) of this problem, the stronger the acid, the weaker its conjugate base. $HX$ is the strongest acid of the three and therefore its conjugate base, $X^-$, is the weakest. With all three salts having equal concentration, the weakest base will produce a solution with the lowest pH. Therefore, the salt solution with the lowest pH is $\text{NaX}$.

15.96 We first find the number of moles of CO$_2$ produced in the reaction:

\[
0.350 \text{ g NaHCO}_3 \times \frac{1 \text{ mol NaHCO}_3}{84.01 \text{ g NaHCO}_3} \times \frac{1 \text{ mol CO}_2}{1 \text{ mol NaHCO}_3} = 4.17 \times 10^{-3} \text{ mol CO}_2
\]

\[
V_{CO_2} = \frac{n_{CO_2}RT}{P} = \frac{(4.17 \times 10^{-3} \text{ mol})(0.0821 \text{ L atm/K mol})(37.0 + 273)K}{(1.00 \text{ atm})} = 0.106 \text{ L}
\]

15.97 Choice (c) because 0.70 $M$ KOH has a higher pH than 0.60 $M$ NaOH. Adding an equal volume of 0.60 $M$ NaOH lowers the $[OH^-]$ to 0.65 $M$, hence lowering the pH.

15.98 If we assume that the unknown monoprotic acid is a strong acid that is 100% ionized, then the $[H^+]$ concentration will be 0.0642 $M$.

\[
\text{pH} = -\log (0.0642) = 1.19
\]

Since the actual pH of the solution is higher, the acid must be a weak acid.

15.99 (a) For the forward reaction $\text{NH}_4^+$ and $\text{NH}_3$ are the conjugate acid and base pair, respectively. For the reverse reaction $\text{NH}_3$ and $\text{NH}_2^-$ are the conjugate acid and base pair, respectively.

(b) $H^+$ corresponds to $\text{NH}_4^+$; $\text{OH}^-$ corresponds to $\text{NH}_2^-$. For the neutral solution, $[\text{NH}_4^+] = [\text{NH}_2^-]$.

15.100 The reaction of a weak acid with a strong base is driven to completion by the formation of water. Irrespective of whether the strong base is reacting with a strong monoprotic acid or a weak monoprotic acid, the same number of moles of acid is required to react with a constant number of moles of base. Therefore the volume of base required to react with the same concentration of acid solutions (either both weak, both strong, or one strong and one weak) will be the same.
15.101 \[ K_a = \frac{[H^+][A^-]}{[HA]} \]

\[ [HA] \approx 0.1 \text{ M} \]
\[ [A^-] \approx 0.1 \text{ M} \]

Therefore,
\[ K_a = [H^+] = \frac{K_w}{[OH^-]} \]
\[ [OH^-] = \frac{K_w}{K_a} \]

15.102 High oxidation state leads to covalent compounds and low oxidation state leads to ionic compounds.
Therefore, CrO is ionic and basic and CrO₃ is covalent and acidic.

15.103 \[ \text{HCOOH} \Leftrightarrow \text{HCOO}^- + \text{H}^+ \quad K_a = 1.7 \times 10^{-4} \]
\[ \text{H}^+ + \text{OH}^- \Leftrightarrow \text{H}_2\text{O} \quad K_w' = \frac{1}{K_w} = \frac{1}{1.0 \times 10^{-14}} = 1.0 \times 10^{14} \]
\[ \text{HCOOH} + \text{OH}^- \Leftrightarrow \text{HCOO}^- + \text{H}_2\text{O} \]

\[ K = K_a K_w' = (1.7 \times 10^{-4})(1.0 \times 10^{14}) = 1.7 \times 10^{10} \]

15.104 We can write two equilibria that add up to the equilibrium in the problem.

\[ \text{CH}_3\text{COOH} (aq) \Leftrightarrow \text{H}^+(aq) + \text{CH}_3\text{COO}^- (aq) \quad K_a = \frac{[H^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5} \]
\[ \text{H}^+(aq) + \text{NO}_2^- (aq) \Leftrightarrow \text{HNO}_2 (aq) \quad K_a' = \frac{1}{K_a'(\text{HNO}_2)} = \frac{1}{4.5 \times 10^{-4}} = 2.2 \times 10^3 \]
\[ K_a' = \frac{[\text{HNO}_2]}{[\text{H}^+][\text{NO}_2^-]} \]

\[ \text{CH}_3\text{COOH} (aq) + \text{NO}_2^- (aq) \Leftrightarrow \text{CH}_3\text{COO}^- (aq) + \text{HNO}_2 (aq) \]

\[ K = \frac{[\text{CH}_3\text{COO}^-][\text{HNO}_2]}{[\text{CH}_3\text{COOH}][\text{NO}_2^-]} = K_a \times K_a' \]

The equilibrium constant for this sum is the product of the equilibrium constants of the component reactions.

\[ K = K_a \times K_a' = (1.8 \times 10^{-5})(2.2 \times 10^3) = 4.0 \times 10^{-2} \]

15.105 (a) \[ \text{H}^- + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}_2 \]
\[ \text{base}_1 + \text{acid}_2 \rightarrow \text{base}_2 + \text{acid}_1 \]

(b) \[ \text{H}^- \] is the reducing agent and \( \text{H}_2\text{O} \) is the oxidizing agent.

15.106 In this specific case the \( K_a \) of ammonium ion is the same as the \( K_b \) of acetate ion \[ K_a(\text{NH}_4^+) = 5.6 \times 10^{-10}, \]
\[ K_b(\text{CH}_3\text{COO}^-) = 5.6 \times 10^{-10}. \] The two are of exactly (to two significant figures) equal strength. The solution will have pH 7.00.

What would the pH be if the concentration were 0.1 M in ammonium acetate? 0.4 M?
15.107 \( K_b = 8.91 \times 10^{-6} \)

\[ K_a = \frac{K_w}{K_b} = 1.1 \times 10^{-9} \]

\[ \frac{[\text{acid}]}{[\text{conjugate base}]} = \frac{K_a}{[H^+] = 3.98 \times 10^{-8}} = 0.028 \]

15.108 The fact that fluorine attracts electrons in a molecule more strongly than hydrogen should cause NF3 to be a poor electron pair donor and a poor base. NH3 is the stronger base.

15.109 Because the P–H bond is weaker, there is a greater tendency for PH4+ to ionize. Therefore, PH3 is a weaker base than NH3.

15.110 The autoionization for deuterium-substituted water is: \( \text{D}_2\text{O} \rightleftharpoons \text{D}^+ + \text{OD}^- \)

\[ [\text{D}^+][\text{OD}^-] = 1.35 \times 10^{-15} \quad (1) \]

(a) The definition of pD is: \( \text{pD} = -\log[D^+] = -\log(1.35 \times 10^{-15}) = 7.43 \)

(b) To be acidic, the pD must be < 7.43.

