17. ACID-BASE EQUILIBRIA

### Solutions to Exercises

*Note on significant figures:* If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multiple-step problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

17.1 Abbreviate the formula of lactic acid as HL. To solve, assemble a table of starting, change, and equilibrium concentrations.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HL</th>
<th>$H_2O$</th>
<th>$H_3O^+$</th>
<th>$L^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Starting</strong></td>
<td>0.025</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td><strong>Change</strong></td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
<td></td>
</tr>
<tr>
<td><strong>Equilibrium</strong></td>
<td>0.025-x</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

Substituting into the equilibrium-constant equation gives

$$K_a = \frac{[H_3O^+][L^-]}{[HL]} = \frac{(x)^2}{(0.025 - x)}$$

The value of $x$ equals the value of the molarity of the $H_3O^+$ ion, which can be obtained from the pH:

$$[H_3O^+] = \text{antilog (-pH)} = \text{antilog (-2.75)} = 0.00178 \text{ M}$$

(continued)
Substitute this value for \( x \) into the equation to get

\[
K_a = \frac{(x)^2}{(0.025 - x)} = \frac{(0.00178)^2}{(0.025 - 0.00178)} = 1.36 \times 10^{-4} = 1.4 \times 10^{-4}
\]

The degree of ionization is

\[
\text{Degree of ionization} = \frac{0.00178}{0.025} = 0.071
\]

### 17.2

To solve, assemble a table of starting, change, and equilibrium concentrations. Use \( \text{HAc} \) as the symbol for acetic acid.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HAc</th>
<th>H(_2)O</th>
<th>H(_3)O(^+) + Ac(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.10</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.10 - x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

Now, substitute these concentrations and the value of \( K_a \) into the equilibrium-constant equation for acid ionization:

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{Ac}^-]}{[\text{HAc}]} = \frac{(x)^2}{(0.10 - x)} = 1.7 \times 10^{-5}
\]

Solve the equation for \( x \), assuming \( x \) is much smaller than 0.10, so \((0.10 - x) \approx 0.10\).

\[
\frac{(x)^2}{(0.10)} \approx 1.7 \times 10^{-5}
\]

\[
x^2 \approx 1.7 \times 10^{-5} \times 0.10 = 1.7 \times 10^{-6}
\]

\[
x \approx 0.00130 \text{ M}
\]

Check to make sure the assumption that \((0.10 - x) \approx 0.10\) is valid:

\[
0.10 - 0.00130 = 0.0987, = 0.10 \quad \text{(to two significant figures)}
\]

The concentrations of hydronium ion and acetate ion are

\[
[\text{H}_3\text{O}^+] = [\text{Ac}^-] = x = 0.0013 = 1.3 \times 10^{-3} \text{ M}
\]

(continued)
The pH of the solution is

\[ \text{pH} = -\log [H_3O^+] = -\log (0.00130) = 2.884 = 2.88 \]

The degree of ionization is

\[ \text{Degree of ionization} = \frac{0.00130}{0.10} = 0.013 \]

Abbreviate the formula for pyruvic acid as HPy. To solve, assemble a table of starting, change, and equilibrium concentrations:

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HPy</th>
<th>( H_2O )</th>
<th>( H_3O^+ )</th>
<th>( Py^- )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.0030</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.0030 - x</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

Substitute the equilibrium concentrations and the value of \( K_a \) into the equilibrium-constant equation to get

\[ K_a = \frac{[H_3O^+][Py^-]}{[HPy]} = \frac{(x)^2}{(0.0030 - x)} = 1.4 \times 10^{-4} \]

Note that the concentration of acid divided by \( K_a \) is \( 0.0030/1.4 \times 10^{-4} = 21 \), which is considerably smaller than 100. Thus, you can expect that \( x \) cannot be ignored compared with 0.0030. The quadratic formula must be used. Rearrange the preceding equation to put it into the form \( ax^2 + bx + c = 0 \).

\[ x^2 + 1.4 \times 10^{-4} x - 4.20 \times 10^{-7} = 0 \]

Substitute into the quadratic formula to get

\[ x = \frac{-1.4 \times 10^{-4} \pm \sqrt{(1.4 \times 10^{-4})^2 + 4(4.20 \times 10^{-7})}}{2} \]

\[ = \frac{-1.4 \times 10^{-4} \pm 1.303 \times 10^{-3}}{2} \]

Using the positive root: \( x = [H_3O^+] = 5.81 \times 10^{-4} \, \text{M} \). Now you can calculate the pH.

\[ \text{pH} = -\log [H_3O^+] = -\log (5.82 \times 10^{-4}) = 3.2350 = 3.24 \]
17.4 To solve, note that $K_{a1} = 1.3 \times 10^{-2} > K_{a2} = 6.3 \times 10^{-3}$, and hence the second ionization and $K_{a2}$ can be ignored. Assemble a table of starting, change, and equilibrium concentrations:

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>H$_2$SO$_3$ + H$_2$O</th>
<th>H$_3$O$^+$ + HSO$_3^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.25</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.25 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

Substitute into the equilibrium-constant equation for the first ionization.

$$K_{a1} = \frac{[H_3O^+][HSO_3^-]}{[H_2SO_3]} = \frac{(x)^2}{(0.25 - x)} = 1.3 \times 10^{-2} = 0.013$$

This gives $x^2 + 0.013x - 0.00325 = 0$

Note that the concentration of acid divided by $K_a$ is $0.25/0.013 = 19$, which is considerably smaller than 100. Thus, you can expect that $x$ cannot be ignored compared with 0.25. Reorganize the above equilibrium-constant expression into the form $ax^2 + bx + c = 0$, and substitute for $a$, $b$, and $c$ in the quadratic formula.

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Using the positive root, $x = [H_3O^+] = 0.05087$ M.

$$pH = -\log (0.05087) = 1.293$$

To calculate [SO$_3^{2-}$], which will be represented by $y$, use the second ionization. Assume the starting concentrations of $H_3O^+$ and HSO$_3^-$ are those from the first equilibrium.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HSO$_3^-$ + H$_2$O</th>
<th>H$_3$O$^+$ + SO$_3^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.05087</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-y</td>
<td>+y</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.0508 - y</td>
<td>0.0508 + y</td>
</tr>
</tbody>
</table>

(continued)
Now, substituting into the $K_{a2}$ expression for the second ionization.

$$K_{a2} = \frac{[H_3O^+][SO_3^{2-}]}{[HSO_3^-]} = \frac{(0.0508 + y)(y)}{(0.0508 - y)} = 6.3 \times 10^{-8}$$

Assuming $y$ is much smaller than 0.0508, note that the $(0.0508 + y)$ cancels the $(0.0508 - y)$ term leaving $y \approx K_{a2}$, or

$$y = [SO_3^{2-}] = 6.3 \times 10^{-8} \text{ M}$$

17.5 First, convert the pH to pOH, and then to $[OH^-]$:

$$pOH = 14.00 - \text{pH} = 14.00 - 9.84 = 4.16$$

$$[OH^-] = \text{antilog} (-4.16) = 6.92 \times 10^{-5} \text{ M}$$

Using the symbol Qu for quinine, assemble a table of starting, change, and equilibrium concentrations.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>Qu + H$_2$O</th>
<th>HQu$^+$ + OH$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.0015</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.0015 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

Note $x = 6.92 \times 10^{-5}$. Substitute into the equilibrium-constant equation to get

$$K_b = \frac{[HQ^+][OH^-]}{[Qu]} = \frac{(x)^2}{(0.0015 - x)} = \frac{(6.92 \times 10^{-5})^2}{(0.0015 - 6.92 \times 10^{-5})}$$

$$= 3.346 \times 10^{-6} = 3.3 \times 10^{-6}$$

17.6 Assemble a table of starting, change, and equilibrium concentrations:

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>NH$_3$ + H$_2$O</th>
<th>NH$_4^+$ + OH$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.20</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
</tbody>
</table>
| Equilibrium| 0.20 - x        | x                 | x                 | (continued)
Assume $x$ is small enough to ignore compared with 0.20. Substitute into the equilibrium-constant equation to get:

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(x)^2}{(0.20 - x)} \approx \frac{(x)^2}{(0.20)} = 1.8 \times 10^{-6}$$

Solving for $x$ gives

$$x^2 = (0.20) \times 1.8 \times 10^{-6} = 3.6 \times 10^{-6}$$

$$x = [\text{OH}^-] \approx 1.89 \times 10^{-3} \text{ M} \text{ (Note $x$ is negligible compared to 0.20.)}$$

Now calculate the hydronium ion concentration.

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{1.89 \times 10^{-3}} = 5.29 \times 10^{-12} = 5.3 \times 10^{-12} \text{ M}$$

17.7  a. Acidic. $\text{NH}_4\text{NO}_3$ is the salt of a weak base (NH$_4$OH) and a strong acid (HNO$_3$), so a solution of $\text{NH}_4\text{NO}_3$ is acidic because of the hydrolysis of NH$_4^+$.

b. Neutral. KNO$_3$ is the salt of a strong base (KOH) and a strong acid (HNO$_3$), so a solution of $\text{NH}_4\text{NO}_3$ is neutral because none of the ions hydrolyze.

c. Acidic. Al(NO$_3$)$_3$ is the salt of a weak base [Al(OH)$_3$] and a strong acid (HNO$_3$), so a solution of Al(NO$_3$)$_3$ is acidic because of the hydrolysis of Al$^{3+}$.

17.8  a. Calculate $K_b$ of the F$^-$ ion from the $K_a$ of its conjugate acid, HF:

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}} = 1.47 \times 10^{-11} = 1.5 \times 10^{-11}$$

b. Calculate $K_a$ of C$_6$H$_5$NH$_3^+$ from $K_b$ of its conjugate base, C$_6$H$_5$NH$_2$:

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.2 \times 10^{-10}} = 2.38 \times 10^5 = 2.4 \times 10^5$$
17.9  Assemble the usual table, writing HBen for benzoic acid and Ben\(^-\) for the benzoate ion. Let 0.015 - x equal the equilibrium concentration of the benzoate anion.

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>Ben(^-) + H(_2)O</th>
<th>HBen + OH(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.015</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.015 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

Calculate \(K_b\) for the Benzoate ion from \(K_a\) for HBen.

\[
K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.3 \times 10^{-5}} = 1.58 \times 10^{-10}
\]

Substitute into the equilibrium-constant equation. Assume x is much smaller than 0.015.

\[
K_b = \frac{[\text{HBen}][\text{OH}^-]}{[\text{Ben}^-]} = \frac{(x)^2}{(0.015 - x)} = 1.58 \times 10^{-10}
\]

\[
x = [\text{HBen}] = [\text{OH}^-] \approx 1.539 \times 10^{-6} \text{ M} \quad (x \text{ is negligible compared to } 0.015.)
\]

Thus, the concentration of benzoic acid in the solution is 1.5 \times 10^{-6} M. The pH is

\[
pOH = -\log [\text{OH}^-] = -\log (1.539 \times 10^{-6}) = 5.812
\]

\[
pH = 14.00 - 5.812 = 8.188 = 8.19
\]

17.10  Assemble the usual table, using starting \([\text{H}_3\text{O}^+] = 0.20 \text{ M}\) from 0.20 M HCl and letting HFo symbolize HCHO\(_2\).
Assume $x$ is negligible compared to 0.10 M and 0.20 M, and substitute into the equilibrium-constant equation to get

$$K_a = \frac{[H_3O^+] [Fo^-]}{[HFo]} = \frac{(0.20 + x)(x)}{(0.10 - x)} \approx \frac{(0.20)(x)}{(0.10)} = 1.7 \times 10^{-4}$$

$$x = [Fo] = 8.50 \times 10^{-5} = 8.5 \times 10^{-5} \text{ M}$$

The degree of ionization is

$$\text{Degree of ionization} = \frac{8.50 \times 10^{-5}}{0.10} = 8.50 \times 10^{-4} = 8.5 \times 10^{-4}$$

17.11 Assemble the usual table, using a starting $[\text{CHO}_2^-]$ of 0.018 M from 0.018 M NaCHO$_2$ and symbolizing HCHO$_2$ as HFo and the CHO$_2^-$ anion as Fo$^-$. 

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HFo + H$_2$O</th>
<th>H$_3$O$^+$ + Fo$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.025</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.025 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

Substitute into the equilibrium-constant equation. Assume $x$ is negligible compared to 0.025 M and 0.018 M.

$$K_a = \frac{[H_3O^+] [Fo^-]}{[HFo]} = \frac{(0.018 + x)(x)}{(0.025 - x)} \approx \frac{(0.018)(x)}{(0.025)} = 1.7 \times 10^{-4}$$

$$x = [H_3O^+] = 2.36 \times 10^{-4} \text{ M}$$

The pH can now be calculated.

$$\text{pH} = -\log [H_3O^+] = -\log (2.36 \times 10^{-4}) = 3.627 = 3.63$$

17.12 Let HOAc represent HC$_2$H$_5$O$_2$ and OAc$^-$ represent C$_2$H$_3$O$_2^-$. The total volume of the buffer is

$$\text{Total volume} = 30.0 \text{ mL} + 70.0 \text{ mL} = 100.0 \text{ mL} = 0.1000 \text{ L}$$

The moles of HOAc and OAc$^-$ in the buffer are

$$\text{mol HOAc} = 0.15 \text{ M} \times 0.0300 \text{ L} = 0.00450 \text{ mol}$$

$$\text{mol OAc}^- = 0.0700 \text{ M} \times 0.0700 \text{ L} = 0.0140 \text{ mol}$$

(continued)
The concentrations of HOAc and OAc\textsuperscript{-} in the buffer are

\[ [\text{HOAc}] = \frac{0.00450 \text{ mol}}{0.1000 \text{ L}} = 0.0450 \text{ M} \]

\[ [\text{OAc}^-] = \frac{0.0140 \text{ mol}}{0.1000 \text{ L}} = 0.140 \text{ M} \]

Now, substitute these starting concentrations into a table.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HOAc</th>
<th>H\textsubscript{2}O</th>
<th>H\textsuperscript{3}O\textsuperscript{+}</th>
<th>OAc\textsuperscript{-}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.0450</td>
<td>0</td>
<td>0.140</td>
<td></td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.0450 - x</td>
<td>x</td>
<td>0.140 + x</td>
<td></td>
</tr>
</tbody>
</table>

Substitute the equilibrium concentrations into the equilibrium-constant expression; then assume \( x \) is negligible compared to the starting concentrations of both HOAc and OAc\textsuperscript{-}.

\[ K_a = \frac{[\text{H}_3\text{O}^+] [\text{OAc}^-]}{[\text{HOAc}]} = \frac{(0.140 + x)(x)}{(0.0450 - x)} \]

\[ x = [\text{H}_3\text{O}^+] \approx 5.46 \times 10^{-6} \text{ M} \]

You can now calculate the pH.

\[ \text{pH} = - \log [\text{H}_3\text{O}^+] = - \log (5.46 \times 10^{-6}) = 5.262 = 5.26 \]

17.13 First, do the stoichiometric calculation. From Exercise 17.11, [HFO\textsubscript{2}] = 0.025 M and [Fo\textsuperscript{-}] = 0.018 M. In one liter of buffer, there are 0.025 mol HFO\textsubscript{2} and 0.018 mol Fo\textsuperscript{-}. The moles of OH\textsuperscript{-} (equal to moles NaOH) added are:

\[ (0.10 \text{ M}) \times 0.0500 \text{ L} = 0.00500 \text{ mol OH}^- \]

The total volume of solution is:

\[ \text{Total volume} = 1 \text{ L} + 0.0500 \text{ L} = 1.0500 \text{ L} \]

After reaction with the OH\textsuperscript{-}, the moles of HFO\textsubscript{2} and Fo\textsuperscript{-} remaining in the solution are:

\[ \text{Mol HFO} = (0.025 - 0.00500) \text{ mol} = 0.0200 \text{ mol} \]

\[ \text{Mol Fo}^- = (0.018 + 0.00500) \text{ mol} = 0.0230 \text{ mol} \]

(continued)
The concentrations are

\[
[\text{HFo}] = \frac{0.0200 \text{ mol}}{1.0500 \text{ L}} = 0.0190 \text{ M}
\]

\[
[\text{Fo}^-] = \frac{0.0230 \text{ mol}}{1.0500 \text{ L}} = 0.0219 \text{ M}
\]

Now account for the ionization of HFo to Fo\(^-\) at equilibrium by assembling the usual table.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HFo + H(_2)O</th>
<th>H(_3)O(^+) + Fo(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.0190</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.0190 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

Assume x is negligible compared to 0.0190 M and 0.0219 M, and substitute into the equilibrium-constant equation to get

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{Fo}^-]}{[\text{HFo}]} = \frac{(0.0219 + x)(x)}{(0.0190 - x)} \approx \frac{(0.0219)(x)}{(0.0190)} = 1.7 \times 10^{-4}
\]

\[
x = [\text{H}_3\text{O}^+] = 1.47 \times 10^{-4} \text{ M}
\]

Now, calculate the pH.

\[
pH = -\log [\text{H}_3\text{O}^+] = -\log (1.47 \times 10^{-4}) = 3.831 = 3.83
\]

17.14 All the OH\(^-\) reacts with the H\(_3\)O\(^+\) from HCl. Calculate the stoichiometric amounts of OH\(^-\) and H\(_3\)O\(^+\).

\[
\text{Mol H}_3\text{O}^+ = (0.10 \text{ mol/L}) \times 0.025 \text{ L} = 0.0025 \text{ mol}
\]

\[
\text{Mol OH}^- = (0.10 \text{ mol NaOH/L}) \times 0.015 \text{ L} = 0.0015 \text{ mol}
\]

The total volume of solution is

\[
\text{Total volume} = 0.025 \text{ L} + 0.015 \text{ L} = 0.040 \text{ L}
\]

(continued)
Subtract the mol of OH\(^-\) from the mol of H\(_3\)O\(^+\), and divide by the total volume to get the concentration of H\(_3\)O\(^+\).

\[
\text{Mol H}_3\text{O}^+ \text{ left } = (0.0025 - 0.0015) \text{ mol} = 0.0010 \text{ mol}
\]

\[
[\text{H}_3\text{O}^+] = \frac{0.0010 \text{ mol}}{0.040 \text{ L}} = 0.0250 \text{ M}
\]

Now calculate the pH.

\[
pH = -\log [\text{H}_3\text{O}^+] = -\log (0.0250) = 1.602 = 1.6
\]

17.15 At the equivalence point, the solution will contain NaF. The molar amount of F\(^-\) is equal to the molar amount of HF and is calculated as follows.

\[
(0.10 \text{ mol HF/L}) \times 0.025 \text{ L} = 0.0025 \text{ mol F}^-
\]

The volume of 0.15 M NaOH added and the total volume of solution are calculated next.

\[
\text{Volume NaOH} = \frac{M_{\text{acid}}V_{\text{acid}}}{M_{\text{base}}} = \frac{(0.10 \text{ M})(25 \text{ mL})}{0.15} = 16.6 \text{ mL}
\]

\[
\text{Total volume} = 25 \text{ mL} + 16.6 \text{ mL} = 41.6 \text{ mL} = 0.0416 \text{ L}
\]

The concentration of F\(^-\) at the equivalence point can now be calculated.

\[
[F^-] = \frac{0.0025 \text{ mol}}{0.0416 \text{ L}} = 0.0600 \text{ M}
\]

Next, consider the hydrolysis of F\(^-\). Start by calculating the hydrolysis constant of F\(^-\) from the \(K_a\) of its conjugate acid, HF.

\[
K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}} = 1.47 \times 10^{-11}
\]

Now, assemble the usual table of concentrations, assume x is negligible compared to 0.0600, and calculate [OH\(^-\)].