(c) Taking \(-\log\) of both sides of equation (1) above:

\[ -\log[D^+] + -\log[\text{OD}^-] = -\log(1.35 \times 10^{-15}) \]

\[ \text{pD} + \text{pOD} = 14.87 \]

15.111 (a) HNO2  (b) HF  (c) BF3  (d) NH3  (e) H2SO3  (f) HCO3− and CO32−

The reactions for (f) are: HCO3−(aq) + H+(aq) → CO2(g) + H2O(l)

\[ \text{CO}_3^{2−}(aq) + 2\text{H}^+(aq) \rightarrow \text{CO}_2(g) + \text{H}_2\text{O}(l) \]

15.112 First we must calculate the molarity of the trifluoromethane sulfonic acid. (Molar mass = 150.1 g/mol)

\[ \text{Molarity} = \frac{0.616 \text{ g} \times \frac{1 \text{ mol}}{150.1 \text{ g}}}{0.250 \text{ L}} = 0.0164 \text{ M} \]

Since trifluoromethane sulfonic acid is a strong acid and is 100% ionized, the [H+] is 0.0165 M.

\[ \text{pH} = -\log(0.0164) = 1.79 \]
15.113  (a)  The Lewis structure of H$_3$O$^+$ is:

\[
\begin{array}{c}
\text{H} \\
\text{O} \\
\text{H} \\
\end{array}
\]

Note that this structure is very similar to the Lewis structure of NH$_3$. The geometry is **trigonal pyramidal**.

(b) H$_4$O$^{2+}$ does **not** exist because the positively charged H$_3$O$^+$ has no affinity to accept the positive H$^+$ ion. If H$_4$O$^{2+}$ existed, it would have a tetrahedral geometry.

15.114  The reactions are

\[ \text{HF} \rightleftharpoons \text{H}^+ + \text{F}^- \]  

\[ \text{F}^- + \text{HF} \rightleftharpoons \text{HF}_2^- \]

Note that for equation (2), the equilibrium constant is relatively large with a value of 5.2. This means that the equilibrium lies to the right. Applying Le Châtelier’s principle, as HF ionizes in the first step, the F$^-$ that is produced is partially removed in the second step. More HF must ionize to compensate for the removal of the F$^-$, at the same time producing more H$^+$.

15.115  The equations are:

\[ \text{Cl}_2(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCl}(aq) + \text{HClO}(aq) \]

\[ \text{HCl}(aq) + \text{AgNO}_3(aq) \rightleftharpoons \text{AgCl(s) + HNO}_3(aq) \]

In the presence of OH$^-$ ions, the first equation is shifted to the right:

\[ \text{H}^+ \text{ (from HCl) + OH}^- \rightarrow \text{H}_2\text{O} \]

Therefore, the concentration of HClO increases. (The ‘bleaching action’ is due to ClO$^-$ ions.)

15.116  (a)  We must consider both the complete ionization of the strong acid, and the partial ionization of water.

\[ \text{HA} \rightarrow \text{H}^+ + \text{A}^- \]

\[ \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \]

From the above two equations, the [H$^+$] in solution is:

\[ [\text{H}^+] = [\text{A}^-] + [\text{OH}^-] \]  

We can also write:

\[ [\text{H}^+][\text{OH}^-] = K_w \]

\[ [\text{OH}^-] = \frac{K_w}{[\text{H}^+]} \]
Substituting into Equation (1):

\[
[H^+] = [A^-] + \frac{K_w}{[H^+]}
\]

\[
[H^+]^2 = [A^-][H^+] + K_w
\]

\[
[H^+]^2 - [A^-][H^+] - K_w = 0
\]

Solving a quadratic equation:

\[
[H^+] = \frac{[A^-] \pm \sqrt{[A^-]^2 + 4K_w}}{2}
\]

(b) For the strong acid, HCl, with a concentration of \(1.0 \times 10^{-7} M\), the \([Cl^-]\) will also be \(1.0 \times 10^{-7} M\).

\[
[H^+] = \frac{[Cl^-] \pm \sqrt{[Cl^-]^2 + 4K_w}}{2} = \frac{1 \times 10^{-7} \pm \sqrt{(1 \times 10^{-7})^2 + 4(1 \times 10^{-14})}}{2}
\]

\[
[H^+] = 1.6 \times 10^{-7} M \text{ (or } -6.0 \times 10^{-8} M, \text{ which is impossible)}
\]

\[
\text{pH} = -\log[1.6 \times 10^{-7}] = 6.80
\]

15.117 We examine the hydrolysis of the cation and anion separately.

\[
\text{NH}_4\text{CN}(aq) \rightarrow \text{NH}_4^+(aq) + \text{CN}^-(aq)
\]

**Cation:** \(\text{NH}_4^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_3(aq) + \text{H}_3\text{O}^+(aq)\)

Initial (M): 2.00  0  0
Change (M):  \(-x\)  \(+x\)  \(+x\)
Equilibrium (M): 2.00  \(-x\)  \(x\)  \(x\)

\[
K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}
\]

\[
5.6 \times 10^{-10} = \frac{x^2}{2.00 - x} \approx \frac{x^2}{2.00}
\]

\[
x = 3.35 \times 10^{-5} M = [\text{H}_3\text{O}^+]
\]

**Anion:** \(\text{CN}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCN}(aq) + \text{OH}^-(aq)\)

Initial (M): 2.00  0  0
Change (M):  \(-x\)  \(+x\)  \(+x\)
Equilibrium (M): 2.00  \(-x\)  \(x\)  \(x\)

\[
K_b = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]}
\]

\[
2.0 \times 10^{-5} = \frac{y^2}{2.00 - y} \approx \frac{y^2}{2.00}
\]

\[
y = 6.32 \times 10^{-3} M = [\text{OH}^-]
\]
CN\(^-\) is stronger as a base than NH\(_4^+\) is as an acid. Some OH\(^-\) produced from the hydrolysis of CN\(^-\) will be neutralized by H\(_3\)O\(^+\) produced from the hydrolysis of NH\(_4^+\).

\[
\begin{array}{c}
\text{H}_3\text{O}^+(aq) + \text{OH}^-(aq) \rightarrow 2\text{H}_2\text{O}(l)
\end{array}
\]

<table>
<thead>
<tr>
<th>Initial ((M))</th>
<th>Change ((M))</th>
<th>Final ((M))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3.35 \times 10^{-2})</td>
<td>(-3.35 \times 10^{-5})</td>
<td>(0)</td>
</tr>
<tr>
<td>(6.32 \times 10^{-3})</td>
<td>(-3.35 \times 10^{-5})</td>
<td>(6.29 \times 10^{-3})</td>
</tr>
</tbody>
</table>

\([\text{OH}^-] = 6.29 \times 10^{-3}\ M\)

\(\text{pOH} = 2.20\)

\(\text{pH} = 11.80\)

**15.118** The solution for the first step is standard:

\[
\begin{array}{c}
\text{H}_3\text{PO}_4(aq) \rightleftharpoons \text{H}^+(aq) + \text{H}_2\text{PO}_4^-(aq)
\end{array}
\]

<table>
<thead>
<tr>
<th>Initial ((M))</th>
<th>Change ((M))</th>
<th>Equil. ((M))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.100</td>
<td>-x</td>
<td>(0.100 - x)</td>
</tr>
<tr>
<td>0.000</td>
<td>+x</td>
<td>x</td>
</tr>
<tr>
<td>0.000</td>
<td>+x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[
K_{a1} = \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}
\]

\(7.5 \times 10^{-3} = \frac{x^2}{(0.100 - x)}\)

In this case we probably cannot say that \((0.100 - x) \approx 0.100\) due to the magnitude of \(K_a\). We obtain the quadratic equation:

\[x^2 + (7.5 \times 10^{-3})x - (7.5 \times 10^{-4}) = 0\]

The positive root is \(x = 0.0239\ M\). We have:

\([\text{H}^+] = [\text{H}_2\text{PO}_4^-] = 0.0239\ M\)

\([\text{H}_3\text{PO}_4] = (0.100 - 0.0239)M = 0.076\ M\)

For the second ionization:

\[
\begin{array}{c}
\text{H}_2\text{PO}_4^-(aq) \rightleftharpoons \text{H}^+(aq) + \text{HPO}_4^{2-}(aq)
\end{array}
\]

<table>
<thead>
<tr>
<th>Initial ((M))</th>
<th>Change ((M))</th>
<th>Equil ((M))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0239</td>
<td>-y</td>
<td>(0.0239 - y)</td>
</tr>
<tr>
<td>0.0239</td>
<td>+y</td>
<td>(0.0239 + y)</td>
</tr>
<tr>
<td>0.000</td>
<td>+y</td>
<td>y</td>
</tr>
</tbody>
</table>

\[
K_{a2} = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}
\]

\(6.2 \times 10^{-8} = \frac{(0.0239 + y)(y)}{(0.0239 - y)} = \frac{(0.0239)(y)}{(0.0239)}\)

\(y = 6.2 \times 10^{-8}\ M\).

Thus,

\([\text{H}^+] = [\text{H}_2\text{PO}_4^-] = 0.0239\ M\)

\([\text{HPO}_4^{2-}] = y = 6.2 \times 10^{-8}\ M\)
We set up the problem for the third ionization in the same manner.

\[
\text{HPO}_4^{2-}(aq) \rightleftharpoons \text{H}^+(aq) + \text{PO}_4^{3-}(aq)
\]

<table>
<thead>
<tr>
<th>Initial (M)</th>
<th>Change (M)</th>
<th>Equil. (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(6.2 \times 10^{-8})</td>
<td>(-z)</td>
<td>(6.2 \times 10^{-8})</td>
</tr>
<tr>
<td>0.0239</td>
<td>(+z)</td>
<td>0.0239 + z</td>
</tr>
<tr>
<td>0</td>
<td>(+z)</td>
<td>(z)</td>
</tr>
</tbody>
</table>

\[
K_{a3} = \frac{[\text{H}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} = 4.8 \times 10^{-13}
\]

\[
4.8 \times 10^{-13} = \frac{(0.0239 + z)(z)}{(6.2 \times 10^{-8}) - z} \approx \frac{(0.239)(z)}{(6.2 \times 10^{-8})}
\]

\[
z = 1.2 \times 10^{-18} \text{ M}
\]

The equilibrium concentrations are:

\[
[\text{H}^+] = [\text{H}_2\text{PO}_4^-] = 0.0239 \text{ M}
\]

\[
[\text{H}_3\text{PO}_4] = 0.076 \text{ M}
\]

\[
[\text{HPO}_4^{2-}] = 6.2 \times 10^{-8} \text{ M}
\]

\[
[\text{PO}_4^{3-}] = 1.2 \times 10^{-18} \text{ M}
\]

15.119 (a) We carry an additional significant figure throughout this calculation to minimize rounding errors.

Number of moles NaOH = \(M \times \text{vol (L)} = 0.0568 \text{ M} \times 0.0138 \text{ L} = 7.838 \times 10^{-4} \text{ mol}\)

If the acid were all dimer, then:

\[
\text{mol of dimer} = \frac{\text{mol NaOH}}{2} = \frac{7.838 \times 10^{-4} \text{ mol}}{2} = 3.919 \times 10^{-4} \text{ mol}
\]

If the acetic acid were all dimer, the pressure that would be exerted would be:

\[
P = \frac{nRT}{V} = \frac{(3.919 \times 10^{-4} \text{ mol})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(324 \text{ K})}{0.360 \text{ L}} = 0.02896 \text{ atm}
\]

However, the actual pressure is 0.0342 atm. If \(\alpha\) mol of dimer dissociates to monomers, then \(2\alpha\) monomer forms.

\[
(\text{CH}_3\text{COOH})_2 \rightleftharpoons 2\text{CH}_3\text{COOH}
\]

\[
1 - \alpha \quad 2\alpha
\]

The total moles of acetic acid is:

\[
\text{moles dimer} + \text{monomer} = (1 - \alpha) + 2\alpha = 1 + \alpha
\]

Using partial pressures:

\[
P_{\text{observed}} = P(1 + \alpha)
\]

0.0342 atm = \((0.02896 \text{ atm})(1 + \alpha)\)

\[
\alpha = 0.181
\]
(b) The equilibrium constant is:

\[ K_p = \frac{P_{\text{CH}_2\text{COOH}}^2}{P_{\text{CH}_2\text{COOH}}^2} = \frac{\left(\frac{2\alpha}{1 + \alpha}\right)^2}{\left(\frac{1 - \alpha}{1 + \alpha}\right)^2} P_{\text{observed}}^2 = \frac{4\alpha^2 P_{\text{observed}}}{1 - \alpha^2} = 4.63 \times 10^{-3} \]

15.120 \[ 0.100 \text{ M Na}_2\text{CO}_3 \rightarrow 0.200 \text{ M Na}^+ + 0.100 \text{ M CO}_3^{2-} \]

First stage:

\[ \text{CO}_3^{2-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCO}_3^-(aq) + \text{OH}^-(aq) \]

| Initial (M) | 0.100 | 0 | 0 |
| Change (M) | -x | +x | +x |
| Equilibrium (M) | 0.100 - x | x | x |

\[ K_1 = \frac{K_w}{K_2} = \frac{1.0 \times 10^{-14}}{4.8 \times 10^{-11}} = 2.1 \times 10^{-4} \]

\[ K_1 = \frac{[\text{HCO}_3^-][\text{OH}^-]}{[\text{CO}_3^{2-}]} \]

\[ 2.1 \times 10^{-4} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100} \]

\[ x = 4.6 \times 10^{-3} M = [\text{HCO}_3^-] = [\text{OH}^-] \]

Second stage:

\[ \text{HCO}_3^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{CO}_3(aq) + \text{OH}^-(aq) \]

| Initial (M) | 4.6 \times 10^{-3} | 0 | 4.6 \times 10^{-3} |
| Change (M) | -y | +y | +y |
| Equilibrium (M) | (4.6 \times 10^{-3}) - y | y | (4.6 \times 10^{-3}) + y |

\[ K_2 = \frac{[\text{H}_2\text{CO}_3][\text{OH}^-]}{[\text{HCO}_3^-]} \]

\[ 2.4 \times 10^{-8} = \frac{y[(4.6 \times 10^{-3}) + y]}{(4.6 \times 10^{-3}) - y} \approx \frac{(y)(4.6 \times 10^{-3})}{(4.6 \times 10^{-3})} \]

\[ y = 2.4 \times 10^{-8} M \]