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>F(^-) + H(_2)O</th>
<th>HF + OH(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.0600</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.0600 - x</td>
<td>x</td>
</tr>
</tbody>
</table>
Substitute into the equilibrium-constant equation to get

\[ K_b = \frac{[HF][OH^-]}{[F^-]} = \frac{(x)^2}{(0.0600 - x)} \approx \frac{(x)^2}{(0.0600)} = 1.47 \times 10^{-11} \]

\[ x = [OH^-] = 9.39 \times 10^{-7} \text{ M} \]

Finally, calculate the pOH and then the pH.

\[ \text{pOH} = - \log [OH^-] = - \log (9.39 \times 10^{-7}) = 6.026 \]

\[ \text{pH} = 14.00 - 6.026 = 7.974 = 7.97 \]

17.16 At the equivalence point, the solution will contain NH\(_4^+\). The molar amount of NH\(_4^+\) is equal to the molar amount of NH\(_3\) and is calculated as follows.

\[ (0.20 \text{ mol NH}_3/\text{L}) \times 0.035 \text{ L} = 0.00700 \text{ mol NH}_4^+ \]

The volume of 0.12 M HCl added and the total volume of solution are calculated next.

\[ \text{Volume HCl} = \frac{M_{\text{base}} V_{\text{base}}}{M_{\text{acid}}} = \frac{(0.20 \text{ M})(35 \text{ mL})}{0.12 \text{ M}} = 58.3 \text{ mL} \]

\[ \text{Total volume} = 35 \text{ mL} + 58.3 \text{ mL} = 93.3 \text{ mL} = 0.0933 \text{ L} \]

The concentration of NH\(_4^+\) at the equivalence point can now be calculated.

\[ [\text{NH}_4^+] = \frac{0.00700 \text{ mol}}{0.0933 \text{ L}} = 0.0750 \text{ M} \]

Next, consider the hydrolysis of NH\(_4^+\). Start by calculating the hydrolysis constant of NH\(_4^+\) from the K\(_b\) of its conjugate base, NH\(_3\).

\[ K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{5.56 \times 10^{-10}} = 5.56 \times 10^{-14} \]

Now, assemble the usual table of concentrations, assume x is negligible compared to 0.0750, and calculate [H\(_3\)O\(^+\)].

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>(\text{NH}_4^+ + \text{H}_2\text{O})</th>
<th>(\text{NH}_3 + \text{H}_3\text{O}^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.0750</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.0750 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

(continued)
ACID-BASE EQUILIBRIA

Substitute into the equilibrium-constant equation to get

\[ K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]^2} = \frac{(x)^2}{(0.0750 - x)} \approx \frac{(x)^2}{(0.0750)} = 5.56 \times 10^{-10} \]

\[ x = [\text{H}_3\text{O}^+] = 6.46 \times 10^{-6} \text{ M} \]

Finally, calculate the pH.

\[ \text{pH} = - \log [\text{H}_3\text{O}^+] = - \log (6.46 \times 10^{-6}) = 5.19 \]

Answers to Concept Checks

17.1 You would probably guess the pH's of the acid solutions depend on their respective \( K_a \)'s; the larger the \( K_a \), the greater the acidity or the lower the pH. We can put this on a firm basis by looking at the acid ionization equilibrium. An acid, HA, ionizes in water as follows:

\[ \text{HA}(aq) + \text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{O}^+(aq) + \text{A}^-(aq) \]

The corresponding equilibrium constant, \( K_a \), equals \( [\text{H}_3\text{O}^+][\text{A}^-]/[\text{HA}] \). When you start with the same concentration of HA, the concentration of HA in solution is essentially the same for each acid. Also, \( [\text{H}_3\text{O}^+] = [\text{A}^-] \). This means \( K_a \) is proportional to \( [\text{H}_3\text{O}^+]^2 \), or \( \text{pH} = - \log [\text{H}_3\text{O}^+] \) is proportional to - log \( K_a \). Therefore, the larger the \( K_a \), the lower the pH. As an example, compare two acids, one with \( K_a = 10^{-5} \) and the other with \( K_a \) equal to \( 10^{-4} \). The corresponding - log \( K_a \) values are five and four, respectively. The second acid (the one with the greater \( K_a \)) would have the lower pH. If you look at Table 17.1, the acid with the largest \( K_a \) of those listed in the problem statement is HF. So the ranking from lowest to highest pH is: HCN < HC\(_2\)H\(_3\)O\(_2\) < HNO\(_2\), HF.

17.2 By examining the contents of the beaker, you see there are three different species present, the ions BH\(^+\) and OH\(^-\) as well as unreacted B molecules. This represents a weak base. The ionization reaction for this base is

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

17.3 Ammonia, NH\(_3\), is a weak base; the other compounds are salts. You can decide the acidity or basicity of salt solutions by noting whether the corresponding acid and base are strong or weak. For example, NH\(_4\)Br is the salt of a weak base (NH\(_3\)) and a strong acid (HBr), so the salt is acidic. Similarly, NaF is basic (it is the salt of a strong base, NaOH, and a weak acid, HF). NaCl is neutral. This means two of the solutions are basic (NH\(_3\) and NaF), one solution is neutral (NaCl), and the other is acidic (NH\(_4\)Br). Although a salt might be as basic as NH\(_3\), this occurs only when the acid from which the salt formed is quite weak (for example, NaCN is quite basic). So, the solution with highest pH is 0.1 M NH\(_3\) (a), and the solution of lowest pH is 0.1 M NH\(_4\)Br (b).
17.4 The amount of any substance in a solution is proportional to the volume times molarity. Let’s look at each solution:

a. The 1.5 mL of 1 M HCl just neutralizes 15 mL of 0.1 M NaOH, giving a solution of NaCl. Thus, the pH of the original solution changes from very basic to neutral (pH = 7) after the addition of HCl.

b. The solution of acetic acid changes from weakly acidic to strongly acidic with the addition of HCl.

c. Equal amounts of NaOH and HC$_2$H$_3$O$_2$ in the original solution exactly neutralize each other to produce the salt, NaC$_2$H$_3$O$_2$, which is slightly basic. The addition of the strong acid, HCl, gives an acidic solution.

d. The 30 mL of NaOH reacts with 30 mL of HC$_2$H$_3$O$_2$ to give the salt, NaC$_2$H$_3$O$_2$, leaving an equal amount of the corresponding acid, HC$_2$H$_3$O$_2$. The result is a buffer solution. The addition of HCl to the buffer does not change the pH appreciably. (This is true as long as the amount of added acid does not overwhelm the capacity of the buffer. In this case, it does not. The amount of acid and base conjugates in the buffer is twice the amount of added acid.)

Only d does not change appreciably in pH.

17.5 a. When two formula units of NaOH are added to the beaker on the left, a reaction occurs consuming two HA molecules and forming two A\(^-\) ions. This results in a solution with two HA molecules and five A\(^-\) ions, which is depicted in beaker Y.

b. Since the original buffer contains three A\(^-\) ions, three HCl molecules could be added before the buffer capacity would be exceeded.

c. The beaker would contain seven HA molecules. In addition, the extra HCl molecules would dissociate into H$_3$O\(^+\) and Cl\(^-\) ions. This could be represented by the following diagram:
Answers to Review Questions

17.1 The equation is

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

The equilibrium-constant expression is

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

17.2 HCN is the weakest acid. Its \( K_a \) of \( 4.9 \times 10^{-10} \) is < \( K_a \) of \( 1.7 \times 10^{-5} \) of HC\(_2\)H\(_3\)O\(_2\); HClO\(_4\) is a strong acid, of course.

17.3 Both methods involve direct measurement of the concentrations of the hydronium ion and the anion of the weak acid and calculation of the concentration of the un-ionized acid. All concentrations are substituted into the \( K_a \) expression to obtain a value for \( K_a \). In the first method, the electrical conductivity of a solution of the weak acid is measured. The conductivity is proportional to the concentration of the hydronium ion and anion. In the second method, the pH of a known starting concentration of weak acid is measured. The pH is converted to [\( \text{H}_3\text{O}^+ \)], which will be equal to the [anion].

17.4 The degree of ionization of a weak acid decreases as the concentration of the acid added to the solution increases. Compared to low concentrations, at high concentrations, there is less water for each weak acid molecule to react with as the weak acid ionizes:

\[ \text{HA(aq) + H}_2\text{O(l)} \rightarrow \text{H}_3\text{O}^+(aq) + \text{A}^-(aq) \]

17.5 You can neglect x if \( C_u/K \geq 100 \). In this case, \( C_u/K = \left[ (0.0010 \text{ M} \div 6.8 \times 10^{-4} \right) = 1.47 \), which is significantly less than 100, and x cannot be neglected in the \((0.0010 - x)\) term. This says the degree of ionization is significant.

17.6 The ionization of the first \( \text{H}_3\text{O}^+ \) is

\[ \text{H}_2\text{PO}_4^-(aq) + \text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{O}^+(aq) + \text{HPO}_4^{2-}(aq) \]

The equilibrium-constant expression is

\[ K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \]

(continued)
The ionization of the second $H_3O^+$ is

$$HPHO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PHO_3^{2-}(aq)$$

The equilibrium-constant expression is

$$K_{a2} = \frac{[H_3O^+][PHO_3^{2-}]}{[HPHO_3^-]}$$

17.7 As shown in Example 17.4, the concentration of a -2 anion of a polyprotic acid in a solution of the diprotic acid alone is approximately equal to the value of $K_{a2}$. For oxalic acid, begin by noting that the $[H_3O^+] \simeq [HC_2O_4^-]$. Then, substitute $[H_3O^+]$ for the $[HC_2O_4^-]$ term in the equilibrium-constant equation for $K_{a2}$:

$$K_{a2} = \frac{[H_3O^+][C_2O_4^{2-}]}{[HC_2O_4^-]} \simeq \frac{[H_3O^+][C_2O_4^{2-}]}{[H_3O^+]^2} = [C_2O_4^{2-}]$$

17.8 The balanced chemical equation for the ionization of aniline is

$$C_6H_5NH_2(aq) + H_2O(l) \rightleftharpoons C_6H_5NH_3^+(aq) + OH^-(aq)$$

The equilibrium-constant equation, or expression for $K_b$, is defined without an $[H_2O]$ term; this term is included in the value for $K_b$ as discussed in Section 17.3. The expression is

$$K_b = \frac{[C_6H_5NH_3^+][OH^-]}{[C_6H_5NH_2]}$$

17.9 First, decide whether any of the three is a strong base or not. Because all the molecules are among the nitrogen-containing weak bases listed in Table 17.2, none is a strong base. Next, recognize the greater the $[OH^-]$, the stronger the weak base. Because $[OH^-]$ can be calculated from the square root of the product of $K_b$ and concentration, the larger the $K_b$, the greater the $[OH^-]$ and the stronger the weak base. Thus, $CH_3NH_2$ is the strongest of these three weak bases because its $K_b$ is the largest.

17.10 Anilinium chloride is not a weak base nor a weak acid but a salt that contains the anilinium ion, $C_6H_5NH_3^+$, and the $Cl^-$ ion. The chloride ion does not hydrolyze because it could only form $HCl$, a strong acid. The anilinium ion does hydrolyze as follows:

$$C_6H_5NH_3^+ + H_2O(l) \rightleftharpoons C_6H_5NH_2 + H_3O^+$$

(continued)
The equilibrium-constant expression for this reaction is

$$K_a = \frac{[C_6H_5NH_2][H_3O^+]}{[C_6H_5NH_3^+]}$$

 Obtain the value for $K_a$ by calculating the value of $K_w/K_b$, where $K_b$ is the ionization constant for aniline, $C_6H_5NH_2$.

17.11 The common-ion effect is the shift in an ionic equilibrium caused by the addition of a solute that furnishes an ion that is common to, or takes part in, the equilibrium. If the equilibrium involves the ionization of a weak acid, then the common ion is usually the anion formed by the ionization of the weak acid. If the equilibrium involves the ionization of a weak base, then the common ion is usually the cation formed by the ionization of the weak base. An example is the addition of $F^-$ ion (as NaF) to a solution of the weak acid HF, which ionizes as shown below:

$$HF(aq) + H_2O(l) \rightarrow H_3O^+(aq) + F^-(aq)$$

The effect of adding $F^-$ to this equilibrium is that it causes a shift in the equilibrium composition to the left. The additional $F^-$ reacts with $H_3O^+$, lowering its concentration and raising the concentration of HF.

17.12 The addition of $CH_3NH_3Cl$ to 0.10 M $CH_3NH_2$ exerts a common-ion effect that causes the equilibrium below to exhibit a shift in composition to the left:

$$CH_3NH_2(aq) + H_2O(l) \rightarrow CH_3NH_3^+(aq) + OH^-(aq)$$

This shift lowers the equilibrium concentration of the $OH^-$ ion, which increases the $[H_3O^+]$. An increase in $[H_3O^+]$ lowers the pH below 11.8. The shift in composition to the left occurs according to Le Chatelier’s principle, which states that a system shifts to counteract any change in composition.

17.13 A buffer is most often a solution of a mixture of two substances that is able to resist pH changes when limited amounts of acid or base are added to it. A buffer must contain a weak acid and its conjugate (weak) base. Strong acids and/or bases cannot form effective buffers because a buffer acts by converting $H_3O^+$ (strong acid) to the un-ionized (weak) buffer acid and by converting $OH^-$ (strong base) to the un-ionized (weak) buffer base. An example of a buffer pair is a mixture of $H_2CO_3$ and $HCO_3^-$, the principal buffer in the blood.

17.14 The capacity of a buffer is the amount of acid or base with which the buffer can react before exhibiting a significant pH change. (A significant change in blood pH might mean 0.01-0.02 pH units; for other systems a significant change might mean 0.5 pH units.) A high-capacity buffer might be of the type discussed for Figure 17.10: one mol of buffer acid and one mol of buffer base. A low-capacity buffer might involve quite a bit less than these amounts: 0.01-0.05 mol of buffer acid and buffer base.
17.15 The pH of a weak base before titration is relatively high, around pH 10 for a 0.1 M solution of a typical weak base. As a strong acid titrant is added, the [OH\(^-\)] decreases, and the pH decreases. At 50 percent neutralization, a buffer of equal amounts of buffer acid and base is formed. The [OH\(^-\)] equals the K\(_b\), or the pOH equals the pK\(_b\). At the equivalence point, the pH is governed by the hydrolysis of the salt of the weak base formed and is usually in the pH 4-6 region. After the equivalence point, the pH decreases to a level just greater than the pH of the strong acid titrant.

17.16 If the pH is 8.0, an indicator that changes color in the basic region would be needed. Of the indicators mentioned in the text, phenolphthalein (pH 8.2-10.0) and thymol blue would work. In actual practice, cresol red (pH 7.2-8.8) would be the best choice because the pH should be closer to the middle of the range than to one end.

## Answers to Conceptual Problems

17.17 A solution of the weak acid, HA, will contain hydronium ions (H\(_3\)O\(^+\)) and anions (A\(^-\)) in equal amounts as well as some undissociated acid (HA) molecules. This is represented by the solution in container A, which contains six HA molecules, two H\(_3\)O\(^+\) and two A\(^-\) ions. The solution in container B contains eight HA molecules and represents an undissociated acid. In container C, all of the HA molecules have dissociated, so this represents a strong acid.

17.18 For equal molar solutions,

a. The greater the pH of the solution, the less H\(_3\)O\(^+\) present in solution. When comparing the three acid solutions of equal concentration, HX produced the least amount of H\(_3\)O\(^+\) in solution (highest pH), so it must be the least ionized.

b. When comparing the three acids, HZ was the most ionized in solution (lowest pH) producing the greatest concentration of H\(_3\)O\(^+\). Therefore, HZ must be the strongest acid with the largest K\(_a\).