At equilibrium:

\[ [\text{Na}^+] = 0.200 \text{ M} \]

\[ [\text{HCO}_3^-] = (4.6 \times 10^{-3}) M - (2.4 \times 10^{-8}) M \approx 4.6 \times 10^{-3} M \]

\[ [\text{H}_2\text{CO}_3] = 2.4 \times 10^{-8} \text{ M} \]

\[ [\text{OH}^-] = (4.6 \times 10^{-3}) M + (2.4 \times 10^{-8}) M \approx 4.6 \times 10^{-3} M \]

\[ [\text{H}^+] = \frac{1.0 \times 10^{-14}}{4.6 \times 10^{-3}} = 2.2 \times 10^{-12} \text{ M} \]
15.121 \[
\text{[CO}_2\text{]} = k_P = (2.28 \times 10^{-3} \text{ mol/L atm})(3.20 \text{ atm}) = 7.30 \times 10^{-3} \text{ M}
\]
\[
\text{CO}_2(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+(\text{aq}) + \text{HCO}_3^-(\text{aq})
\]
\[(7.30 \times 10^{-3} - x) M \quad x M \quad x M
\]
\[
K_a = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]}
\]
\[
4.2 \times 10^{-7} = \frac{x^2}{(7.30 \times 10^{-3}) - x} \approx \frac{x^2}{7.30 \times 10^{-3}}
\]
\[
x = 5.5 \times 10^{-5} \text{ M} = [\text{H}^+]
\]
\[\text{pH} = 4.26\]

15.122 When NaCN is treated with HCl, the following reaction occurs.
\[
\text{NaCN} + \text{HCl} \rightarrow \text{NaCl} + \text{HCN}
\]
HCN is a very weak acid, and only partially ionizes in solution.
\[
\text{HCN}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{CN}^-(\text{aq})
\]
The main species in solution is HCN which has a tendency to escape into the gas phase.
\[
\text{HCN}(\text{aq}) \rightleftharpoons \text{HCN}(g)
\]
Since the HCN(g) that is produced is a highly poisonous compound, it would be dangerous to treat NaCN with acids without proper ventilation.

15.123 When the pH is 10.00, the pOH is 4.00 and the concentration of hydroxide ion is \(1.0 \times 10^{-4}\) M. The concentration of HCN must be the same. (Why?) If the concentration of NaCN is \(x\), the table looks like:

| Initial (M) | | | | |
|---|---|---|---|
| CN\(^-\) (aq) + H\(_2\)O(l) \rightleftharpoons HCN(aq) + OH\(^-\) (aq) | x | 0 | 0 |
| Change (M) | | | |
| -1.0 \times 10^{-4} | +1.0 \times 10^{-4} | +1.0 \times 10^{-4} |
| Equilibrium (M) | | | |
| \((x - 1.0 \times 10^{-4})\) | \((1.0 \times 10^{-4})\) | \((1.0 \times 10^{-4})\) |

\[
K_b = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]}
\]
\[
2.0 \times 10^{-5} = \frac{(1.0 \times 10^{-4})^2}{(x - 1.0 \times 10^{-4})}
\]
\[
x = 6.0 \times 10^{-4} \text{ M} = [\text{CN}^-]_0
\]

Amount of NaCN = \[
250 \text{ mL} \times \frac{6.0 \times 10^{-4} \text{ mol NaCN}}{1000 \text{ mL}} \times \frac{49.01 \text{ g NaCN}}{1 \text{ mol NaCN}} = 7.4 \times 10^{-3} \text{ g NaCN}
\]
15.124 \[ \text{pH} = 2.53 = -\log[H^+] \]

\[ [H^+] = 2.95 \times 10^{-3} \text{ M} \]

Since the concentration of $H^+$ at equilibrium is $2.95 \times 10^{-3} \text{ M}$, that means that $2.95 \times 10^{-3} \text{ M} \text{ HCOOH}$ ionized. Let $I$ represent the initial concentration of HCOOH as $I$. The equation representing the ionization of formic acid is:

\[ \text{HCOOH(aq)} \rightleftharpoons \text{H}^+(aq) + \text{HCOO}^-(aq) \]

<table>
<thead>
<tr>
<th>Initial (M)</th>
<th>$I$</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change (M)</td>
<td>$-2.95 \times 10^{-3}$</td>
<td>$+2.95 \times 10^{-3}$</td>
<td>$+2.95 \times 10^{-3}$</td>
</tr>
<tr>
<td>Equilibrium (M)</td>
<td>$I - (2.95 \times 10^{-3})$</td>
<td>$2.95 \times 10^{-3}$</td>
<td>$2.95 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

\[ K_a = \frac{[H^+][\text{HCOO}^-]}{[\text{HCOOH}]} \]

\[ 1.7 \times 10^{-4} = \frac{(2.95 \times 10^{-3})^2}{I - (2.95 \times 10^{-3})} \]

\[ I = 0.054 \text{ M} \]

There are 0.054 moles of formic acid in 1000 mL of solution. The mass of formic acid in 100 mL is:

\[ 100 \text{ mL} \times \frac{0.054 \text{ mol formic acid}}{1000 \text{ mL soln}} \times \frac{46.03 \text{ g formic acid}}{1 \text{ mol formic acid}} = 0.25 \text{ g formic acid} \]

15.125 The equilibrium is established:

\[ \text{CH}_3\text{COOH(aq)} \rightleftharpoons \text{CH}_3\text{COO}^-(aq) + \text{H}^+(aq) \]

<table>
<thead>
<tr>
<th>Initial (M)</th>
<th>0.150</th>
<th>0</th>
<th>0.100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change (M)</td>
<td>$-x$</td>
<td>$+x$</td>
<td>$+x$</td>
</tr>
<tr>
<td>Equilibrium (M)</td>
<td>$(0.150 - x)$</td>
<td>$x$</td>
<td>$(0.100 + x)$</td>
</tr>
</tbody>
</table>

\[ K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \]

\[ 1.8 \times 10^{-5} = \frac{x(0.100 + x)}{0.150 - x} \approx \frac{0.100x}{0.150} \]

\[ x = 2.7 \times 10^{-5} \text{ M} \]

$2.7 \times 10^{-5} \text{ M}$ is the $[H^+]$ contributed by CH$_3$COOH. HCl is a strong acid that completely ionizes. It contributes a $[H^+]$ of 0.100 M to the solution.

\[ [H^+]_{\text{total}} = [0.100 + (2.7 \times 10^{-5})] \text{ M} \approx 0.100 \text{ M} \]

\[ \text{pH} = 1.000 \]

The pH is totally determined by the HCl and is independent of the CH$_3$COOH.
The balanced equation is:  
\[ 
\text{Mg} + 2\text{HCl} \rightarrow \text{MgCl}_2 + \text{H}_2 
\]

\[
\text{mol of Mg} = \frac{1.87 \text{ g Mg}}{24.31 \text{ g/Mg}} = 0.0769 \text{ mol}
\]

From the balanced equation:

\[
\text{mol of HCl required for reaction} = 2 \times \text{mol Mg} = (2)(0.0769 \text{ mol}) = 0.154 \text{ mol HCl}
\]

The concentration of HCl:

\[
\text{pH} = -0.544, \text{ thus } [\text{H}^+] = 3.50 M
\]

\[
\text{initial mol HCl} = M \times \text{Vol (L)} = (3.50 M)(0.0800 \text{ L}) = 0.280 \text{ mol HCl}
\]

Moles of HCl left after reaction:

\[
\text{initial mol HCl} - \text{mol HCl reacted} = 0.280 \text{ mol} - 0.154 \text{ mol} = 0.126 \text{ mol HCl}
\]

Molarity of HCl left after reaction:

\[
M = \frac{\text{mol}/L}{0.126 \text{ mol}/0.080 \text{ L}} = 1.58 M
\]

\[
\text{pH} = -\log(1.58) = -0.20
\]

(a) The pH of the solution of HA would be lower. (Why?)

(b) The electrical conductance of the HA solution would be greater. (Why?)

(c) The rate of hydrogen evolution from the HA solution would be greater. Presumably, the rate of the reaction between the metal and hydrogen ion would depend on the hydrogen ion concentration (i.e., this would be part of the rate law). The hydrogen ion concentration will be greater in the HA solution.

The important equation is the hydrolysis of NO₂⁻:  
\[ 
\text{NO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_2 + \text{OH}^-
\]

(a) Addition of HCl will result in the reaction of the H⁺ from the HCl with the OH⁻ that was present in the solution. The OH⁻ will effectively be removed and the equilibrium will shift to the right to compensate (more hydrolysis).

(b) Addition of NaOH is effectively addition of more OH⁻ which places stress on the right hand side of the equilibrium. The equilibrium will shift to the left (less hydrolysis) to compensate for the addition of OH⁻.

(c) Addition of NaCl will have no effect.

(d) Recall that the percent ionization of a weak acid increases with dilution (see Figure 15.4 of the text). The same is true for weak bases. Thus dilution will cause more hydrolysis, shifting the equilibrium to the right.

Like carbon dioxide, sulfur dioxide behaves as a Lewis acid by accepting a pair of electrons from the Lewis base water. The Lewis acid-base adduct rearranges to form sulfurous acid in a manner exactly analogous to the rearrangement of the carbon dioxide-water adduct to form carbonic acid that is presented on page 700 of the textbook.

In Chapter 11, we found that salts with their formal electrostatic intermolecular attractions had low vapor pressures and thus high boiling points. Ammonia and its derivatives (amines) are molecules with dipole-dipole attractions; as long as the nitrogen has one direct N–H bond, the molecule will have hydrogen
bonding. Even so, these molecules will have much higher vapor pressures than ionic species. Thus, if we could convert the neutral ammonia-type molecules into salts, their vapor pressures, and thus associated odors, would decrease. Lemon juice contains acids which can react with neutral ammonia-type (amine) molecules to form ammonium salts.

\[
\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+ \\
\text{RNH}_2 + \text{H}^+ \rightarrow \text{RNH}_3^+
\]

**15.131**  
\[\text{pH} = 10.64\]  
\[\text{pOH} = 3.36\]  
\[\text{[OH}^-\text{]} = 4.4 \times 10^{-4} \text{ M}\]

\[
\text{CH}_3\text{NH}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{NH}_3^+(aq) + \text{OH}^-(aq)
\]

\[x - 4.4 \times 10^{-4} \text{ M} \quad 4.4 \times 10^{-4} \text{ M} \quad 4.4 \times 10^{-4} \text{ M}\]

\[
K_b = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]}
\]

\[4.4 \times 10^{-4} = \frac{(4.4 \times 10^{-4})(4.4 \times 10^{-4})}{x - (4.4 \times 10^{-4})}\]

\[4.4 \times 10^{-4}x - 1.9 \times 10^{-7} = 1.9 \times 10^{-7}\]

\[x = 8.6 \times 10^{-4} \text{ M}\]

The molar mass of CH₃NH₂ is 31.06 g/mol.

The mass of CH₃NH₂ in 100.0 mL is:

\[100.0 \text{ mL} \times \frac{8.6 \times 10^{-4} \text{ mol CH}_3\text{NH}_2}{1000 \text{ mL}} \times \frac{31.06 \text{ g CH}_3\text{NH}_2}{1 \text{ mol CH}_3\text{NH}_2} = 2.7 \times 10^{-3} \text{ g CH}_3\text{NH}_2\]

**15.132**  
\[\text{HCOOH} \rightleftharpoons \text{H}^+ + \text{HCOO}^-\]

Initial (\(M\)): 0.400 0 0  
Change (\(M\)): \(-x\) \(+x\) \(+x\)  
Equilibrium (\(M\)): 0.400 \(-x\) \(x\) \(x\)

Total concentration of particles in solution: \((0.400 - x) + x + x = 0.400 + x\)

Assuming the molarity of the solution is equal to the molality, we can write:

\[
\Delta T_f = K_{\text{f,m}}
\]

\[0.758 = (1.86)(0.400 + x)\]

\[x = 0.00753 = [\text{H}^+] = [\text{HCOO}^-]\]

\[
K_a = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = \frac{(0.00753)(0.00753)}{0.400 - 0.00753} = 1.4 \times 10^{-4}
\]
15.133  (a)  \( \text{NH}_2^- + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{OH}^- \)
\[ \text{N}_3^- + 3\text{H}_2\text{O} \rightarrow \text{NH}_3 + 3\text{OH}^- \]

(b)  \( \text{N}_3^- \) is the stronger base since each ion produces 3 \( \text{OH}^- \) ions.

15.134  \( \text{SO}_2(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+(aq) + \text{HSO}_3^-(aq) \)

Recall that 0.12 ppm \( \text{SO}_2 \) would mean 0.12 parts \( \text{SO}_2 \) per 1 million \( (10^6) \) parts of air by volume. The number of particles of \( \text{SO}_2 \) per volume will be directly related to the pressure.

\[
\rho_{\text{SO}_2} = \frac{0.12 \text{ parts } \text{SO}_2}{10^6 \text{ parts air}} = 1.2 \times 10^{-7} \text{ atm}
\]

We can now calculate the \( [\text{H}^+] \) from the equilibrium constant expression.

\[
K = \frac{[\text{H}^+][\text{HSO}_3^-]}{\rho_{\text{SO}_2}}
\]

\[
1.3 \times 10^{-2} = \frac{x^2}{1.2 \times 10^{-7}}
\]

\[
x^2 = (1.3 \times 10^{-2})(1.2 \times 10^{-7})
\]

\[
x = 3.9 \times 10^{-5} M = [\text{H}^+]
\]

\[
\text{pH} = -\log(3.9 \times 10^{-5}) = 4.40
\]

15.135  \[
\frac{[\text{H}^+][\text{ClO}^-]}{[\text{HClO}]} = 3.0 \times 10^{-8}
\]

A pH of 7.8 corresponds to \( [\text{H}^+] = 1.6 \times 10^{-8} M \)