17.19 a. When HF is dissolved in water, the F\(^-\) hydrolyzes. The reaction is

\[
HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)
\]

b. When NaF is dissolved in water, F\(^-\) hydrolyzes. The reaction is

\[
F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq)
\]

c. When C\(_6\)H\(_5\)NH\(_2\) is dissolved in water, the following reaction occurs:

\[
C_6H_5NH_2(aq) + H_2O(l) \rightleftharpoons C_6H_5NH_3^+(aq) + OH^-(aq)
\] (continued)
d. When $C_6H_5NH_3Cl$ is dissolved in water, $C_6H_5NH_3^+$ hydrolyzes. The reaction is

$$C_6H_5NH_3^+(aq) + H_2O(l) \rightarrow C_6H_5NH_2(aq) + OH^-(aq)$$

17.20 The KBr solution is made from a neutral salt. Thus, it should have a pH of 7.0. The HBr solution is a strong acid with pH < 7.0. The CH₃NH₂ solution is a weak base with pH > 7.0. The NH₄Cl solution is made from a salt with a weak acid cation, NH₄⁺, with pH < 7.0. Therefore, the ranking from lowest to highest hydroxide concentrations is: HBr < NH₄Cl < KBr < CH₃NH₂.

17.21 A solution of ranitidine hydrochloride should be acidic. Let Ran represent ranitidine. Then RanHCl is the chloride salt, ranitidinium chloride. The cation ranitidinium, RanH⁺, should hydrolyze according to the following equation

$$RanH^+(aq) + H_2O(l) \rightarrow Ran(aq) + H_3O^+(aq)$$

17.22 NH₃ is a weak base; therefore, the solution would have pH > 7. The NH₄Br solution is made from a salt with a weak acid cation, NH₄⁺, with pH < 7.0. The NaF solution is made from a salt with a basic anion, F⁻, with a pH > 7. The NaCl solution is made from a neutral salt; therefore, it should have a pH = 7. In order to rank the relative strengths of the F⁻ and NH₃, you should estimate $K_b$ for each. Using data from Appendices E and F of your text, $K_b$ for NH₃ is about $10^{-5}$ and about $10^{-10}$ for F⁻, which indicates NH₃ is a stronger base than F⁻. Therefore, the ranking from highest to lowest pH is: NH₃ > NaF > NaCl > NH₄Br.

17.23 To prepare a buffer solution that has a pH equal to the pKₐ of the acid, you need equal amounts of acid and conjugate base in the solution. The easiest way to make the buffer is to mix equal volumes of equal molar solutions of HA and NaA. Thus, mix 100 mL of 0.10 M NaA with the 100 mL of 0.10 M HA to prepare the buffer.

17.24 Of the three titrations, the weak base-strong acid titration is easiest to identify. The attributes to look for are a high pH at the start and a gradual decrease in pH as the titration proceeds. The other two titrations both start with low pH and increase in pH as the titration proceeds. Of the two, the strong acid-strong base titration should show a more rapid increase in pH before the endpoint is reached along with a well-defined, sharp equivalence point at pH 7. The weak acid-strong base titration will show a more gradual change in pH before the equivalence point, which should be less sharply defined and occur at a pH above seven.

17.25 a. First, since the pH of the solution is less than seven at the beginning of the titration, you can conclude that an acid is being titrated with a base.

b. The pH of the equivalence point is about 8.5. Therefore, the acid being titrated is a weak acid.

(continued)
c. You need to pick an indicator that changes color in the pH range of about 7 to 10. Therefore, thymol blue or phenolphthalein would work fine for this titration.

17.26 a. The balanced chemical equation for the titration of aqueous NaOH with HCl is

\[ \text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)} \]

b. Beaker A contains four Cl\(^-\) ions and four water molecules. There are no OH\(^-\) ions present. This represents the equivalence point. Beaker B contains two OH\(^-\) and two Cl\(^-\) ions and two water molecules. Since some OH\(^-\) is still present, this represents the titration at a point before the equivalence point. Beaker C contains six Cl\(^-\) and two H\(_3\)O\(^+\) ions and four water molecules. This represents the titration at a point after the equivalence point.

c. The solution in beaker A is at the equivalence point and is neutral. The solution in beaker B contains OH\(^-\) ions and is basic. The solution in beaker C contains H\(_3\)O\(^+\) ions and is acidic.

### Solutions to Practice Problems

**Note on significant figures:** If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multiple-step problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

17.27 a. \( \text{HBrO(aq)} + \text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{O}^+(aq) + \text{BrO}^-(aq) \)

b. \( \text{HClO}_2(aq) + \text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{O}^+(aq) + \text{ClO}_2^-(aq) \)

c. \( \text{HNO}_2(aq) + \text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{O}^+(aq) + \text{NO}_2^-(aq) \)

d. \( \text{HCN(aq)} + \text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{O}^+(aq) + \text{CN}^-(aq) \)

17.28 a. \( \text{HCO}_2\text{H(aq)} + \text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{O}^+(aq) + \text{HCO}_2^-(aq) \)

b. \( \text{HF(aq)} + \text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{O}^+(aq) + \text{F}^-(aq) \)

c. \( \text{HN}_3(aq) + \text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{O}^+(aq) + \text{N}_3^-(aq) \)

d. \( \text{HOCN(aq)} + \text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{O}^+(aq) + \text{OCN}^-(aq) \)
HAc will be used throughout as an abbreviation for acrylic acid and Ac\(^-\) for the acrylate ion. At the start, the H\(_3\)O\(^+\) from the self-ionization of water is so small it is approximately zero. Once the acrylic acid solution is prepared, some of the 0.10 M HAc ionizes to H\(_3\)O\(^+\) and Ac\(^-\). Then, let x equal the mol/L of HAc that ionize, forming x mol/L of H\(_3\)O\(^+\) and x mol/L of Ac\(^-\) and leaving (0.10 - x) M HAc in solution. We can summarize the situation in tabular form:

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>HAc + H(_2)O</th>
<th>H(_3)O(^+) + Ac(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.10</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.10 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

The equilibrium-constant equation is:

\[
K_a = \frac{[H_3O^+] [Ac^-]}{[HAc]} = \frac{x^2}{(0.10 - x)}
\]

The value of x can be obtained from the pH of the solution:

\[
x = [H_3O^+] = \text{antilog (-pH)} = \text{antilog (-2.63)} = 2.34 \times 10^{-3} = 0.00234 \text{ M}
\]

Note that (0.10 - x) = (0.10 - 0.00234) = 0.09766, which is significantly different from 0.10, so x cannot be ignored in the calculation. Thus, we substitute for x in both the numerator and denominator to obtain the value of \(K_a\):

\[
K_a = \frac{x^2}{(0.10 - x)} = \frac{(0.00234)^2}{(0.10 - 0.00234)} = 5.606 \times 10^{-5} = 5.6 \times 10^{-5}
\]

HN\(_3\) will be used throughout as an abbreviation for hydrazoic acid and N\(_3\)\(^-\) for the hydrazoate ion. At the start, the H\(_3\)O\(^+\) from the self-ionization of water is so small it is approximately zero. Once the hydrazoic acid solution is prepared, some of the 0.20 M HN\(_3\) ionizes to H\(_3\)O\(^+\) and N\(_3\)\(^-\). Then, let x equal the mol/L of HN\(_3\) that ionizes, forming x mol/L of H\(_3\)O\(^+\) and x mol/L of N\(_3\)\(^-\) and leaving (0.20 - x) M HN\(_3\) in solution. We can summarize the situation in tabular form:

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>HN(_3) + H(_2)O</th>
<th>H(_3)O(^+) + N(_3)(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.20</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.20 - x</td>
<td>x</td>
</tr>
</tbody>
</table>
The equilibrium-constant equation is:

\[ K_a = \frac{[\text{H}_3\text{O}^+][\text{N}_3^-]}{[\text{HN}_3]} = \frac{x^2}{(0.20 - x)} \]

The value of \(x\) can be obtained from the pH of the solution:

\[ x = [\text{H}_3\text{O}^+] = \text{antilog}(-\text{pH}) = \text{antilog}(-3.21) = 6.16 \times 10^{-4} = 0.000616 \text{ M} \]

Note that \((0.20 - x) = (0.20 - 0.000616) = 0.1993\), which is not significantly different from 0.20, so \(x\) can be ignored in the calculation. Thus, we substitute for \(x\) in only the numerator, not the denominator, to obtain the value of \(K_a\):

\[ K_a = \frac{x^2}{(0.20 - x)} \approx \frac{(0.000616)^2}{(0.20)} \approx 1.89 \times 10^{-6} = 1.9 \times 10^{-6} \]

17.31 To solve, assemble a table of starting, change, and equilibrium concentrations. Use HBo as the symbol for boric acid and Bo\(^+\) as the symbol for B(OH)\(^4^-\).

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HBo + H(_2)O</th>
<th>H(_3)O(^+) + Bo(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.021</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.021 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

The value of \(x\) equals the value of the molarity of the H\(_3\)O\(^+\) ion, which can be obtained from the equilibrium-constant expression. Substitute into the equilibrium-constant expression, and solve for \(x\).

\[ K_a = \frac{[\text{H}_3\text{O}^+][\text{Bo}^-]}{[\text{HBo}]} = \frac{(x)^2}{(0.021 - x)} = 5.9 \times 10^{-10} \]

Solve the equation for \(x\), assuming \(x\) is much smaller than 0.021.

\[ \frac{(x)^2}{(0.021 - x)} \approx \frac{(x)^2}{(0.021)} = 5.9 \times 10^{-10} \]

\[ x^2 = 5.9 \times 10^{-10} \times 0.021 = 1.239 \times 10^{-11} \]

\[ x = [\text{H}_3\text{O}^+] = 3.519 \times 10^{-8} \text{ M} \]

(continued)
ACID-BASE EQUILIBRIA  ■  611

Check to make sure the assumption that \((0.021 - x) \cong 0.021\) is valid:

\[
0.021 - (3.519 \times 10^{-6}) = 0.02099, \text{ or } \cong 0.021 \text{ to two sig. figs.}
\]

\[
pH = - \log [H_3O^+] = - \log (3.519 \times 10^{-6}) = 5.453 = 5.45
\]

The degree of ionization is

\[
\text{degree of ionization} = \frac{3.519 \times 10^{-6}}{(0.021)} = 0.000167 = 0.00017 = 1.7 \times 10^{-4}
\]

17.32 To solve, assemble a table of starting, change, and equilibrium concentrations. Use HFo as the symbol for formic acid and Fo\(^-\) as the symbol for CHO\(_2\)\(^-\).

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HFo + H(_2)O</th>
<th>H(_3)O(^+) + Fo(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.10</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.10 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

The value of \(x\) equals the value of the molarity of the H\(_3\)O\(^+\) ion, which can be obtained from the equilibrium-constant expression. Substitute into the equilibrium-constant expression, and solve for \(x\).

\[
K_a = \frac{[H_3O^+][Fo^-]}{[HFo]} = \frac{(x)^2}{(0.10 - x)} = 1.7 \times 10^{-4}
\]

Solve the equation for \(x\), assuming \(x\) is much smaller than 0.10.

\[
\frac{(x)^2}{(0.10 - x)} = \frac{(x)^2}{(0.10)} = 1.7 \times 10^{-4}
\]

\[
x^2 = 1.7 \times 10^{-4} \times (0.10) = 1.7 \times 10^{-5}
\]

\[
x = [H_3O^+] = 4.123 \times 10^{-3} = 0.0041 \text{ M}
\]

Check to make sure the assumption that \((0.10 - x) \cong 0.10\) is valid:

\[
0.10 - (0.004123) = 0.0958, \text{ or } \cong 0.10 \text{ to two sig. figs}
\]

\[
pH = - \log [H_3O^+] = - \log (4.123 \times 10^{-3}) = 2.384 = 2.38
\]

The degree of ionization is

\[
\text{Degree of ionization} = \frac{0.0041}{(0.10)} = 0.0412 = 0.041
\]
17.33 To solve, assemble a table of starting, change, and equilibrium concentrations. Use HPaba as a symbol for p-aminobenzoic acid (PABA), and use Paba\(^-\) as the symbol for the -1 anion.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HPaba + H(_2)O</th>
<th>H(_3)O(^+) + Paba(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.055</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.055 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms x and (0.055 - x):

\[
K_a = \frac{[H_3O^+][Paba^-]}{[HPaba]} = \frac{(x)^2}{(0.055 - x)} = 2.2 \times 10^{-5}
\]

Solve the equation for x, assuming x is smaller than 0.055.

\[
x^2 = (2.2 \times 10^{-5}) \times 0.055 = 1.21 \times 10^{-6}
\]

\[
x = [H_3O^+] = [Paba^-] \approx 1.10 \times 10^{-3} = 0.0011 = 1.1 \times 10^{-3} \text{ M}
\]

Check to make sure the assumption that (0.055 - x) \(\approx\) 0.055 is valid.

\[
0.055 - 0.00110 = 0.0539, \text{ or } 0.054
\]

17.34 To solve, assemble a table of starting, change, and equilibrium concentrations. Use HBar as a symbol for barbituric acid and Bar\(^-\) as the symbol for the -1 anion.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HBar + H(_2)O</th>
<th>H(_3)O(^+) + Bar(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.15</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.15 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms x and (0.15 - x):

\[
K_a = \frac{[H_3O^+][Bar^-]}{[HBar]} = \frac{(x)^2}{(0.15 - x)} = 9.8 \times 10^{-5}
\]

Solve the equation for x, assuming x is negligible compared to 0.15.

\[
x^2 \approx (9.8 \times 10^{-5}) \times 0.15 = 1.47 \times 10^{-5}
\]

\[
x = [H_3O^+] = [Bar^-] \approx 3.83 \times 10^{-3} = 0.0038 \text{ M}
\]
17.35  To solve, first convert the pH to $[\text{H}_3\text{O}^+]$, which also equals $[\text{C}_2\text{H}_3\text{O}_2^-]$, here symbolized as $[\text{Ac}^-]$. Then, assemble the usual table, and substitute into the equilibrium-constant expression to solve for $[\text{HC}_2\text{H}_3\text{O}_2]$ here symbolized as $[\text{HAc}]$.

$$[\text{H}_3\text{O}^+] = \text{antilog }(-2.68) = 2.089 \times 10^{-3} \text{ M}$$

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HAc</th>
<th>H$_2$O</th>
<th>H$_3$O$^+$</th>
<th>Ac$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>x</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-2.089 $\times 10^{-3}$</td>
<td>+2.089 $\times 10^{-3}$</td>
<td>+2.089 $\times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>x - (2.089 $\times 10^{-3}$)</td>
<td>2.089 $\times 10^{-3}$</td>
<td>2.089 $\times 10^{-3}$</td>
<td></td>
</tr>
</tbody>
</table>

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the x and the x - (2.089 $\times 10^{-3}$) terms into the expression:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Ac}^-]}{[\text{HAc}]} = \frac{(2.089 \times 10^{-3})^2}{(x - 2.089 \times 10^{-3})} = 1.7 \times 10^{-5}$$

Solve the equation for x, assuming 0.002089 is much smaller than x.

$$x = [\text{HAc}] \approx \frac{(2.089 \times 10^{-3})^2}{(1.7 \times 10^{-5})} = 0.256 = 0.26 \text{ M}$$

17.36  To solve, first convert the pH to $[\text{H}_3\text{O}^+]$, which also equals the $[\text{C}_3\text{H}_5\text{O}_3^-]$, here symbolized as $[\text{Lac}^-]$. Then, assemble the usual table, and substitute into the equilibrium-constant expression to solve for $[\text{HC}_3\text{H}_5\text{O}_3]$ here symbolized as $[\text{HLac}]$.

$$[\text{H}_3\text{O}^+] = \text{antilog }(-2.51) = 3.09 \times 10^{-3} \text{ M}$$

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HLac</th>
<th>H$_2$O</th>
<th>H$_3$O$^+$</th>
<th>Lac$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>x</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-3.09 $\times 10^{-3}$</td>
<td>+3.09 $\times 10^{-3}$</td>
<td>+3.09 $\times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>x - (3.09 $\times 10^{-3}$)</td>
<td>3.09 $\times 10^{-3}$</td>
<td>3.09 $\times 10^{-3}$</td>
<td></td>
</tr>
</tbody>
</table>

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the x and the x - (3.09 $\times 10^{-3}$) terms into the expression:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Lac}^-]}{[\text{HLac}]} = \frac{(3.09 \times 10^{-3})^2}{(x - 3.09 \times 10^{-3})} = 1.4 \times 10^{-4}$$

(continued)
Solve the equation for x. It appears $3.09 \times 10^{-3}$ is not much smaller than x, so do not ignore x in the denominator.

$$\frac{(3.09 \times 10^{-3})^2}{1.4 \times 10^{-4}} = 0.0682 = (x - 3.09 \times 10^{-3})$$

$$x = [\text{HLac}] = 0.0682 + 0.00309 = 0.0712 = 0.071 \text{ M}$$

17.37 To solve, assemble the usual table of starting, change, and equilibrium concentrations of HF and F⁻ ions.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HF + H₂O</th>
<th>(H_3O^+) + F⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.040</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.040 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms x and (0.040 - x):

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = \frac{(x)^2}{(0.040 - x)} = 6.8 \times 10^{-4}$$

In this case, x cannot be ignored compared to 0.040 M. (If it is ignored, subtracting the calculated \(H_3O^+\) from 0.040 yields a significant change.) The quadratic formula must be used. Reorganize the equilibrium-constant expression into the form $ax^2 + bx + c = 0$, and substitute for a, b, and c in the quadratic formula.

$$x^2 + (6.8 \times 10^{-4})x - (2.72 \times 10^{-5}) = 0$$

$$x = \frac{-6.8 \times 10^{-4} \pm \sqrt{(6.8 \times 10^{-4})^2 + 4(2.72 \times 10^{-5})}}{2}$$

$$x = \frac{-6.8 \times 10^{-4} \pm 0.01045}{2}$$

Use the positive root.