Substitute \( [\text{H}^+] \) into the equation above to solve for the \( \frac{[\text{ClO}^-]}{[\text{HClO}]} \) ratio.

\[
\frac{[\text{ClO}^-]}{[\text{HClO}]} = \frac{3.0 \times 10^{-8}}{1.6 \times 10^{-8}} = 1.9
\]

This indicates that to obtain a pH of 7.8, the \( [\text{ClO}^-] \) must be 1.9 times greater than the \( [\text{HClO}] \). We can write:

\[
\% \text{ClO}^- = \frac{\text{part } \text{ClO}^-}{\text{part } \text{ClO}^- + \text{part } \text{HClO}} \times 100% = \frac{1.9}{1.9 + 1.0} \times 100% = 66%
\]

By difference, \( \% \text{HClO} = 34% \)

15.136  In inhaling the smelling salt, some of the powder dissolves in the basic solution. The ammonium ions react with the base as follows:

\[
\text{NH}_4^+(aq) + \text{OH}^-(aq) \rightarrow \text{NH}_3(aq) + \text{H}_2\text{O}
\]

It is the pungent odor of ammonia that prevents a person from fainting.
15.137 (a) The overall equation is

$$\text{Fe}_2\text{O}_3(s) + 6\text{HCl}(aq) \rightarrow 2\text{FeCl}_3(aq) + 3\text{H}_2\text{O}(l)$$

and the net ionic equation is

$$\text{Fe}_2\text{O}_3(s) + 6\text{H}^+(aq) \rightarrow 2\text{Fe}^{3+}(aq) + 3\text{H}_2\text{O}(l)$$

Since HCl donates the H\(^+\) ion, it is the Brønsted acid. Each Fe\(_2\)O\(_3\) unit accepts six H\(^+\) ions; therefore, it is the Brønsted base.

(b) The first stage is

$$\text{CaCO}_3(s) + \text{HCl}(aq) \rightarrow \text{Ca}^{2+}(aq) + \text{HCO}_3^-(aq) + \text{Cl}^- (aq)$$

and the second stage is

$$\text{HCl}(aq) + \text{HCO}_3^-(aq) \rightarrow \text{CO}_2(g) + \text{Cl}^-(aq) + \text{H}_2\text{O}(l)$$

The overall equation is

$$\text{CaCO}_3(s) + 2\text{HCl}(aq) \rightarrow \text{CaCl}_2(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g)$$

The CaCl\(_2\) formed is soluble in water.

(c) We need to find the concentration of the HCl solution in order to determine its pH. Let's assume a volume of 1.000 L = 1000 mL. The mass of 1000 mL of solution is:

$$1000 \text{ mL} \times \frac{1.073 \text{ g}}{1 \text{ mL}} = 1073 \text{ g}$$

The number of moles of HCl in a 15 percent solution is:

$$\frac{15\% \text{ HCl}}{100\% \text{ soln}} \times 1073 \text{ g soln} = (1.6 \times 10^2 \text{ g HCl}) \times \frac{1 \text{ mol HCl}}{36.46 \text{ g HCl}} = 4.4 \text{ mol HCl}$$

Thus, there are 4.4 moles of HCl in one liter of solution, and the concentration is 4.4 M. The pH of the solution is

$$\text{pH} = -\log(4.4) = -0.64$$

This is a highly acidic solution (note that the pH is negative), which is needed to dissolve large quantities of rocks in the oil recovery process.

15.138 (c) does not represent a Lewis acid-base reaction. In this reaction, the F–F single bond is broken and single bonds are formed between P and each F atom. For a Lewis acid-base reaction, the Lewis acid is an electron-pair acceptor and the Lewis base is an electron-pair donor.

15.139 (a) False. A Lewis acid such as CO\(_2\) is not a Brønsted acid. It does not have a hydrogen ion to donate.

(b) False. Consider the weak acid, NH\(_4^+\). The conjugate base of this acid is NH\(_3\), which is neutral.

(c) False. The percent ionization of a base decreases with increasing concentration of base in solution.

(d) False. A solution of barium fluoride is basic. The fluoride ion, F\(^-\), is the conjugate base of a weak acid. It will hydrolyze to produce OH\(^-\) ions.
15.140 From the given pH's, we can calculate the $[H^+]$ in each solution.

Solution (1): $[H^+] = 10^{-pH} = 10^{-4.12} = 7.6 \times 10^{-5} \text{ M}$
Solution (2): $[H^+] = 10^{-5.76} = 1.7 \times 10^{-6} \text{ M}$
Solution (3): $[H^+] = 10^{-5.34} = 4.6 \times 10^{-6} \text{ M}$

We are adding solutions (1) and (2) to make solution (3). The volume of solution (2) is 0.528 L. We are going to add a given volume of solution (1) to solution (2). Let's call this volume $x$. The moles of $H^+$ in solutions (1) and (2) will equal the moles of $H^+$ in solution (3).

$$\text{mol } H^+ \text{ soln (1)} + \text{mol } H^+ \text{ soln (2)} = \text{mol } H^+ \text{ soln (3)}$$

Recall that mol = $M \times L$. We have:

$$(7.6 \times 10^{-5} \text{ mol/L})(x \text{ L}) + (1.7 \times 10^{-6} \text{ mol/L})(0.528 \text{ L}) = (4.6 \times 10^{-6} \text{ mol/L})(0.528 + x) \text{ L}$$

$$(7.6 \times 10^{-5})x + (9.0 \times 10^{-7}) = (2.4 \times 10^{-6}) + (4.6 \times 10^{-6})x$$

$$7.1 \times 10^{-5}x = 1.5 \times 10^{-6}$$

$$x = 0.021 \text{ L} = 21 \text{ mL}$$

15.141 Set up a table showing initial and equilibrium concentrations.

<table>
<thead>
<tr>
<th>HNO$_2$(aq)</th>
<th>$\rightleftharpoons$</th>
<th>$H^+(aq) + NO_2^-(aq)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial (M):</td>
<td>0.80</td>
<td>0.00</td>
</tr>
<tr>
<td>Change (M):</td>
<td>$-x$</td>
<td>$+x$</td>
</tr>
<tr>
<td>Equilibrium (M):</td>
<td>$(0.80 - x)$</td>
<td>$x$</td>
</tr>
</tbody>
</table>

Using the value of $K_a$ from Table 15.3 of the text:

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

$$4.5 \times 10^{-4} = \frac{x^2}{(0.80 - x)}$$

We assume that $x$ is small so $(0.80 - x) \approx 0.80$

$$4.5 \times 10^{-4} = \frac{x^2}{0.80}$$

$$x = 0.019 \text{ M} = [H^+]$$

$$\text{pH} = -\log(0.019) = 1.72$$

Percent ionization $= \frac{0.019 \text{ M}}{0.80 \text{ M}} \times 100\% = 2.4\%$

15.142 First, determine the molarity of each of the acids.

$$M \ (HX) = \frac{16.9 \ g \ HX}{1 \ L \ \text{soln}} \times \frac{1 \ \text{mol} \ HX}{180 \ g \ HX} = 0.0939 \text{ M}$$

$$M \ (HY) = \frac{9.05 \ g \ HY}{1 \ L \ \text{soln}} \times \frac{1 \ \text{mol} \ HY}{78.0 \ g \ HY} = 0.116 \text{ M}$$
Because both of these solutions have the same pH, they have the same concentration of $H_3O^+$ in solution. The acid with the lower concentration ($HX$) has the greater percent ionization and is therefore the stronger acid.