$$x = [H_3O^+] = 4.88 \times 10^{-3} = 0.0049 = 4.9 \times 10^{-3} \text{ M}$$

$$pH = -\log (4.88 \times 10^{-3}) = 2.311 = 2.31$$
17.38 To solve, assemble the usual table of starting, change, and equilibrium concentrations of \( {\text{HC}_2\text{H}_2\text{ClO}_2} \), symbolized as HCl, and the \( {\text{C}_2\text{H}_2\text{ClO}}^- \) ion, symbolized as Cl'.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HCl + H₂O</th>
<th>H₃O⁺ + Cl⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.015</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.015 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms x and (0.015 - x):

\[
K_a = \frac{[\text{H}_3\text{O}^+] [\text{Cl}^-]}{[\text{HCl}]} = \frac{(x)^2}{(0.015 - x)} = 1.3 \times 10^{-3} = 0.0013
\]

In this case, x cannot be ignored compared to 0.015 M. (If it is ignored, subtracting the calculated \([\text{H}_3\text{O}^+]\) from 0.015 yields a significant change.) The quadratic formula must be used. Reorganize the equilibrium-constant expression into the form \( ax^2 + bx + c = 0 \), and substitute for \( a, b, \) and \( c \) in the quadratic formula.

\[
x^2 + (0.0013) x - 1.95 \times 10^{-5} = 0
\]

\[
x = \frac{-0.0013 \pm \sqrt{(0.0013)^2 + 4(1.95 \times 10^{-5})}}{2}
\]

\[
x = \frac{-0.0013 \pm 0.008926}{2}
\]

Use the positive root.

\[
x = [\text{H}_3\text{O}^+] = 3.813 \times 10^{-3} = 0.0038 \text{ M}
\]

\[
\text{pH} = - \log (3.813 \times 10^{-3}) = 2.418 = 2.42
\]

17.39 To solve, assemble the usual table of starting, change, and equilibrium concentrations of \( (\text{NO}_2)_2\text{C}_6\text{H}_5\text{CO}_2\text{H} \), symbolized as HDin, and the \( (\text{NO}_2)_2\text{C}_6\text{H}_5\text{CO}_2^- \) ion, symbolized as Din'.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HDin + H₂O</th>
<th>H₃O⁺ + Din⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>2.00</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>2.00 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

(continued)
Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms $x$ and $(2.00 - x)$:

$$K_a = \frac{[H_3O^+][Din^-]}{[HDin]} = \frac{(x)^2}{(2.00 - x)} = 7.94 \times 10^{-2} = 0.0794$$

In this case, $x$ cannot be ignored compared to 2.00 M. (If it is ignored, subtracting the calculated $[H_3O^+]$ from 2.00 yields a significant change.) The quadratic formula must be used. Reorganize the equilibrium-constant expression into the form $ax^2 + bx + c = 0$, and substitute for $a$, $b$, and $c$ in the quadratic formula.

$$x^2 + (0.0794)x - 0.1588 = 0$$

$$x = \frac{-0.0794 \pm \sqrt{(0.0794)^2 + 4(0.1588)}}{2}$$

$$x = \frac{-0.0794 \pm 0.8009}{2}$$

Use the positive root.

$$x = [H_3O^+] = 0.3607 = 0.361 \text{ M}$$

17.40 To solve, assemble the usual table of starting, change, and equilibrium concentrations of $\text{BrCaH}_4\text{CO}_2\text{H}$, symbolized as $\text{HpBr}$, and the $\text{BrCaH}_4\text{CO}_2^-$ ion, symbolized as $\text{pBr}^-$. 

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HpBr + H₂O</th>
<th>H₃O⁺</th>
<th>pBr⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>2.00 x 10⁻⁴</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>(2.00 x 10⁻⁴ - x)</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms $x$ and $(2.00 \times 10^{-4} - x)$:

$$K_a = \frac{[H_3O^+] [pBr^-]}{[HpBr]} = \frac{(x)^2}{(2.00 \times 10^{-4} - x)} = 1.00 \times 10^{-4}$$

In this case, $x$ cannot be ignored compared to $2.00 \times 10^{-4}$ M. (If it is ignored, subtracting the calculated $[H_3O^+]$ from $2.00 \times 10^{-4}$ yields a significant change.) The quadratic formula must be used. Reorganize the equilibrium-constant expression into the form $ax^2 + bx + c = 0$, and substitute for $a$, $b$, and $c$ in the quadratic formula.

$$x^2 + (1.00 \times 10^{-4})x - 2.00 \times 10^{-8} = 0$$

(continued)
Plugging into the quadratic formula gives

\[
x = \frac{-1.00 \times 10^{-4} \pm \sqrt{(1.00 \times 10^{-4})^2 + 4(2.00 \times 10^{-8})}}{2}
\]

\[
x = \frac{-1.00 \times 10^{-4} \pm 3.00 \times 10^{-4}}{2}
\]

Use the positive root.

\[
x = [H_3O^+] = 1.000 \times 10^{-4} = 1.00 \times 10^{-4} \text{ M}
\]

17.41 a. To solve, note that \(K_{a1} = 1.2 \times 10^{-3} > K_{a2} = 3.9 \times 10^{-6}\), and hence the second ionization and \(K_{a2}\) can be neglected. Assemble a table of starting, change, and equilibrium concentrations. Let \(H_2\text{Ph} = H_2\text{C}_8\text{H}_4\text{O}_4\) and \(H\text{Ph}^- = H\text{C}_8\text{H}_4\text{O}_4^-\).

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>(H_2\text{Ph})</th>
<th>(H_2\text{O})</th>
<th>(H_3\text{O}^+)</th>
<th>HPh^-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.015</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.015 - x</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute \(x\) and \((0.015 - x)\):

\[
K_{a1} = \frac{[H_3\text{O}^+][\text{HPh}^-]}{[H_2\text{Ph}]} = \frac{(x)^2}{(0.015 - x)} = 1.2 \times 10^{-3} = 0.0012
\]

In this case, \(x\) cannot be ignored in the \((0.015 - x)\) term. (If it is ignored, the calculated \([H_3\text{O}^+]\) when subtracted from 0.0015 M yields a significant change.) The quadratic formula must be used. Reorganize the equilibrium-constant expression into the form \(ax^2 + bx + c = 0\), and substitute for \(a\), \(b\), and \(c\) in the quadratic formula.

\[
x^2 + (0.0012)x - 1.80 \times 10^{-5} = 0
\]

\[
x = \frac{-0.0012 \pm \sqrt{(0.0012)^2 - 4(-1.80 \times 10^{-5})}}{2}
\]

\[
x = \frac{-0.0012 \pm 0.008569}{2}
\]

Use the positive root.

\[
x = [H_3\text{O}^+] \cong 3.684 \times 10^{-3} = 0.0037 = 3.7 \times 10^{-3} \text{ M}
\]

(continued)
b. Because \([\text{HPh}^-] \equiv [\text{H}_3\text{O}^+]\), these terms cancel in the \(K_{a2}\) expression. This reduces to

\[
[\text{Ph}^2] = K_{a2} = 3.9 \times 10^{-6} \text{ M}
\]

17.42 a. To solve, note that \(K_{a1} = 4.3 \times 10^{-7} > K_{a2} = 4.8 \times 10^{-11}\), and hence the second ionization and \(K_{a2}\) can be neglected. Assemble a table of starting, change, and equilibrium concentrations.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>(\text{H}_2\text{CO}_3)</th>
<th>(+\text{H}_2\text{O})</th>
<th>(+\text{H}_3\text{O}^+)</th>
<th>(+\text{HCO}_3^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>5.45 \times 10^{-4}</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>(5.45 \times 10^{-4} - x)</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute \(x\) and \((5.45 \times 10^{-4} - x)\):

\[
K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{(x)^2}{(5.45 \times 10^{-4} - x)} = 4.3 \times 10^{-7}
\]

In this case, \(x\) cannot be ignored compared to 5.45 \times 10^{-4} \text{ M}. (If it is ignored, the calculated \([\text{H}_3\text{O}^+]\) when subtracted from 5.45 \times 10^{-4} \text{ M yields a significant change.})

The quadratic formula must be used. Reorganize the equilibrium-constant expression into the form \(ax^2 + bx + c = 0\), and substitute for \(a\), \(b\), and \(c\) in the quadratic formula.

\[
x^2 + (4.3 \times 10^{-7})x - 2.3435 \times 10^{-10} = 0
\]

\[
x = \frac{-4.3 \times 10^{-7} \pm \sqrt{(4.3 \times 10^{-7})^2 + 4(2.3435 \times 10^{-10})}}{2}
\]

\[
x = \frac{-4.3 \times 10^{-7} \pm 3.06 \times 10^{-5}}{2}
\]

Use the positive root.

\[
x = [\text{H}_3\text{O}^+] = 1.51 \times 10^{-5} = 1.5 \times 10^{-5} \text{ M}
\]

(continued)
b. To calculate \([\text{CO}_3^{2-}] = y\), note from the equilibrium concentrations in the table above that \([\text{HCO}_3^-] \equiv [\text{H}_2\text{O}^+]\). In exact terms, \([\text{H}_2\text{O}^+] = (1.5 \times 10^{-5} + y)\) from the ionization of \(\text{HCO}_3^-\), and \([\text{HCO}_3^-] = (1.5 \times 10^{-5} - y)\) from ionization. Substituting into the \(K_{a2}\) expression gives

\[
K_{a2} = \frac{[\text{H}_3\text{O}^+] [\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \frac{(1.5 \times 10^{-5} + y)(y)}{(1.5 \times 10^{-5} - y)} = 4.8 \times 10^{-11}
\]

Assuming \(y\) is much smaller than \(1.5 \times 10^{-5}\), note the \((1.5 \times 10^{-5}) + y\) term cancels the \((1.5 \times 10^{-5}) - y\) term, leaving

\([\text{CO}_3^{2-}] \cong K_{a2} = 4.8 \times 10^{-11}\) M

17.43 The equation is

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

The \(K_b\) expression is

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

17.44 The equation is

\[
\text{C}_6\text{H}_5\text{NH}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+(\text{aq}) + \text{OH}^-(\text{aq})
\]

The \(K_b\) expression is

\[
K_b = \frac{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{NH}_2]}
\]

17.45 To solve, convert the pH to [OH⁻]:

\[
p\text{OH} = 14.00 - \text{pH} = 14.00 - 11.34 = 2.66
\]

\[
[\text{OH}^-] = \text{antilog}(-2.66) = 2.188 \times 10^{-3}\ \text{M}
\]

Using the symbol EtN for ethanolamine, assemble a table of starting, change, and equilibrium concentrations.

(continued)
### CHAPTER 17

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>EtN + H₂O</th>
<th>HEtN⁺ + OH⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Starting</strong></td>
<td>0.15</td>
<td>0</td>
</tr>
<tr>
<td><strong>Change</strong></td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td><strong>Equilibrium</strong></td>
<td>0.15 - (2.188 x 10⁻³)</td>
<td>2.188 x 10⁻³</td>
</tr>
</tbody>
</table>

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms, and solve for $K_b$:

$$K_b = \frac{[HEtN^⁺][OH⁻]}{[EtN]} = \frac{(2.188 \times 10^{-3})^2}{(0.15 - 2.188 \times 10^{-3})} = 3.23 \times 10^{-5} = 3.2 \times 10^{-5}$$

**17.46** To solve, convert the pH to [OH⁻]:

$$pOH = 14.00 - pH = 14.00 - 11.63 = 2.37$$

$$[OH⁻] = antilog (-2.37) = 4.266 \times 10^{-3} \text{ M}$$

Using the symbol TMeN for trimethylamine, assemble a table of starting, change, and equilibrium concentrations.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>TMeN + H₂O</th>
<th>HTMeN⁺ + OH⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Starting</strong></td>
<td>0.25</td>
<td>0</td>
</tr>
<tr>
<td><strong>Change</strong></td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td><strong>Equilibrium</strong></td>
<td>0.25 - (4.266 x 10⁻³)</td>
<td>4.266 x 10⁻³</td>
</tr>
</tbody>
</table>

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms, and solve for $K_b$:

$$K_b = \frac{[HTMeN^⁺][OH⁻]}{[TMeN]} = \frac{(4.266 \times 10^{-3})^2}{(0.25 - 4.266 \times 10^{-3})} = 7.40 \times 10^{-5} = 7.4 \times 10^{-5}$$

**17.47** To solve, assemble a table of starting, change, and equilibrium concentrations:

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>CH₃NH₂ + H₂O</th>
<th>CH₃NH₃⁺ + OH⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Starting</strong></td>
<td>0.060</td>
<td>0</td>
</tr>
<tr>
<td><strong>Change</strong></td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td><strong>Equilibrium</strong></td>
<td>0.060 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

(continued)
Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms and the value of $K_b$:

$$K_b = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]} = \frac{(x)^2}{(0.060 - x)} = 4.4 \times 10^{-4}$$

In this case, $x$ cannot be ignored compared to 0.060 M. (If it is ignored, subtracting the calculated $[\text{H}_3\text{O}^+]$ from 0.060 yields a significant change.) The quadratic formula must be used. Reorganize the equilibrium-constant expression into the form $ax^2 + bx + c = 0$, and substitute for $a$, $b$, and $c$ in the quadratic formula.

$$x^2 + (4.4 \times 10^{-4})x - 2.64 \times 10^{-5} = 0$$

$$x = \frac{-4.4 \times 10^{-4} \pm \sqrt{(4.4 \times 10^{-4})^2 + 4(2.64 \times 10^{-5})}}{2}$$

$$x = \frac{-4.4 \times 10^{-4} \pm 0.01028}{2}$$

Use the positive root.

$$x = [\text{OH}^-] = 4.92 \times 10^{-3} = 0.0049 = 4.9 \times 10^{-3} \text{ M}$$

$$p\text{OH} = -\log (4.92 \times 10^{-3}) = 2.307$$

$$p\text{H} = 14.00 - 2.307 = 11.692 = 11.69$$

17.48 To solve, assemble a table of starting, change, and equilibrium concentrations:

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HONH$_2$ + H$_2$O</th>
<th>HONH$_3^+$</th>
<th>OH$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.18</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.18 - x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms and the value of $K_b$:

$$K_b = \frac{[\text{HONH}_3^+][\text{OH}^-]}{[\text{HONH}_2]} = \frac{(x)^2}{(0.18 - x)} = 1.1 \times 10^{-8}$$

(continued)
Solve the equation for \(x\), assuming \(x\) can be ignored compared to 0.18 M.

\[
\frac{(x)^2}{(0.18 - x)} \cong \frac{(x)^2}{(0.18)} = 1.1 \times 10^{-8}
\]

\[x^2 = 1.1 \times 10^{-8} \times (0.18)\]

\[x = [OH^-] = 4.44 \times 10^{-5} = 4.4 \times 10^{-5} \text{ M}\]

\[pOH = - \log (4.44 \times 10^{-5}) = 4.351\]

\[pH = 14.00 - 4.351 = 9.649 = 9.65\]

17.49 a. No hydrolysis occurs because the nitrate ion (NO\(_3^-\)) is the anion of a strong acid.

b. Hydrolysis occurs. Equation:

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

Equilibrium-constant expression:

\[
K_b = \frac{K_w}{K_a} = \frac{[\text{HOCl}] [\text{OH}^-]}{[\text{OCl}^-]}
\]

c. Hydrolysis occurs. Equation:

\[
\text{NH}_2\text{NH}_3^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NH}_2\text{NH}_2\]

Equilibrium-constant expression:

\[
K_a = \frac{K_w}{K_b} = \frac{[\text{H}_3\text{O}^+] [\text{NH}_2\text{NH}_2]}{[\text{NH}_2\text{NH}_3^+]}\]

d. No hydrolysis occurs because the bromide ion (Br\(^-\)) is the anion of a strong acid.

17.50 a. Hydrolysis occurs. Equation:

\[
\text{CH}_3\text{NH}_3^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_3\text{NH}_2\]

Equilibrium-constant expression:

\[
K_a = \frac{K_w}{K_b} = \frac{[\text{H}_3\text{O}^+] [\text{CH}_3\text{NH}_2]}{[\text{CH}_3\text{NH}_3^+]}\]

(continued)
b. No hydrolysis occurs because the iodide ion (I\(^-\)) is the anion of a strong acid.

c. Hydrolysis occurs. Equation:

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

Equilibrium-constant expression:

\[
K_b = \frac{K_w}{K_a} = \frac{[\text{HClO}_2][\text{OH}^-]}{[\text{ClO}_2^-]} \\
\]

d. Hydrolysis occurs. Equation:

\[
\text{PO}_4^{3-} + \text{H}_2\text{O} \rightleftharpoons \text{HPO}_4^{2-} + \text{OH}^- \\
\]

Equilibrium-constant expression:

\[
K_b = \frac{K_w}{K_{a_3}} = \frac{[\text{HPO}_4^{2-}][\text{OH}^-]}{[\text{PO}_4^{3-}]} \\
\]

17.51 Acid ionization is

\[
\text{Zn(H}_2\text{O)}_6^{2+}(\text{aq}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{Zn(H}_2\text{O)}_5(\text{OH})^+(_\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \\
\]

17.52 Acid ionization is

\[
\text{Cu(H}_2\text{O)}_6^{2+}(\text{aq}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{Cu(H}_2\text{O)}_5(\text{OH})^+(_\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \\
\]

17.53 a. \text{Fe(NO}_3)_3\text{ is a salt of a weak base, Fe(OH)}_3\text{, and a strong acid, HNO}_3\text{, so it would be expected to be acidic. Fe}^{3+}\text{ is not in Group I A or IIA, so it would be expected to form a metal hydrate ion that would hydrolyze to form an acidic solution.}

b. \text{Na}_2\text{CO}_3\text{ is a salt of a strong base, NaOH, and the anion of a weak acid, HCO}_3^-\text{, so it would be expected to be basic.}

c. \text{Ca(CN)}_2\text{ is a salt of a strong base, Ca(OH)}_2\text{, and a weak acid, HCN, so it would be expected to be basic.}

d. \text{NH}_4\text{ClO}_4\text{ is a salt of a weak base, NH}_3\text{, and a strong acid, HClO}_4\text{, so it would be expected to be acidic.}
17.54 a. \( \text{Na}_2\text{S} \) is a salt of a strong base, NaOH, and the anion of a weak acid, \( \text{HS}^- \), so it would be expected to be basic.

b. Cu(NO\(_3\))\(_2\) is a salt of a weak base, Cu(OH)\(_2\), and a strong acid, HNO\(_3\), so it would be expected to be acidic. Cu\(^{2+}\) is not in Group IA or IIA, so it would be expected to form a metal hydrate ion that would hydrolyze to form an acidic solution.

c. KClO\(_4\) is a salt of a strong base, KOH, and a strong acid, HClO\(_4\), so no reaction would occur to change the neutral pH (7.00) of water.

d. \( \text{C}_2\text{NH}_3\text{Cl} \) is a salt of a weak base, CH\(_3\)NH\(_2\), and a strong acid, HCl, so it would be expected to be acidic.

17.55 a. Both ions hydrolyze:

\[
\begin{align*}
\text{NH}_4^+ + \text{H}_2\text{O} & \rightarrow \text{NH}_3 + \text{H}_3\text{O}^+ \\
\text{C}_2\text{H}_3\text{O}_2^- + \text{H}_2\text{O} & \rightarrow \text{HC}_2\text{H}_3\text{O}_2 + \text{OH}^-
\end{align*}
\]

Calculate the \( K_a \) and \( K_b \) constants of each to compare them:

\[
\begin{align*}
\text{NH}_4^+ \text{ as an acid: } K_a &= \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.55 \times 10^{-10} \\
\text{C}_2\text{H}_3\text{O}_2^- \text{ as a base: } K_b &= \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-5}} = 5.88 \times 10^{-10}
\end{align*}
\]

Because the \( K_b \) for the hydrolysis of \( \text{C}_2\text{H}_3\text{O}_2^- \) is slightly larger than the constant, \( K_a \), for the hydrolysis of \( \text{NH}_4^+ \), the solution will be slightly basic but close to pH 7.0.

b. Both ions hydrolyze:

\[
\begin{align*}
\text{C}_6\text{H}_5\text{NH}_3^+ + \text{H}_2\text{O} & \rightarrow \text{C}_6\text{H}_5\text{NH}_2 + \text{H}_3\text{O}^+ \\
\text{C}_2\text{H}_3\text{O}_2^- + \text{H}_2\text{O} & \rightarrow \text{HC}_2\text{H}_3\text{O}_2 + \text{OH}^-
\end{align*}
\]

Calculate the \( K_a \) and \( K_b \) constants of each to compare them:

\[
\begin{align*}
\text{C}_6\text{H}_5\text{NH}_3^+ \text{ as an acid: } K_a &= \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.2 \times 10^{-10}} = 2.38 \times 10^{-5}
\end{align*}
\]

(continued)
C$_2$H$_3$O$_2$$^-$ as a base: $K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-5}} = 5.88 \times 10^{-10}$

Because the constant, $K_a$, for the hydrolysis of C$_6$H$_5$NH$_3^+$ is larger than the hydrolysis constant, $K_b$, for the hydrolysis of C$_2$H$_3$O$_2^-$, the solution will be acidic and significantly less than pH 7.0.

17.56 a. Both ions hydrolyze:

NH$_4^+$ + H$_2$O $\rightleftharpoons$ NH$_3$ + H$_3$O$^+$

CNO$^-$ + H$_2$O $\rightleftharpoons$ HCNO + OH$^-$

Calculate the $K_a$ and $K_b$ constants of each to compare them:

NH$_4^+$ as an acid: $K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.55 \times 10^{-10}$

CNO$^-$ as a base: $K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{3.5 \times 10^{-4}} = 2.86 \times 10^{-11}$

Because the constant, $K_a$, for the hydrolysis of NH$_4^+$ is larger than the hydrolysis constant, $K_b$, for the hydrolysis of CNO$^-$, the solution will be acidic and significantly less than pH 7.0.

b. Both ions hydrolyze:

C$_6$H$_5$NH$_3^+$ + H$_2$O $\rightleftharpoons$ C$_6$H$_5$NH$_2$ + H$_3$O$^+$

CNO$^-$ + H$_2$O $\rightleftharpoons$ HCNO + OH$^-$

Calculate the $K_a$ and $K_b$ constants of each to compare them:

C$_6$H$_5$NH$_3^+$ as an acid: $K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.2 \times 10^{-10}} = 2.38 \times 10^{-5}$

CNO$^-$ as a base: $K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{3.5 \times 10^{-4}} = 2.86 \times 10^{-11}$

Because the constant, $K_a$, for the hydrolysis of C$_6$H$_5$NH$_3^+$ is larger than the hydrolysis constant, $K_b$, for the hydrolysis of CNO$^-$, the solution will be acidic and significantly less than pH 7.0.
17.57 a. The reaction is
\[
\text{NO}_2^- + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + \text{OH}^-
\]
The constant, \(K_b\), is obtained by dividing \(K_w\) by the \(K_a\) of the conjugate acid, \(\text{HNO}_2\):
\[
K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.5 \times 10^{-4}} = 2.22 \times 10^{-11} = 2.2 \times 10^{-11}
\]
b. The reaction is
\[
\text{C}_5\text{H}_5\text{NH}^+ + \text{H}_2\text{O} \rightarrow \text{C}_5\text{H}_5\text{N} + \text{H}_3\text{O}^+
\]
The constant, \(K_a\), is obtained by dividing \(K_w\) by the \(K_b\) of the conjugate base, \(\text{C}_5\text{H}_5\text{N}^\cdot\):
\[
K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-9}} = 7.14 \times 10^{-6} = 7.1 \times 10^{-6}
\]

17.58 a. The reaction is
\[
\text{ClO}^- + \text{H}_2\text{O} \rightarrow \text{HClO} + \text{OH}^-
\]
The constant, \(K_b\), is obtained by dividing \(K_w\) by the \(K_a\) of the conjugate acid, \(\text{HClO}\):
\[
K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{3.5 \times 10^{-8}} = 2.857 \times 10^{-7} = 2.9 \times 10^{-7}
\]
b. The reaction is
\[
\text{NH}_3\text{OH}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{NH}_2\text{OH}
\]
The constant, \(K_a\), is obtained by dividing \(K_w\) by the \(K_b\) of the conjugate base, \(\text{NH}_2\text{OH}\):
\[
K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.1 \times 10^{-8}} = 9.09 \times 10^{-7} = 9.1 \times 10^{-7}
\]
Assemble the usual table, letting \([Pr^-]\) equal the equilibrium concentration of the propionate anion (the only ion that hydrolyzes). Then, calculate the \(K_b\) of the \(Pr^-\) ion from the \(K_a\) of its conjugate acid, HPr. Assume \(x\) is much smaller than the 0.025 M concentration in the denominator, and solve for \(x\) in the numerator of the equilibrium-constant expression. Finally, calculate pOH from the \([OH^-]\) and pH from the pOH.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>(Pr^- + H_2O)</th>
<th>(HPr + OH^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.025</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.025 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[
K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.3 \times 10^{-5}} = 7.69 \times 10^{-10}
\]

Substitute into the equilibrium-constant equation.

\[
K_b = \frac{[HPr][OH^-]}{[Pr^-]} = \frac{(x)^2}{(0.025 - x)} \approx \frac{(x)^2}{(0.025)} = 7.69 \times 10^{-10}
\]

\[
x = [OH^-] = [HPr] \approx 4.38 \times 10^{-6} = 4.4 \times 10^{-6} \text{ M}
\]

\[
pOH = -\log [OH^-] = -\log (4.38 \times 10^{-6}) = 5.358
\]

\[
pH = 14.00 - 5.358 = 8.642 = 8.64
\]

Assemble the usual table, letting \([CN^-]\) equal the equilibrium concentration of the cyanide anion (the only ion that hydrolyzes). Then, calculate the \(K_b\) of the \(CN^-\) ion from the \(K_a\) of its conjugate acid, HCN. Assume \(x\) is much smaller than the 0.010 M concentration in the denominator, and solve for \(x\) in the numerator of the equilibrium-constant expression. (This is a borderline case, but the quadratic equation gives a value of 4.415 \times 10^{-4} \text{ M} for \(x\), not much different than the approximation.) Finally, calculate pOH from the \([OH^-]\) and pH from the pOH.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>(CN^- + H_2O)</th>
<th>(HCN + OH^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.010</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.010 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[
K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.9 \times 10^{-10}} = 2.04 \times 10^{-5}
\]

(continued)
Substitute into the equilibrium-constant equation.

\[ K_b = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} = \frac{(x)^2}{(0.010 - x)} \cong \frac{(x)^2}{(0.010)} = 2.04 \times 10^{-6} \]

\[ x = [\text{OH}^-] = [\text{HCN}] \cong 4.52 \times 10^{-4} = 4.5 \times 10^{-4} \text{ M} \]

\[ \text{pOH} = -\log [\text{OH}^-] = -\log (4.52 \times 10^{-4}) = 3.3448 \]

\[ \text{pH} = 14.00 - 3.3448 = 10.6552 = 10.66 \]

The cyanide ion concentration is

\[ [\text{CN}^-] = 0.010 - x = 0.010 - 4.52 \times 10^{-4} = 0.009548 = 0.0095 \text{ M} \]

17.61 Assemble the usual table, letting [PyNH$^+$] equal the equilibrium concentration of the pryridinium cation (the only ion that hydrolyzes). Then, calculate the $K_a$ of the PyNH$^+$ ion from the $K_b$ of its conjugate base, PyN. Assume $x$ is much smaller than the 0.15 M concentration in the denominator, and solve for $x$ in the numerator of the equilibrium-constant expression. Finally, calculate pH from the [H$_3$O$^+$].

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>PyNH$^+$</th>
<th>H$_2$O</th>
<th>H$_3$O$^+$</th>
<th>PyN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.15</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.15 - x</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

\[ K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-9}} = 7.14 \times 10^{-6} \]

Write the equilibrium-constant expression in terms of chemical symbols and then substitute the terms and solve for $K_a$:

\[ K_a = \frac{[\text{PyN}][\text{H}_3\text{O}^+]}{[\text{PyNH}^+]} = \frac{(x)^2}{(0.15 - x)} \cong \frac{(x)^2}{(0.15)} = 7.14 \times 10^{-6} \]

\[ x = [\text{H}_3\text{O}^+] = [\text{PyN}] \cong 1.03 \times 10^{-3} = 0.0010 = 1.0 \times 10^{-3} \text{ M} \]

\[ \text{pH} = -\log [\text{H}^+] = -\log (1.03 \times 10^{-3}) = 2.987 = 2.99 \]
17.62 Assemble the usual table, letting [MeNH$_3^+$] equal the equilibrium concentration of the methylammonium cation (the only ion that hydrolyzes). Then, calculate the $K_a$ of the MeNH$_3^+$ ion from the $K_b$ of its conjugate base, MeNH$_2$. Assume $x$ is much smaller than the 0.35 M concentration in the denominator, and solve for $x$ in the numerator of the equilibrium-constant expression. Finally, calculate pH from the [H$_3$O$^+$].

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>MeNH$_3^+$ + H$_2$O</th>
<th>H$_3$O$^+$ + MeNH$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.35</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.35 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

$$K_a = \frac{K_{w}}{K_b} = \frac{1.0 \times 10^{-14}}{4.4 \times 10^{-4}} = 2.27 \times 10^{-11}$$

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms and solve for $K_a$:

$$K_a = \frac{[\text{MeNH}_2][\text{H}_3\text{O}^+]}{[\text{MeNH}_3^+]} = \frac{(x)^2}{(0.35 - x)} \approx \frac{(x)^2}{(0.35)} = 2.27 \times 10^{-11}$$

$x = [\text{H}_3\text{O}^+] = [\text{MeNH}_2] \approx 2.82 \times 10^{-6} = 2.8 \times 10^{-6}$ M

$pH = -\log [\text{H}_3\text{O}^+] = -\log (2.82 \times 10^{-6}) = 5.549 = 5.55$

17.63 To solve, assemble a table of starting, change, and equilibrium concentrations for each part. For each part, assume $x$ is much smaller than the 0.75 M starting concentration of HF. Then, solve for $x$ in the numerator of each equilibrium-constant expression by using the product of $6.8 \times 10^{-4}$ and other terms.

a. 0.75 M Hydrofluoric acid, HF:

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HF + H$_2$O</th>
<th>H$_3$O$^+$ + F$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.75</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.75 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = \frac{(x)^2}{(0.75 - x)} \approx \frac{(x)^2}{(0.75)} = 6.8 \times 10^{-4}$$

$x^2 = 6.8 \times 10^{-4} \times (0.75)$ (continued)
\[ x = [\text{H}_3\text{O}^+] = 0.02258 \text{ M} \]

Check to see if the assumption is valid.

\[ 0.75 - (0.02258) = 0.727 = 0.73 \]

This is a borderline case; the quadratic equation gives \([\text{H}_3\text{O}^+] = 0.02224 \text{ M}\), not much different. The degree of ionization is

\[ \text{Degree of ionization} = \frac{0.02258}{0.75} = 0.0301 = 0.030 \]

b. 0.75 \text{ M} \text{ HF with} 0.12 \text{ M} \text{ HCl}:

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HF + H_2O</th>
<th>H_3O^+ + F^-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.75</td>
<td>0.12</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.75 - x</td>
<td>0.12 + x</td>
</tr>
</tbody>
</table>

Assuming \( x \) is negligible compared to 0.12 and to 0.75, substitute into the equilibrium-constant expression 0.12 for \([\text{H}_3\text{O}^+]\) from 0.12 \text{ M} \text{ HCl and 0.75 from the HF}:

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = \frac{(0.12 + x)(x)}{(0.75 - x)} \approx \frac{(0.12)(x)}{(0.75)} = 6.8 \times 10^{-4}
\]

\[
x = [\text{F}^-] = \frac{(0.75)(6.8 \times 10^{-4})}{(0.12)} \approx 4.250 \times 10^{-3} \text{ M}
\]

Check to see if the assumptions are valid:

\[ 0.75 - (4.250 \times 10^{-3}) = 0.7457 = 0.75 \]

\[ 0.12 + (4.250 \times 10^{-3}) = 0.1242 = 0.12 \]

\[ \text{Degree of ionization} = \frac{4.25 \times 10^{-3}}{0.75} = 0.00566 = 0.0057 \]
17.64 To solve, assemble a table of starting, change, and equilibrium concentrations for each part. For each part, assume $x$ is much smaller than the 0.22 M starting concentration of HCHO$_2$. Then, solve for $x$ in each equilibrium-constant expression by using the product of $1.7 \times 10^{-4}$ and each starting molarity of formic acid.

a. 0.22 M HCHO$_2$

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HCHO$_2$ + H$_2$O [H_3O^+ + \text{CHO}_2^-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.22</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.22 - x</td>
</tr>
</tbody>
</table>

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms and solve for $K_a$:

$$K_a = \frac{[H_3O^+]\text{[CHO}_2^-]}{[\text{HCHO}_2]} = \frac{(x)^2}{(0.22 - x)} = \frac{(x)^2}{(0.22)} = 1.7 \times 10^{-4}$$

$$x^2 = 1.7 \times 10^{-4} \times (0.22 \text{ M})$$

$$x = [\text{H}_3\text{O}^+] \approx 6.11 \times 10^{-3} \text{ M}$$

Check to see if the assumption is valid:

$$0.22 - (6.11 \times 10^{-3}) = 0.213 = 0.21$$

The degree of ionization is:

$$\text{Degree of ionization} = \frac{6.11 \times 10^{-3}}{0.22} = 0.0277 = 0.028$$

b. 0.22 M HCHO$_2$ with 0.12 M HCl:

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HCHO$_2$ + H$_2$O [H_3O^+ + \text{CHO}_2^-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.22</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.22 - x</td>
</tr>
</tbody>
</table>

(continued)
Assuming \( x \) is negligible compared to 0.12 and to 0.22, substitute into the equilibrium-constant expression 0.12 for \([H_3O^+]\) from 0.12 M HCl and 0.22 from the HCHO₂:

\[
K_a = \frac{[H_3O^+] [CHO_2^-]}{[HCHO_2]} = \frac{(0.12 + x)(x)}{(0.22 - x)} \approx \frac{(0.12)(x)}{(0.22)} = 1.7 \times 10^{-4}
\]

\[
x = [CHO_2^-] = \frac{(0.22)(1.7 \times 10^{-4})}{(0.12)} \approx 3.11 \times 10^{-4} \text{ M}
\]

Check to see if the assumptions are valid:

\[
0.12 + 3.11 \times 10^{-4} = 0.1203 = 0.12
\]
\[
0.22 - (3.11 \times 10^{-4}) = 0.219 = 0.22
\]

The degree of ionization is

\[
\text{Degree of ionization} = \frac{(3.11 \times 10^{-4})}{0.22} = 0.00141 = 0.0014
\]

17.65 Assemble the usual table, using a starting NO₂⁻ of 0.10 M, from 0.10 M KNO₂, and a starting HNO₂ of 0.15 M. Assume \( x \) is negligible compared to 0.10 M and 0.15 M, and solve for the \( x \) in the numerator.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HNO₂ + H₂O</th>
<th>H₃O⁺ + NO₂⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.15</td>
<td>0.10</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.15 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[
K_a = \frac{[H_3O^+] [NO_2^-]}{[HNO_2]} = \frac{(0.10 + x)(x)}{(0.15 - x)} \approx \frac{(0.10)(x)}{(0.15)} = 4.5 \times 10^{-4}
\]

\[
x = [H_3O^+] = 6.75 \times 10^{-4} \text{ M}
\]

\[
pH = - \log [H_3O^+] = - \log (6.75 \times 10^{-4}) = 3.170 = 3.17
\]