15.143 Given the equation: $HbH^+ + O_2 \rightleftharpoons HbO_2 + H^+$

(a) From the equilibrium equation, high oxygen concentration puts stress on the left side of the equilibrium and thus shifts the concentrations to the right to compensate. $HbO_2$ is favored.

(b) High acid, $H^+$ concentration, places stress on the right side of the equation forcing concentrations on the left side to increase, thus releasing oxygen and increasing the concentration of $HbH^+$.

(c) Removal of CO$_2$ decreases $H^+$ (in the form of carbonic acid), thus shifting the reaction to the right. More $HbO_2$ will form. Breathing into a paper bag increases the concentration of CO$_2$ (re-breathing the exhaled CO$_2$), thus causing more O$_2$ to be released as explained above.

15.144 The balanced equations for the two reactions are:

$$MCO_3(s) + 2HCl(aq) \rightarrow MCl_2(aq) + CO_2(g) + H_2O(l)$$

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

First, let’s find the number of moles of excess acid from the reaction with NaOH.

$$0.03280 L \times \frac{0.588 \text{ mol NaOH}}{1 \text{ L soln}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}} = 0.0193 \text{ mol HCl}$$

The original number of moles of acid was:

$$0.500 L \times \frac{0.100 \text{ mol HCl}}{1 \text{ L soln}} = 0.0500 \text{ mol HCl}$$

The amount of hydrochloric acid that reacted with the metal carbonate is:

$$(0.0500 \text{ mol HCl}) - (0.0193 \text{ mol HCl}) = 0.0307 \text{ mol HCl}$$

The mole ratio from the balanced equation is 1 mole MCO$_3$ : 2 mole HCl. The moles of MCO$_3$ that reacted are:

$$0.0307 \text{ mol HCl} \times \frac{1 \text{ mol MCO}_3}{2 \text{ mol HCl}} = 0.01535 \text{ mol MCO}_3$$

We can now determine the molar mass of MCO$_3$, which will allow us to identify the metal.

$$\text{molar mass MCO}_3 = \frac{1.294 \text{ g MCO}_3}{0.01535 \text{ mol MCO}_3} = 84.3 \text{ g/mol}$$

We subtract off the mass of CO$_3^{2-}$ to identify the metal.

$$\text{molar mass M} = 84.3 \text{ g/mol} - 60.01 \text{ g/mol} = 24.3 \text{ g/mol}$$

The metal is magnesium.
We start with the equation for the hydrolysis of a weak acid.

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

At equilibrium, \([\text{H}_3\text{O}^+] = [\text{A}^-]\).

\[ K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}_3\text{O}^+]^2}{[\text{HA}]} \]

Because this is a weak acid, the concentration of HA at equilibrium is approximately equal to its initial concentration: \([\text{HA}] \approx [\text{HA}]_0\). Substituting into the above equation gives,

\[ K_a \approx \frac{[\text{H}_3\text{O}^+]^2}{[\text{HA}]_0} \]

\[ [\text{H}_3\text{O}^+] = \sqrt{K_a[\text{HA}]_0} \]

By definition,

\[ \% \text{ ionization} = \frac{[\text{H}_3\text{O}^+]}{[\text{HA}]_0} \times 100\% = \sqrt{K_a[\text{HA}]_0} \frac{[\text{HA}]}{[\text{HA}]_0} = \sqrt{K_a} \]

Looking at this equation for \% ionization, when \([\text{HA}]_0\) is decreased by a factor of 10 to \([\text{HA}]_0 / 10\), \% ionization increases by \(\sqrt{10}\). This result is in accord with LeChâtelier’s principle, which predicts that ionization should increase with dilution.

Because HF is a much stronger acid than HCN, we can assume that the pH is largely determined by the ionization of HF.

\[ \text{HF(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{F}^-(aq) \]

\begin{align*}
\text{Initial (M)}: & \quad 1.00 & 0 & 0 \\
\text{Change (M)}: & \quad -x & +x & +x \\
\text{Equilibrium (M)}: & \quad 1.00 - x & x & x \\
\end{align*}

\[ K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} \]

\[ 7.1 \times 10^{-4} = \frac{x^2}{1.00 - x} \approx \frac{x^2}{1.00} \]

\[ x = 0.027 \text{ M} = [\text{H}_3\text{O}^+] \]

\[ \text{pH} = 1.57 \]

HCN is a very weak acid, so at equilibrium, \([\text{HCN}] \approx 1.00 \text{ M}\).

\[ K_a = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]} \]

\[ 4.9 \times 10^{-10} = \frac{(0.027)[\text{CN}^-]}{1.00} \]

\[ [\text{CN}^-] = 1.8 \times 10^{-8} \text{ M} \]
In a 1.00 \( M \) HCN solution, the concentration of \( [CN^-] \) would be:

\[
\text{HCN}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CN}^-(aq)
\]

<table>
<thead>
<tr>
<th>Initial (M)</th>
<th>Change (M)</th>
<th>Equilibrium (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>-x</td>
<td>1.00 - x</td>
</tr>
<tr>
<td>0</td>
<td>+x</td>
<td>x</td>
</tr>
<tr>
<td>0</td>
<td>+x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]}
\]

\[
4.9 \times 10^{-10} = \frac{x^2}{1.00 - x} \approx \frac{x^2}{1.00}
\]

\[
x = 2.2 \times 10^{-5} \text{ M} = [\text{CN}^-]
\]

[CN\(^-\)] is greater in the 1.00 \( M \) HCN solution compared to the 1.00 \( M \) HCN/1.00 \( M \) HF solution. According to LeChâtelier’s principle, the high [H\(3\)O\(^+\)] (from HF) shifts the HCN equilibrium from right to left decreasing the ionization of HCN. The result is a smaller [CN\(^-\)] in the presence of HF.

15.147 Both NaF and SnF\(_2\) provide F\(^-\) ions in solution.

\[
\text{NaF} \rightarrow \text{Na}^+ + \text{F}^-
\]

\[
\text{SnF}_2 \rightarrow \text{Sn}^{2+} + 2\text{F}^-
\]

Because HF is a much stronger acid than H\(_2\)O, it follows that F\(^-\) is a much weaker base than OH\(^-\). The F\(^-\) ions replace OH\(^-\) ions during the remineralization process

\[
5\text{Ca}^{2+} + 3\text{PO}_4^{3-} + \text{F}^- \rightarrow \text{Ca}_5(\text{PO}_4)_3\text{F} \quad \text{(fluorapatite)}
\]

because OH\(^-\) has a much greater tendency to combine with H\(^+\)

\[
\text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O}
\]

than F\(^-\) does.

\[
\text{F}^- + \text{H}^+ \rightleftharpoons \text{HF}
\]

Because F\(^-\) is a weaker base than OH\(^-\), fluorapatite is more resistant to attacks by acids compared to hydroxyapatite.