17.66 Use a starting OCN⁻ of 0.20 M and a starting HOCN of 0.10 M. Assume \( x \) is negligible compared to 0.20 M and 0.10 M.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HOCN + H₂O</th>
<th>H₃O⁺ + OCN⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.10</td>
<td>0.20</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.10 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

(continued)
\[
K_a = \frac{[H_3O^+][OCN^-]}{[HOCN]} = \frac{(0.20+x)(x)}{(0.10-x)} \approx \frac{(0.20)(x)}{(0.10)} = 3.5 \times 10^{-4}
\]

\[x = [H_3O^+] = 1.75 \times 10^{-4} \text{ M}\]

\[pH = - \log [H_3O^+] = - \log (1.75 \times 10^{-4}) = 3.756 = 3.76\]

17.67 Assemble the usual table, using a starting \(\text{CH}_3\text{NH}_3^+\) of 0.15 M, from 0.15 M \(\text{CH}_3\text{NH}_3\text{Cl}\), and a starting \(\text{CH}_3\text{NH}_2\) of 0.10 M. Assume \(x\) is negligible compared to 0.15 M and 0.10 M, and solve for the \(x\) in the numerator.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>(\text{CH}_3\text{NH}_2) + H(_2)O</th>
<th>OH(^-)</th>
<th>(\text{CH}_3\text{NH}_3^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.10</td>
<td>0</td>
<td>0.15</td>
</tr>
<tr>
<td>Change</td>
<td>-(x)</td>
<td>+(x)</td>
<td>+(x)</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.10 - (x)</td>
<td>(x)</td>
<td>0.15 + (x)</td>
</tr>
</tbody>
</table>

\[K_b = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]} = \frac{(0.15+x)(x)}{(0.10-x)} \approx \frac{(0.15)(x)}{(0.10)} = 4.4 \times 10^{-4}\]

\[x = [\text{OH}^-] = 2.93 \times 10^{-4} \text{ M}\]

\[pOH = - \log [\text{OH}^-] = - \log (2.93 \times 10^{-4}) = 3.532\]

\[pH = 14.00 - pOH = 14.00 - 3.532 = 10.468 = 10.47\]

17.68 Assemble the usual table, using a starting \(\text{C}_2\text{H}_5\text{NH}_3^+\) of 0.10 M, from 0.10 M \(\text{C}_2\text{H}_5\text{NH}_3\text{Br}\), and a starting \(\text{C}_2\text{H}_5\text{NH}_2\) of 0.15 M. Assume \(x\) is negligible compared to 0.10 M and 0.15 M, and solve for the \(x\) in the numerator.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>(\text{C}_2\text{H}_5\text{NH}_2) + H(_2)O</th>
<th>OH(^-)</th>
<th>(\text{C}_2\text{H}_5\text{NH}_3^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.15</td>
<td>0</td>
<td>0.10</td>
</tr>
<tr>
<td>Change</td>
<td>-(x)</td>
<td>+(x)</td>
<td>+(x)</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.15 - (x)</td>
<td>(x)</td>
<td>0.10 + (x)</td>
</tr>
</tbody>
</table>

\[K_b = \frac{[\text{C}_2\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_2\text{H}_5\text{NH}_2]} = \frac{(0.10+x)(x)}{(0.15-x)} \approx \frac{(0.10)(x)}{(0.15)} = 4.7 \times 10^{-4}\]

\[x = [\text{OH}^-] = 7.05 \times 10^{-4} \text{ M}\]

\[pOH = - \log [\text{OH}^-] = - \log (7.05 \times 10^{-4}) = 3.151\]

\[pH = 14.00 - pOH = 14.00 - 3.151 = 10.848 = 10.85\]
17.69 Find the mol/L of HF and the mol/L of F\(^-\), and assemble the usual table. Substitute the equilibrium concentrations into the equilibrium-constant expression; then, assume \(x\) is negligible compared to the starting concentrations of both HF and F\(^-\). Solve for \(x\) in the numerator of the equilibrium-constant expression, and calculate the pH from this value.

Total volume = \(0.045 \text{ L} + 0.035 \text{ L} = 0.080 \text{ L}\)

\[(0.10 \text{ mol HF/L}) \times 0.035 \text{ L} = 0.0035 \text{ mol HF} \div 0.080 \text{ L total volume} = 0.04375 \text{ M}\]

\[(0.15 \text{ mol F}^-/\text{L}) \times 0.045 \text{ L} = 0.00675 \text{ mol F}^- \div 0.080 \text{ L total volume} = 0.084375 \text{ M}\]

Now, substitute these starting concentrations into the usual table:

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HF + H(_2)O</th>
<th>H(_3)O(^+) + F(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.04375</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.04375 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[K_a = \frac{[H_3O^+][F^-]}{[HF]} = \frac{(x)(0.084375 + x)}{(0.04375 - x)} \cong \frac{(x)(0.084375)}{(0.04375)} = 6.8 \times 10^{-4}\]

\[x = [H_3O^+] = 3.52 \times 10^{-4} \text{ M}\]

\[\text{pH} = -\log [H_3O^+] = -\log (3.52 \times 10^{-4}) = 3.453 = 3.45\]

17.70 Find the mol/L of NH\(_3\) and the mol/L of NH\(_4^+\), and assemble the usual table. Substitute the equilibrium concentrations into the equilibrium-constant expression; then, assume \(x\) is negligible compared to the starting concentrations of both NH\(_3\) and NH\(_4^+\). Solve for \(x\) in the numerator of the equilibrium-constant expression, and calculate the pH from this value.

Total volume = \(0.115 \text{ L} + 0.145 \text{ L} = 0.260 \text{ L}\)

\[(0.30 \text{ mol NH}_3/\text{L}) \times 0.115 \text{ L} = 0.0345 \text{ mol NH}_3 \div 0.260 \text{ L total vol} = 0.1327 \text{ M}\]

\[(0.15 \text{ mol NH}_4^+/\text{L}) \times 0.145 \text{ L} = 0.02175 \text{ mol NH}_4^+ \div 0.260 \text{ L total vol} = 0.08365 \text{ M}\]

(continued)
Now, substitute these starting concentrations into the usual table:

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>NH\textsubscript{3} + H\textsubscript{2}O</th>
<th>NH\textsubscript{4}\textsuperscript{+} + OH\textsuperscript{-}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.1327</td>
<td>0.08365</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.1327 - x</td>
<td>0.08365 + x</td>
</tr>
</tbody>
</table>

\[ K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(0.08365 + x)(x)}{(0.1327 - x)} \approx \frac{(0.08365)(x)}{(0.1327)} = 1.8 \times 10^{-5} \]

\[ x = [\text{OH}^-] = 2.855 \times 10^{-5} \text{ M} \]

\[ \text{pOH} = - \log [\text{OH}^-] = - \log (2.855 \times 10^{-5}) = 4.544 \]

\[ \text{pH} = 14.00 - \text{pOH} = 14.00 - 4.544 = 9.456 = 9.46 \]

17.71 First, use the 0.10 M NH\textsubscript{3} and 0.10 M NH\textsubscript{4}\textsuperscript{+} to calculate the [OH\textsuperscript{-}] and pH before HCl is added. Assemble a table of starting, change, and equilibrium concentrations. Assume \( x \) is negligible compared to 0.10 M, and substitute the approximate concentrations into the equilibrium-constant expression.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>NH\textsubscript{3} + H\textsubscript{2}O</th>
<th>NH\textsubscript{4}\textsuperscript{+} + OH\textsuperscript{-}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.10 - x</td>
<td>0.10 + x</td>
</tr>
</tbody>
</table>

\[ K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(0.10 + x)(x)}{(0.10 - x)} \approx \frac{(0.10)(x)}{(0.10)} = 1.8 \times 10^{-5} \]

\[ x = [\text{OH}^-] = 1.8 \times 10^{-5} \text{ M} \]

\[ \text{pOH} = - \log [\text{OH}^-] = - \log (1.8 \times 10^{-5}) = 4.744 \]

\[ \text{pH} = 14.00 - \text{pOH} = 14.00 - 4.744 = 9.2552 = 9.26 \text{ (before HCl added)} \]

Now, calculate the pH after the 0.012 L (12 mL) of 0.20 M HCl is added by noting that the H\textsubscript{3}O\textsuperscript{+} ion reacts with the NH\textsubscript{3} to form additional NH\textsubscript{4}\textsuperscript{+}. Calculate the stoichiometric amount of HCl; then, subtract the moles of HCl from the moles of NH\textsubscript{3}. Add the resulting moles of NH\textsubscript{4}\textsuperscript{+} to the 0.0125 starting moles of NH\textsubscript{4}\textsuperscript{+} in the 0.125 L of buffer.

(continued)
(0.20 mol HCl/L) \times 0.012 L = 0.0024 mol HCl (reacts with 0.0024 mol NH₃)

Mol NH₃ left = (0.0125 - 0.0024) mol = 0.0101 mol

Mol NH₄⁺ present = (0.0125 + 0.0024) mol = 0.0149 mol

The concentrations of NH₃ and NH₄⁺ are

\[
[NH₃] = \frac{0.0101 \text{ mol NH₃}}{0.137 \text{ L}} = 0.0737 \text{ M}
\]

\[
[NH₄⁺] = \frac{0.0149 \text{ mol NH₃}}{0.137 \text{ L}} = 0.108 \text{ M}
\]

Now, account for the ionization of NH₃ to NH₄⁺ and OH⁻ at equilibrium by assembling the usual table. Assume x is negligible compared to 0.0737 M and 0.108 M, and solve the equilibrium-constant expression for x in the numerator. Calculate the pH from x, the [OH⁻].

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>NH₃ + H₂O</th>
<th>NH₄⁺</th>
<th>OH⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.0737</td>
<td>0.108</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.0737 - x</td>
<td>0.108 + x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[
K_b = \frac{[NH₄⁺][OH⁻]}{[NH₃]} = \frac{(0.108 + x)(x)}{(0.0737 - x)} \approx \frac{(0.108)(x)}{(0.0737)} = 1.8 \times 10^{-5}
\]

\[
x = [OH⁻] \approx 1.22 \times 10^{-5} \text{ M}
\]

\[
pOH = -\log [OH⁻] = -\log (1.22 \times 10^{-5}) = 4.913
\]

\[
pH = 14.00 - pOH = 14.00 - 4.913 = 9.086 = 9.09 \text{ (after HCl added)}
\]

17.72 First, use the 0.525 L of 0.50 M HCHO₂ (HFO) and 0.475 L of 0.50 M NaCHO₂ (Na⁺Fo⁻) to calculate the [H₃O⁺] and pH before HCl is added. Assemble a table of starting, change, and equilibrium concentrations. Assume x is negligible compared to both concentrations; substitute into the Kₐ expression.

\[
0.50 \text{ M HFO} \times 0.525 \text{ L} = 0.263 \text{ mol HFO (÷ 1.00 L} = 0.263 \text{ M)}
\]

\[
0.50 \text{ M Fo}⁻ \times 0.475 \text{ L} = 0.238 \text{ mol Fo}⁻ (÷ 1.00 L} = 0.238 \text{ M)}
\]

(continued)
Set up the table:

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HFo + H₂O</th>
<th>H₃O⁺ + Fo⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.263</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.263 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{Fo}^-]}{[\text{HFo}]} = \frac{(x)(0.238 + x)}{(0.263 - x)} \approx \frac{(x)(0.238)}{(0.263)} = 1.7 \times 10^{-4}
\]

\[x = [\text{H}_3\text{O}^+] = 1.88 \times 10^{-4} \text{ M}\]

\[\text{pH} = - \log [\text{H}_3\text{O}^+] = - \log (1.88 \times 10^{-4}) = 3.726 = 3.73 \text{ (before HCl added)}\]

Now, calculate the pH after the 0.0085 L (8.5 mL) of 0.15 M HCl is added by noting that the H₃O⁺ ion reacts with the Fo⁻ to form additional HFo. Calculate the stoichiometric amount of HCl; then, subtract the moles of HCl from the moles of Fo⁻. Add the resulting moles of HFo to the 0.02227 starting moles of HFo in the 0.085 L of buffer.

\[(0.15 \text{ mol HCl/L}) \times 0.0085 \text{ L} = 0.00128 \text{ mol HCl (reacts with 0.00128 mol Fo}^-)\]

\[\text{Mol Fo}^- \text{ left} = (0.02023 - 0.00128) \text{ mol} = 0.01895 \text{ mol Fo}^-\]

\[\text{Mol HFo present} = (0.02227 + 0.00128) = 0.02355 \text{ mol HFo}\]

The concentrations of HFo and Fo⁻ are

\[[\text{HFo}] = \frac{0.02355 \text{ mol HFo}}{0.0935 \text{ L}} = 0.2518 \text{ M}\]

\[[\text{Fo}^-] = \frac{0.01895 \text{ mol Fo}^-}{0.0935 \text{ L}} = 0.2026 \text{ M}\]

Now, account for the ionization of HFo to H₃O⁺ and Fo⁻ at equilibrium by assembling the usual table. Assume x is negligible compared to 0.2518 M and 0.2026M, and solve the equilibrium-constant expression for x in the numerator. Calculate the pH from x, the [H₃O⁺].

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HFo + H₂O</th>
<th>H₃O⁺ + Fo⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.2518</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.2518 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

(continued)
Substitute into the equilibrium-constant equation to get

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HFo}]} = \frac{(x)(0.2026 + x)}{(0.2518 - x)} \approx \frac{(x)(0.2026)}{(0.2518)} = 1.7 \times 10^{-4}
\]

\[
x = [\text{H}_3\text{O}^+] = 2.11 \times 10^{-4} \text{ M}
\]

\[
pH = -\log [\text{H}_3\text{O}^+] = -\log (2.11 \times 10^{-4}) = 3.6757 = 3.68 \text{ (after HCl added)}
\]

17.73 Use the Henderson-Hasselbalch equation, where \(pK_a = -\log K_a\).

\[
pH = -\log K_a + \log \frac{([\text{buff. base}])}{([\text{buff. acid}])}
\]

\[
= -\log (1.4 \times 10^{-3}) + \log \left( \frac{0.10 \text{ M}}{0.15 \text{ M}} \right) = 2.677 = 2.68
\]

17.74 Use the Henderson-Hasselbalch equation (\(pK_a = -\log K_a\)), and do the calculations in one step.

\[
pH = -\log K_a + \log \frac{([\text{buff. base}])}{([\text{buff. acid}])}
\]

\[
= -\log (1.3 \times 10^{-5}) + \log \left( \frac{0.20 \text{ M}}{0.10 \text{ M}} \right) = 5.187 = 5.19
\]

17.75 Calculate the \(K_a\) of the pyridinium ion from the \(K_b\) of pyridine, and then use the Henderson-Hasselbalch equation where \(pK_a = -\log K_a\).

\[
K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-9}} = 7.14 \times 10^6
\]

\[
pH = -\log K_a + \log \frac{([\text{buff. base}])}{([\text{buff. acid}])}
\]

\[
= -\log (7.14 \times 10^6) + \log \left( \frac{0.15 \text{ M}}{0.10 \text{ M}} \right) = 5.322 = 5.32
\]
17.76 Calculate the $K_a$ of the methylammonium ion from the $K_b$ of methylamine, and then use the Henderson-Hasselbalch equation where $pK_a = -\log K_a$.

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.4 \times 10^{-14}} = 2.27 \times 10^{-11}$$

$$pH = -\log K_a + \log \frac{[\text{buff. base}]}{[\text{buff. acid}]}$$

$$= -\log (2.27 \times 10^{-11}) + \log \frac{(0.20 \text{ M})}{(0.15 \text{ M})} = 10.768 = 10.77$$

17.77 Symbolize acetic acid as HOAc and sodium acetate as Na’OAc”. Use the Henderson-Hasselbalch equation to find the log of $[\text{OAc}^-]/[\text{HOAc}]$. Then, solve for $[\text{OAc}^-]$ and for moles of NaOAc in the 2.0 L of solution.

$$pH = -\log K_a + \log \frac{[\text{OAc}^-]}{[\text{HOAc}]} = 5.00$$

$$5.00 = -\log (1.7 \times 10^{-5}) + \log \frac{[\text{OAc}^-]}{(0.10 \text{ M})}$$

$$5.00 = 4.770 + \log [\text{OAc}^-] - \log (0.10)$$

$$\log [\text{OAc}^-] = 5.00 - 4.770 - 1.00 = -0.770$$

$$[\text{OAc}^-] = 0.1698 \text{ M}$$

$$\text{Mol NaOAc = 0.1698 mol/L x 2.0 L = 0.3396 = 0.34 mol}$$

17.78 Use the Henderson-Hasselbalch equation to find the log of $[\text{F}^-]/[\text{HF}]$. Then, solve for $[\text{HF}]$ and for moles of HF in the 0.5000 L of solution.

$$pH = -\log K_a + \log \frac{[\text{F}^-]}{[\text{HF}]} = 3.50$$

$$3.50 = -\log (6.8 \times 10^{-4}) + \log \frac{(0.30 \text{ M})}{[\text{HF}]}$$

(continued)
3.50 = 3.167 + log [0.30] - log [HF]

\[
\log [HF] = 3.167 - 0.523 - 3.50 = -0.856
\]

[HF] = 0.1393 M

Mol HF = 0.1393 mol/L x 0.5000 L = 0.06965 = 0.070 mol HF

17.79 All the OH\(^{-}\) (from the NaOH) reacts with the H\(_3\)O\(^{+}\) from HCl. Calculate the stoichiometric amounts of OH\(^{-}\) and H\(_3\)O\(^{+}\), and subtract the mol of OH\(^{-}\) from the mol of H\(_3\)O\(^{+}\). Then, divide the remaining H\(_3\)O\(^{+}\) by the total volume of 0.015 L + 0.025 L, or 0.040 L, to find the [H\(_3\)O\(^{+}\)]. Then calculate the pH.

\[
\text{Mol H}_3\text{O}^{+} = (0.10 \text{ mol HCl/L}) \times 0.025 \text{ L HCl} = 0.0025 \text{ mol H}_3\text{O}^{+}
\]

\[
\text{Mol OH}^{-} = (0.10 \text{ mol NaOH/L}) \times 0.015 \text{ L NaOH} = 0.0015 \text{ mol OH}^{-}
\]

\[
\text{Mol H}_3\text{O}^{+} \text{ left} = (0.0025 - 0.0015) \text{ mol H}_3\text{O}^{+} = 0.0010 \text{ mol H}_3\text{O}^{+}
\]

\[
[\text{H}_3\text{O}^{+}] = 0.0010 \text{ mol H}_3\text{O}^{+} \div 0.040 \text{ L total volume} = 0.0250 \text{ M}
\]

\[
\text{pH} = -\log [\text{H}_3\text{O}^{+}] = -\log (0.0250) = 1.602 = 1.6
\]

17.80 All the H\(^{+}\) (from the HCl) reacts with the OH\(^{-}\) from NaOH. Calculate the stoichiometric amounts of OH\(^{-}\) and H\(_3\)O\(^{+}\), and subtract the mol of H\(_3\)O\(^{+}\) from the mol of OH\(^{-}\). Then, divide the remaining OH\(^{-}\) by the total volume of 0.040 L + 0.025 L, or 0.065 L, to find the [OH\(^{-}\)]. Then calculate the pOH and pH.

\[
\text{Mol OH}^{-} = (0.10 \text{ mol NaOH/L}) \times 0.040 \text{ L NaOH} = 0.0040 \text{ mol OH}^{-}
\]

\[
\text{Mol H}_3\text{O}^{+} = (0.10 \text{ mol HCl/L}) \times 0.025 \text{ L HCl} = 0.0025 \text{ mol H}_3\text{O}^{+}
\]

\[
\text{Mol OH}^{-} \text{ left} = (0.0040 - 0.0025) \text{ mol OH}^{-} = 0.0015 \text{ mol OH}^{-}
\]

\[
[\text{OH}^{-}] = 0.0015 \text{ mol OH}^{-} \div 0.065 \text{ L total volume} = 0.0230 \text{ M}
\]

\[
\text{pOH} = -\log [\text{OH}^{-}] = -\log (0.0230) = 1.636
\]

\[
\text{pH} = 14.00 - \text{pH} = 14.00 - 1.636 = 12.363 = 12.37
\]
17.81 Use HBen to symbolize benzoic acid and Ben\(^-\) to symbolize the benzoate anion. At the equivalence point, equal molar amounts of HBen and NaOH react to form a solution of NaBen. Start by calculating the moles of HBen. Use this to calculate the volume of NaOH needed to neutralize all of the HBen (and use the moles of HBen as the moles of Ben\(^-\) formed at the equivalence point). Add the volume of NaOH to the original 0.050 L to find the total volume of solution.

\[
\text{Mol HBen} = \frac{1.24 \text{ g HBen}}{122.1 \text{ g HBen/mol HBen}} = 0.01016 \text{ mol HBen}
\]

\[
\text{Volume NaOH} = \frac{0.01016 \text{ mol NaOH}}{0.180 \text{ mol NaOH/L}} = 0.05644 \text{ L}
\]

\[
\text{Total volume} = 0.05644 \text{ L} + 0.050 \text{ L HBen soln} = 0.10644 \text{ L}
\]

\[
\text{[Ben}\(^-)\] = \frac{(0.01016 \text{ mol Ben}\(^-)\text{ from HBen})}{0.10644 \text{ L}} = 0.09545 \text{ M}
\]

Because the Ben\(^-\) hydrolyzes to OH\(^-\) and HBen, use this to calculate the [OH\(^-\)]. Start by calculating the \(K_b\) constant of Ben\(^-\) from the \(K_a\) of its conjugate acid, HBen. Then, assemble the usual table of concentrations, assume \(x\) is negligible, and calculate [OH\(^-\)] and pH.

\[
K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.3 \times 10^{-5}} = 1.59 \times 10^{-10}
\]

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>Ben(^-) + H(_2)O</th>
<th>HBen + OH(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.09545</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.09545 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[
K_b = \frac{[\text{HBen}][\text{OH}^-]}{[\text{Ben}^-]} = \frac{(x)^2}{(0.09545 - x)} \approx \frac{(x)^2}{(0.09545)} = 1.59 \times 10^{-10}
\]

\[
x = [\text{OH}^-] = 3.895 \times 10^{-6} \text{ M}
\]

\[
pOH = -\log [\text{OH}^-] = -\log (3.895 \times 10^{-6}) = 5.4094
\]

\[
pH = 14.00 - 5.4094 = 8.5905 \approx 8.59
\]
17.82 Use HPr to symbolize propionic acid and Pr\(^-\) to symbolize the propionate anion. At the equivalence point, equal molar amounts of HPr and NaOH react to form a solution of NaPr. Start by calculating the moles of HPr. Use this to calculate the volume of NaOH needed to neutralize all of the HPr (and use the moles of HPr as the moles of Pr\(^-\) formed at the equivalence point). Add the volume of NaOH to the original 0.050 L to find the total volume of solution.

\[
\text{Mol HPr} = \frac{0.400 \text{ g HPr}}{74.08 \text{ g HPr/mol HPr}} = 0.00540 \text{ mol HPr}
\]

\[
\text{Volume NaOH} = \frac{0.00540 \text{ mol NaOH}}{0.150 \text{ mol NaOH/L}} = 0.03600 \text{ L}
\]

\[
\text{Total volume} = 0.03600 \text{ L} + 0.050 \text{ L HPr soln} = 0.08600 \text{ L}
\]

\[
[\text{Pr}^-] = \frac{0.00540 \text{ mol Pr}^- \text{ from HPr}}{0.08600 \text{ L}} = 0.06279 \text{ M}
\]

Because the Pr\(^-\) hydrolyzes to OH\(^-\) and HPr, use this to calculate the [OH\(^-\)]. Start by calculating the \(K_b\) constant of Pr\(^-\) from the \(K_a\) of its conjugate acid, HPr. Then, assemble the usual table of concentrations, assume \(x\) is negligible, and calculate [OH\(^-\)] and pH.

\[
K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.3 \times 10^{-5}} = 7.69 \times 10^{-10}
\]

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>Pr(^-) + H(_2)O</th>
<th>HPr + OH(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.06279</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.06279 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[
K_b = \frac{[\text{HPr}][\text{OH}^-]}{[\text{Pr}^-]} = \frac{(x)^2}{(0.06279 - x)} \approx \frac{(x)^2}{(0.06279)} = 7.69 \times 10^{-10}
\]

\[
x = [\text{OH}^-] = 6.948 \times 10^{-6} \text{ M}
\]

\[
pOH = -\log [\text{OH}^-] = -\log (6.948 \times 10^{-6}) = 5.158
\]

\[
\text{pH} = 14.00 - 5.158 = 8.841 = 8.84
\]
17.83 Use EtN to symbolize ethylamine and EtNH⁺ to symbolize the ethylammonium cation. At the equivalence point, equal molar amounts of EtN and HCl react to form a solution of EtNHCl. Start by calculating the moles of EtN. Use this to calculate the volume of HCl needed to neutralize all of the EtN (and use the moles of EtN as the moles of EtNH⁺ formed at the equivalence point). Add the volume of HCl to the original 0.032 L to find the total volume of solution.

\[
(0.087 \text{ mol EtN/L}) \times 0.032 \text{ L} = 0.00278 \text{ mol EtN}
\]

Volume HCl = 0.00278 mol HCl ÷ (0.15 mol HCl/L) = 0.0185 L

Total volume = 0.0185 L + 0.032 L EtN soln = 0.0505 L

\[
[\text{EtNH}^+] = \frac{(0.00278 \text{ mol EtNH}^+ \text{ from EtN})}{0.0505 \text{ L}} = 0.0550 \text{ M}
\]

Because the EtNH⁺ hydrolyzes to H₂O⁺ and EtN, use this to calculate the [H₂O⁺]. Start by calculating the \( K_a \) constant of EtNH⁺ from the \( K_b \) of its conjugate base, EtN. Then, assemble the usual table of concentrations, assume x is negligible, and calculate [H₂O⁺] and pH.

\[
K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.7 \times 10^{-4}} = 2.13 \times 10^{-11}
\]

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>EtNH⁺</th>
<th>H₂O⁺</th>
<th>EtN</th>
<th>H₂O⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.0550</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.0550 - x</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

\[
K_a = \frac{[\text{EtN}][\text{H}_2\text{O}^+]}{[\text{EtNH}^+]} = \frac{(x)^2}{(0.0550 - x)} \approx \frac{(x)^2}{(0.0550)} = 2.13 \times 10^{-11}
\]

\[
x = [\text{H}_2\text{O}^+] = 1.98 \times 10^{-6} \text{ M}
\]

\[
pH = -\log [\text{H}_2\text{O}^+] = -\log (1.98 \times 10^{-6}) = 5.9656 = 5.97
\]
17.84 Use $\text{HyN}$ to symbolize hydroxylamine and $\text{HyNH}^+$ to symbolize the hydroxylammonium cation. At the equivalence point, equal molar amounts of $\text{HyN}$ and $\text{HCl}$ react to form a solution of $\text{HyNHCl}$. Start by calculating the moles of $\text{HyN}$. Use this to calculate the volume of $\text{HCl}$ needed to neutralize all of the $\text{HyN}$ (and use the moles of $\text{HyN}$ as the moles of $\text{HyNH}^+$ formed at the equivalence point). Add volumes.

\[
(0.20 \text{ mol } \text{HyN/L}) \times 0.022 \text{ L} = 0.00440 \text{ mol } \text{HyN}
\]

Volume HCl $= 0.00440 \text{ mol } \text{HCl} \div (0.15 \text{ mol } \text{HCl/L}) = 0.0293 \text{ L}$

Total volume $= 0.0293 \text{ L} + 0.022 \text{ L } \text{HyN soln} = 0.0513 \text{ L}$

$[\text{HyNH}^+] = (0.00440 \text{ mol } \text{HyNH}^+ \text{ from } \text{HyN}) \div 0.0513 \text{ L} = 0.0858 \text{ M}$

Use $\text{HyNH}^+$ hydrolysis to calculate the $[\text{H}_3\text{O}^+]$. Calculate the $K_a$ constant of $\text{HyNH}^+$ from the $K_b$ of $\text{HyN}$. Assemble the concentration table; assume $x$ is negligible, and calculate $[\text{H}_3\text{O}^+]$.

\[
K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.1 \times 10^{-8}} = 9.09 \times 10^{-7}
\]

\[
\begin{array}{|c|c|c|c|}
\hline
\text{Conc. (M)} & \text{HyNH}^+ & \text{H}_2\text{O} & \text{HyN} + \text{H}_3\text{O}^+ \\
\hline
\text{Starting} & 0.0858 & 0 & 0 \\
\text{Change} & -x & +x & +x \\
\text{Equilibrium} & 0.0858 - x & x & x \\
\hline
\end{array}
\]

\[
K_a = \frac{[\text{HyN}][\text{H}_3\text{O}^+]}{[\text{HyNH}^+]} = \frac{(x)^2}{(0.0858 - x)} \approx \frac{(x)^2}{(0.0858)} = 9.09 \times 10^{-7}
\]

\[
x = [\text{H}_3\text{O}^+] = 2.79 \times 10^{-4} \text{ M}
\]

\[
pH = -\log [\text{H}_3\text{O}^+] = -\log (2.79 \times 10^{-4}) = 3.554 = 3.55
\]

17.85 Calculate the stoichiometric amounts of $\text{NH}_3$ and $\text{HCl}$, which forms $\text{NH}_4^+$. Then, divide $\text{NH}_3$ and $\text{NH}_4^+$ by the total volume of $0.500 \text{ L} + 0.200 \text{ L} = 0.700 \text{ L}$ to find the starting concentrations. Calculate the $[\text{OH}^-]$, the pOH, and the pH.

\[
\text{Mol } \text{NH}_3 = (0.10 \text{ mol } \text{NH}_3/\text{L}) \times 0.500 \text{ L} = 0.0500 \text{ mol } \text{NH}_3
\]

\[
\text{Mol } \text{HCl} = (0.15 \text{ mol } \text{HCl}/\text{L}) \times 0.200 \text{ L} = 0.0300 \text{ mol } \text{HCl} \ (0.0300 \text{ mol } \text{NH}_4^+)
\]

\[
\text{Mol } \text{NH}_3 \text{ left} = 0.0500 \text{ mol} - 0.0300 \text{ mol } \text{HCl} = 0.0200 \text{ mol } \text{NH}_3
\]

\[
0.0200 \text{ mol } \text{NH}_3 \div 0.700 \text{ L} = 0.0286 \text{ M } \text{NH}_3
\]
0.0300 mol NH₄⁺ ÷ 0.700 L = 0.0429 M NH₄⁺

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>NH₃ + H₂O</th>
<th>NH₄⁺ + OH⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.0286</td>
<td>0.0429</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.0286 - x</td>
<td>0.0429 + x</td>
</tr>
</tbody>
</table>

\[ K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(0.0429 + x)(x)}{(0.0286 - x)} \approx \frac{(0.0429)(x)}{(0.0286)} = 1.8 \times 10^{-5} \]

\[ x = [\text{OH}^-] = 1.20 \times 10^{-5} \text{ M} \]

\[ pOH = - \log [\text{OH}^-] = - \log (1.20 \times 10^{-5}) = 4.920 \]

\[ \text{pH} = 14.00 - \text{pOH} = 14.00 - 4.920 = 9.079 \approx 9.08 \]

Use the symbols HAc for acetic acid and Ac⁻ for the acetate ion from sodium acetate. Calculate the stoichiometric amounts of HAc and Ac⁻. Then, divide the HAc and Ac⁻ by the total volume of 0.035 L + 0.025 L, or 0.060 L, to find the starting concentrations. Calculate the [H₃O⁺] and pH.

\[ \text{Mol HAc} = (0.15 \text{ mol HAc/L}) \times 0.035 \text{ L} \text{ HAc} = 0.00525 \text{ mol HAc} \]

\[ \text{Mol Ac}^- = (0.10 \text{ mol NaAc/L}) \times 0.025 \text{ L NaAc} = 0.00250 \text{ mol Ac}^- \]

\[ 0.00525 \text{ mol HAc} \div 0.060 \text{ L} = 0.0875 \text{ M HAc} \]

\[ 0.00250 \text{ mol Ac}^- \div 0.060 \text{ L} = 0.0417 \text{ M Ac}^- \]

Set up a table.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HAc + H₂O</th>
<th>H₃O⁺ + Ac⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.0875</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.0875 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[ K_a = \frac{[\text{H}_3\text{O}^+][\text{Ac}^-]}{[\text{HAc}]} = \frac{(0.0417 + x)(x)}{(0.0875 - x)} \approx \frac{(0.0417)(x)}{(0.0875)} = 1.7 \times 10^{-5} \]

\[ [\text{H}_3\text{O}^+] \approx 3.57 \times 10^{-5} \text{ M} \]

\[ \text{pH} = - \log [\text{H}_3\text{O}^+] = - \log (3.57 \times 10^{-5}) = 4.447 \approx 4.45 \]
CHAPTER 17

Solutions to General Problems

17.87 To solve, assemble a table of starting, change, and equilibrium concentrations. Use HSal to symbolize salicylic acid, and use Sal\(^-\) for the anion. Start by converting pH to [H\(_3\)O\(^+\)]:

\[
[H_3O^+] = \text{antilog}(-pH) = \text{antilog}(-2.43) = 3.72 \times 10^{-3} \text{ M}
\]

Starting M of HSal = \((2.2 \text{ g} \div 138 \text{ g/mol}) \div 1.00 \text{ L} = 0.0159 \text{ M}\)

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HSal + H(_2)O + H(_3)O(^+)</th>
<th>Sal(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.0159</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
</tbody>
</table>
| Equilibrium | 0.0159 - x               | x       | x

The value of x equals the value of the molarity of the H\(_3\)O\(^+\) ion, which is 3.72 \times 10^{-3} \text{ M}.

Substitute into the equilibrium-constant expression to find \(K_a\):

\[
K_a = \frac{[H_3O^+][\text{Sal}^-]}{[\text{HSal}]} = \frac{(x)^2}{(0.0159 - x)} = \frac{(3.72 \times 10^{-3})^2}{(0.0159 - 3.72 \times 10^{-3})} = 1.13 \times 10^{-3} = 1.1 \times 10^{-3}
\]

17.88 To solve, assemble a table of starting, change, and equilibrium concentrations. Use HCyn to symbolize cyanoacetic acid, and use Cyn\(^-\) for the anion. Start by converting pH to [H\(_3\)O\(^+\)]:

\[
[H_3O^+] = \text{antilog}(-pH) = \text{antilog}(-1.89) = 1.29 \times 10^{-2} \text{ M}
\]

Starting M of HCyn = \((5.0 \text{ g} \div 85.1 \text{ g/mol}) \div 1.00 \text{ L} = 0.0588 \text{ M}\)

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HCyn + H(_2)O + H(_3)O(^+)</th>
<th>Cyn(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.0588</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
</tbody>
</table>
| Equilibrium | 0.0588 - x               | x       | x

The value of x equals the value of the molarity of the H\(_3\)O\(^+\) ion, which is 1.29 \times 10^{-2} \text{ M}.