15.148 The van’t Hoff equation allows the calculation of an equilibrium constant at a different temperature if the value of the equilibrium constant at another temperature and \( \Delta H^o \) for the reaction are known.

\[
\ln \frac{K_1}{K_2} = \frac{\Delta H^o}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

First, we calculate \( \Delta H^o \) for the ionization of water using data in Appendix 3 of the text.

\[
\text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+(aq) + \text{OH}^-(aq)
\]

\[
\Delta H^o = [\Delta H^o_1(\text{H}^+) + \Delta H^o_1(\text{OH}^-)] - \Delta H^o_1(\text{H}_2\text{O})
\]

\[
\Delta H^o = (0 - 229.94 \text{ kJ/mol}) - (-285.8 \text{ kJ/mol})
\]

\[
\Delta H^o = 55.9 \text{ kJ/mol}
\]
We substitute $\Delta H^\circ$ and the equilibrium constant at 25°C (298 K) into the van’t Hoff equation to solve for the equilibrium constant at 100°C (373 K).

\[
\ln \frac{1.0 \times 10^{-14}}{K_2} = \frac{55.9 \times 10^3 \text{ J/mol}}{8.314 \text{ J/mol} \cdot \text{K}} \left( \frac{1}{373 \text{ K}} - \frac{1}{298 \text{ K}} \right)
\]

\[
\frac{1.0 \times 10^{-14}}{K_2} = e^{-4.537}
\]

\[
K_2 = 9.3 \times 10^{-13}
\]

We substitute into the equilibrium constant expression for the ionization of water to solve for $[H^+]$ and then pH.

\[
K_2 = [H^+][OH^-]
\]

\[
9.3 \times 10^{-13} = x^2
\]

\[
x = [H^+] = 9.6 \times 10^{-7} \text{ M}
\]

\[
\text{pH} = -\log(9.6 \times 10^{-7}) = 6.02
\]

Note that the water is not acidic at 100°C because $[H^+] = [OH^-]$.

15.149 To calculate the $K_a$ value of the acid, the molarity of the solution must be determined. The temperature, pressure, and density given will allow the calculation of the molar mass of the acid. Once the molar mass is known, the concentration of the acid can be determined. Knowing the concentration and the pH of the solution, the $K_a$ value can then be calculated.

First, we calculate the moles of HA using the ideal gas equation, and then we calculate the molar mass of HA.

\[
n = \frac{PV}{RT} = \frac{(0.982 \text{ atm})(1.00 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm} / \text{mol} \cdot \text{K})(273 + 28) \text{ K}} = 0.0397 \text{ mol}
\]

\[
molar \ mass = \frac{g \ of \ substance}{mol \ of \ substance} = \frac{1.16 \ g}{0.0397 \ mol} = 29.2 \ g/mol
\]

The molarity of the acid solution is:

\[
M = \frac{\text{mol}}{L} = \frac{2.03 \ g \times \frac{1 \ \text{mol \ HA}}{29.2 \ g}}{1.00 \ \text{L}} = 0.0695 \ \text{M}
\]

<table>
<thead>
<tr>
<th>Initial ($M$)</th>
<th>0.0695</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change($M$)</td>
<td>$-x$</td>
</tr>
<tr>
<td>Equil. ($M$)</td>
<td>0.0695 $-x$</td>
</tr>
</tbody>
</table>

\[
K_a = \frac{[H^+][A^-]}{[HA]} = \frac{x^2}{0.0695 - x}
\]

The concentration of $H^+$, which equals $x$, can be determined from the pH of the solution.

\[
[H^+] = x = 10^{-\text{pH}} = 10^{-5.22} = 6.03 \times 10^{-6}
\]
\[ K_a = \frac{x^2}{0.0695 - x} = \frac{(6.03 \times 10^{-6})^2}{0.0695 - (6.03 \times 10^{-6})} \]

\[ K_a = 5.2 \times 10^{-10} \]

**15.150** The reactions are:

\[ \text{P}_4(\text{s}) + 5\text{O}_2(\text{g}) \rightarrow \text{P}_4\text{O}_{10}(\text{s}) \]
\[ \text{P}_4\text{O}_{10}(\text{s}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow 4\text{H}_3\text{PO}_4(\text{aq}) \]

First, we calculate the moles of \( \text{H}_3\text{PO}_4 \) produced. Next, we can calculate the molarity of the phosphoric acid solution. Finally, we can determine the pH of the \( \text{H}_3\text{PO}_4 \) solution (a weak acid).

\[
10.0 \text{ g P}_4 \times \frac{1 \text{ mol P}_4}{123.9 \text{ g P}_4} \times \frac{1 \text{ mol P}_4}{1 \text{ mol P}_4} \times \frac{4 \text{ mol H}_3\text{PO}_4}{1 \text{ mol P}_4\text{O}_{10}} = 0.323 \text{ mol H}_3\text{PO}_4
\]

Molarity = \( \frac{0.323 \text{ mol}}{0.500 \text{ L}} = 0.646 \text{ M} \)

We set up the ionization of the weak acid, \( \text{H}_3\text{PO}_4 \). The \( K_a \) value for \( \text{H}_3\text{PO}_4 \) can be found in Table 15.5 of the text.

\[
\text{H}_3\text{PO}_4(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{H}_2\text{PO}_4^-(\text{aq})
\]

<table>
<thead>
<tr>
<th>Initial (M)</th>
<th>Change (M)</th>
<th>Equilibrium (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.646</td>
<td>0</td>
<td>0.646 - x +x</td>
</tr>
</tbody>
</table>

\[
K_a = \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = \frac{(x)(x)}{(0.646 - x)}
\]

\[ x^2 + 7.5 \times 10^{-3}x - 4.85 \times 10^{-3} = 0 \]

Solving the quadratic equation,

\[ x = 0.066 \text{ M} = [\text{H}^+] \]

Following the procedure in Problem 15.118 and the discussion in Section 15.8 of the text, we can neglect the contribution to the hydronium ion concentration from the second and third ionization steps. Thus,

\[ \text{pH} = -\log(0.066) = 1.18 \]

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**Answers to Review of Concepts**

Section 15.1 (p. 661) \( \text{(b)} \)
Section 15.4 (p. 670) \( \text{(a) (i) H}_2\text{O} > \text{H}^+, \text{NO}_3^- > \text{OH}^- \). (ii) \( \text{H}_2\text{O} > \text{HF} > \text{H}^+, \text{F}^- > \text{OH}^- \). \( \text{(b) (i) H}_2\text{O} > \text{NH}_3 > \text{NH}_4^+, \text{OH}^- > \text{H}^+. \) (ii) \( \text{H}_2\text{O} > \text{K}^+, \text{OH}^- > \text{H}^+ \). \)
Section 15.7 (p. 681) \( \text{CN}^- \)
Section 15.8 (p. 685) \( \text{(c)} \)
Section 15.10 (p. 694) \( \text{(a) C}^- \). (b) \( \text{B}^- < \text{A}^- < \text{C}^- \).