Substitute into the equilibrium-constant expression to find \(K_a\):

(continued)
\[ K_a = \frac{[H_3O^+][Cyn^-]}{[HCyn]} = \frac{(x)^2}{(0.0588 - x)} = \frac{(1.29 \times 10^{-2})^2}{(0.0588 - 1.29 \times 10^{-2})} \]

\[ = 3.62 \times 10^{-3} = 3.6 \times 10^{-3} \]

17.89 To solve, assemble a table of starting, change, and equilibrium concentrations. Start by converting pH to [H_3O^+]:

\[
[H_3O^+] = \text{antilog (pH)} = \text{antilog (-1.73)} = 1.86 \times 10^{-2} \text{ M}
\]

Starting M of HSO_4^- = 0.050 M

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HSO_4^- + H_2O</th>
<th>H_3O^+ + SO_4^{2-}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.050</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.050 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

The value of x equals the value of the molarity of the H_3O^+ ion, which is 1.86 \times 10^{-2} \text{ M}. Substitute into the equilibrium-constant expression to find \( K_a \):

\[ K_a = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{(x)^2}{(0.050 - x)} = \frac{(1.86 \times 10^{-2})^2}{(0.050 - 1.86 \times 10^{-2})} \]

\[ = 1.10 \times 10^{-2} = 1.1 \times 10^{-2} \]

17.90 To solve, assemble a table of starting, change, and equilibrium concentrations. Start by converting pH to [H_3O^+]:

\[
[H_3O^+] = \text{antilog (pH)} = \text{antilog (-4.10)} = 7.94 \times 10^{-5} \text{ M}
\]

Starting M of H_2PO_4^- = 0.10 M

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>H_2PO_4^- + H_2O</th>
<th>H_3O^+ + HPO_4^{2-}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.10</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.10 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

(continued)
The value of $x$ equals the value of the molarity of the $\text{H}_2\text{O}^+$ ion, which is $7.94 \times 10^{-5}$ M. Substitute into the equilibrium-constant expression to find $K_{a2}$:

$$K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = \frac{(x)^2}{(0.10-x)} = \frac{(7.94 \times 10^{-5})^2}{(0.10-7.94 \times 10^{-5})} = 6.304 \times 10^{-8} = 6.3 \times 10^{-8}$$

17.91 For the base ionization (hydrolysis) of $\text{CN}^-$ to $\text{HCN} + \text{OH}^-$, the base-ionization constant is

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.9 \times 10^{-10}} = 2.0 \times 10^{-5} = 2.0 \times 10^{-5}$$

For the base ionization (hydrolysis) of $\text{CO}_3^{2-}$ to $\text{HCO}_3^- + \text{OH}^-$, the base-ionization constant is calculated from the ionization constant ($K_{a2}$) of $\text{HCO}_3^-$, the conjugate acid of $\text{CO}_3^{2-}$.

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.8 \times 10^{-11}} = 2.0 \times 10^{-5} = 2.1 \times 10^{-5}$$

Because the constant of $\text{CO}_3^{2-}$ is larger, it is the stronger base.

17.92 For the base ionization (hydrolysis) of $\text{PO}_4^{3-}$ to $\text{HPO}_4^{2-} + \text{OH}^-$, the base-ionization constant is calculated from the ionization constant ($K_{a3}$) of $\text{HPO}_4^{2-}$, the conjugate acid of $\text{PO}_4^{3-}$.

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.8 \times 10^{-13}} = 2.0 \times 10^{-2} = 2.1 \times 10^{-2}$$

For the base ionization (hydrolysis) of $\text{SO}_4^{2-}$ to $\text{HSO}_4^- + \text{OH}^-$, the base-ionization constant is calculated from the ionization constant ($K_{a2}$) of $\text{HSO}_4^-$, the conjugate acid of $\text{SO}_4^{2-}$.

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.1 \times 10^{-2}} = 9.09 \times 10^{-13} = 9.1 \times 10^{-13}$$

Because the constant of $\text{PO}_4^{3-}$ is larger, it is the stronger base.
17.93 Assume $\text{Al}^{3+}$ is $\text{Al}^3\text{(H}_2\text{O)}_6^{3+}$. Assemble the usual table to calculate the $[\text{H}_3\text{O}^+]$ and pH. Use the usual equilibrium-constant expression.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>$\text{Al}^3\text{(H}_2\text{O)}_6^{3+}$</th>
<th>$+\text{H}_2\text{O}$</th>
<th>$\text{H}_3\text{O}^+$</th>
<th>$+\text{Al}^3\text{(H}_2\text{O)}_5\text{(OH)}^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.15</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Change</td>
<td>$-x$</td>
<td>$+x$</td>
<td>$+x$</td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>$0.15 - x$</td>
<td>$x$</td>
<td>$x$</td>
<td></td>
</tr>
</tbody>
</table>

$$
K_a = \frac{[\text{Al}^3\text{(H}_2\text{O)}_5\text{(OH)}^{2+}][\text{H}_3\text{O}^+]}{[\text{Al}^3\text{(H}_2\text{O)}_6^{3+}]} = \frac{(x)^2}{(0.15 - x)} \approx \frac{(x)^2}{(0.15)} = 1.4 \times 10^{-5}
$$

$$x = [\text{H}_3\text{O}^+] = 1.449 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.449 \times 10^{-3}) = 2.838 = 2.84$$

17.94 Assume $\text{Zn}^{2+}$ is $\text{Zn}^2\text{(H}_2\text{O)}_6^{2+}$. Assemble the usual table to calculate the $[\text{H}_3\text{O}^+]$ and pH.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>$\text{Zn}^2\text{(H}_2\text{O)}_6^{2+}$</th>
<th>$+\text{H}_2\text{O}$</th>
<th>$\text{H}_3\text{O}^+$</th>
<th>$+\text{Zn}^2\text{(H}_2\text{O)}_5\text{(OH)}^{+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.15</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Change</td>
<td>$-x$</td>
<td>$+x$</td>
<td>$+x$</td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>$0.15 - x$</td>
<td>$x$</td>
<td>$x$</td>
<td></td>
</tr>
</tbody>
</table>

Write the equilibrium-constant expression in terms of chemical symbols and substitute.

$$
K_a = \frac{[\text{Zn}^2\text{(H}_2\text{O)}_5\text{(OH)}^{+}][\text{H}_3\text{O}^+]}{[\text{Zn}^2\text{(H}_2\text{O)}_6^{2+}]} = \frac{(x)^2}{(0.15 - x)} \approx \frac{(x)^2}{(0.15)} = 2.5 \times 10^{-10}
$$

$$x = [\text{H}_3\text{O}^+] = 6.12 \times 10^{-6} \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (6.12 \times 10^{-6}) = 5.213 = 5.21$$
17.95 Calculate the concentrations of the tartaric acid ($\text{H}_2\text{Tar}$) and the hydrogen tartrate ion ($\text{HTar}^-$).

\[
(11.0 \text{ g H}_2\text{Tar} \div 150.1 \text{ g/mol}) \div 1.00 \text{ L} = 0.07328 \text{ M H}_2\text{Tar}
\]

\[
(20.0 \text{ g KHTar}^- \div 188.2 \text{ g/mol}) \div 1.00 \text{ L} = 0.1063 \text{ M [HTar]}
\]

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>$\text{H}_2\text{Tar}$ + $\text{H}_2\text{O}$</th>
<th>$\text{H}_3\text{O}^+$ + $\text{HTar}^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Starting</strong></td>
<td>0.07328</td>
<td>0</td>
</tr>
<tr>
<td><strong>Change</strong></td>
<td>-$x$</td>
<td>+$x$</td>
</tr>
<tr>
<td><strong>Equilibrium</strong></td>
<td>0.07328 - $x$</td>
<td>$x$</td>
</tr>
</tbody>
</table>

Ignoring $x$ compared to 0.07328 and 0.1063 and substituting into the $K_{a1}$ expression gives

\[
K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{HTar}^-]}{[\text{H}_2\text{Tar}]} = \frac{(0.1063 + x)(x)}{(0.07328 - x)} \approx \frac{(0.1063)(x)}{(0.07328)} = 1.0 \times 10^{-3}
\]

\[
x = [\text{H}_3\text{O}^+] = 6.89 \times 10^{-4} \text{ M}
\]

\[
\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (6.89 \times 10^{-4}) = 3.161 = 3.16
\]

17.96 Calculate the concentrations of the dihydrogen phosphate ion ($\text{H}_2\text{PO}_4^-$) and the hydrogen phosphate ion ($\text{HPO}_4^{2-}$).

\[
(13.0 \text{ g NaH}_2\text{PO}_4 \div 120.0 \text{ g/mol}) \div 1.00 \text{ L} = 0.1082 \text{ M H}_2\text{PO}_4^-
\]

\[
(15.0 \text{ g Na}_2\text{HPO}_4 \div 142.0 \text{ g/mol}) \div 1.00 \text{ L} = 0.1056 \text{ M HPO}_4^{2-}
\]

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>$\text{H}_2\text{PO}_4^-$ + $\text{H}_2\text{O}$</th>
<th>$\text{H}_3\text{O}^+$ + $\text{HPO}_4^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Starting</strong></td>
<td>0.1082</td>
<td>0</td>
</tr>
<tr>
<td><strong>Change</strong></td>
<td>-$x$</td>
<td>+$x$</td>
</tr>
<tr>
<td><strong>Equilibrium</strong></td>
<td>0.1082 - $x$</td>
<td>$x$</td>
</tr>
</tbody>
</table>

Ignoring $x$ compared to 0.1082 and 0.1056 and substituting into the $K_{a1}$ expression gives

\[
K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = \frac{(0.1056 + x)(x)}{(0.1082 - x)} \approx \frac{(0.1056)(x)}{(0.1082)} = 6.2 \times 10^{-8}
\]

\[
x = [\text{H}_3\text{O}^+] = 6.35 \times 10^{-8} \text{ M}
\]

\[
\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (6.35 \times 10^{-8}) = 7.197 = 7.20
\]
17.97 Use the Henderson-Hasselbalch equation where $[H_2CO_3] = \text{the buffer acid}$, $[HCO_3^-] = \text{the buffer base}$, and $K_{a1}$ of carbonic acid is the ionization constant.

\[
pH = -\log K_a + \log \frac{[HCO_3^-]}{[H_2CO_3]} = 7.40
\]

\[
7.40 = -\log (4.3 \times 10^{-7}) + \log \frac{[HCO_3^-]}{[H_2CO_3]}
\]

\[
\log \frac{[HCO_3^-]}{[H_2CO_3]} = 7.40 - 6.366 = 1.034
\]

\[
\frac{[HCO_3^-]}{[H_2CO_3]} = \frac{10.81}{1} = 11
\]

17.98 Use the Henderson-Hasselbalch equation where $[C_{18}H_{21}NO_3] = \text{[Cod]} = \text{the buffer base}$, and $[HC_{18}H_{21}NO_3^+] = \text{[HCod]^+} = \text{the buffer acid}$. The ionization constant is calculated as follows:

\[
K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-9}} = 1.61 \times 10^{-6}
\]

\[
pH = -\log K_a + \log \frac{[\text{Cod}]}{[\text{HCod}^+]} = 4.50
\]

\[
4.50 = -\log (1.61 \times 10^{-6}) + \log \frac{[\text{Cod}]}{[\text{HCod}^+]}
\]

\[
\log \frac{[\text{Cod}]}{[\text{HCod}^+]} = 4.50 - 5.793 = -1.293
\]

\[
\log \frac{[\text{HCod}^+]}{[\text{Cod}]} = 1.293
\]

\[
\frac{[\text{HCod}^+]}{[\text{Cod}]} = \frac{19.6}{1} = \frac{20}{1}
\]
17.99 All the OH⁻ (from the NaOH) reacts with the H₃O⁺ from HCl. Calculate the stoichiometric amounts of OH⁻ and H₃O⁺, and subtract the mol of OH⁻ from the mol of H₃O⁺. Then, divide the remaining H₃O⁺ by the total volume of 0.456 L + 0.285 L, or 0.741 L, to find the [H₃O⁺]. Then, calculate the pH.

\[
\text{Mol H}_3\text{O}^+ = (0.10 \text{ mol HCl/L}) \times 0.456 \text{ L HCl} = 0.0456 \text{ mol H}_3\text{O}^+ \\
\text{Mol OH}^- = (0.15 \text{ mol NaOH/L}) \times 0.285 \text{ L NaOH} = 0.0428 \text{ mol OH}^- \\
\text{Mol H}_3\text{O}^+ \text{ left} = (0.0456 - 0.0428) \text{ mol H}_3\text{O}^+ = 0.0028 \text{ mol H}_3\text{O}^+ \\
[H_3O^+] = 0.0028 \text{ mol H}_3\text{O}^+ \div 0.741 \text{ L total volume} = 0.0038 \text{ M} \\
\text{pH} = -\log [H_3O^+] = -\log (0.0038) = 2.42 = 2.4 
\]

17.100 All the H₃O⁺ (from the HClO₄) reacts with the OH⁻ from KOH. Calculate the stoichiometric amounts of OH⁻ and H₃O⁺, and subtract the mol of H₃O⁺ from the mol of OH⁻. Then, divide the remaining OH⁻ by the volume of 0.115 L to find the [OH⁻]. Then, calculate the pOH and pH.

\[
\text{Mol OH}^- = 2.0 \text{ g KOH} \div (56.1 \text{ g KOH/mol KOH}) = 0.0357 \text{ mol OH}^- \\
\text{Mol H}_3\text{O}^+ = (0.19 \text{ mol HClO}_4/L) \times 0.115 \text{ L HCl} = 0.0219 \text{ mol H}_3\text{O}^+ \\
\text{Mol OH}^- \text{ left} = (0.0357 - 0.0219) \text{ mol OH}^- = 0.0138 \text{ mol OH}^- \\
[OH^-] = 0.0138 \text{ mol OH}^- \div 0.115 \text{ L volume} = 0.120 \text{ M} \\
pOH = -\log [OH^-] = -\log (0.120) = 0.9208 \\
pH = 14.00 - pOH = 14.00 - 0.9208 = 13.079 = 13.08 
\]

17.101 Use BzN to symbolize benzylamine and BzNH⁺ to symbolize the benzylammonium cation. At the equivalence point, equal molar amounts of BzN and HCl react to form a solution of BzNHCl. Start by calculating the moles of BzN. Use this number to calculate the volume of HCl needed to neutralize all the BzN (and use the moles of BzN as the moles of BzNH⁺ formed at the equivalence point). Add the volume of HCl to the original 0.025 L to find the total volume of solution.

\[
(0.025 \text{ mol BzN/L}) \times 0.065 \text{ L} = 0.00162 \text{ mol BzN} \\
\text{Volume HCl} = 0.00162 \text{ mol HCl} \div (0.050 \text{ mol HCl/L}) = 0.0324 \text{ L} \\
\text{Total volume} = 0.025 \text{ L} + 0.0324 \text{ L} = 0.0574 \text{ L} \\
[BzNH^+] = (0.00162 \text{ mol BzNH}^+ \text{ from BzN}) \div 0.0574 \text{ L} = 0.0282 \text{ M} 
\]

(continued)
Because the BzNH$^+$ hydrolyzes to $\text{H}_3\text{O}^+$ and BzN, use this to calculate the [H$_3$O$^+$]. Start by calculating the $K_a$ constant of BzNH$^+$ from the $K_b$ of its conjugate base, BzN. Then, assemble the usual table of concentrations, assume x is negligible, and calculate [H$_3$O$^+$] and pH.

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.7 \times 10^{-10}} = 2.13 \times 10^{-5}$$

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>BzNH$^+$ + $\text{H}_2\text{O}$</th>
<th>$\text{H}_3\text{O}^+$</th>
<th>BzN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.0282</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.0282 - x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

Substitute into the equilibrium-constant equation.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{BzN}]}{[\text{BzNH}^+]} = \frac{(x)^2}{(0.0282 - x)} \cong \frac{(x)^2}{(0.0282)} = 2.13 \times 10^{-5}$$

$$x = [\text{H}_3\text{O}^+] = 7.7502 \times 10^{-4} \text{ M}$$

$$pH = -\log [\text{H}_3\text{O}^+] = -\log (7.7502 \times 10^{-4}) = 3.1106 = 3.11$$

17.102 At the equivalence point, equal molar amounts of HSO$_4^-$ and NaOH react to form a solution of Na$_2$SO$_4$. Start by calculating the moles of HSO$_4^-$. Use this number to calculate the volume of NaOH needed to neutralize all the HSO$_4^-$ (and use the moles of HSO$_4^-$ as the moles of SO$_4^{2-}$ formed at the equivalence point). Add the volume of NaOH to the original 0.050 L to find the total volume of solution.

Mol HSO$_4^-$ = 1.24 g NaHSO$_4$ ÷ (120.1 g NaHSO$_4$/mol NaHSO$_4$)

= 0.01032 mol HSO$_4^-$

Volume NaOH = 0.01032 mol NaOH ÷ (0.180 mol NaOH/L) = 0.05733 L

Total volume = 0.05733 L + 0.0500 L HSO$_4^-$ soln = 0.1073 L

[SO$_4^{2-}$] = (0.01032 mol SO$_4^{2-}$ from HSO$_4^-$) ÷ 0.1073 L = 0.0962 M

Because the SO$_4^{2-}$ hydrolyzes to OH$^-$ and HSO$_4^-$, use this number to calculate the [OH$^-$]. Start by calculating the $K_a$ constant of SO$_4^{2-}$ from the $K_b$ of its conjugate acid, HSO$_4^-$. Assemble the usual table of concentrations, assume x is negligible, and calculate [OH$^-$] and pH. (continued)
$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.1 \times 10^{-2}} = 9.09 \times 10^{-13}$$

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>$SO_4^{2-}$ + $H_2O$</th>
<th>$HSO_4^-$ + $OH^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.0962</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-$x$</td>
<td>$+x$</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.0962 - $x$</td>
<td>$x$</td>
</tr>
</tbody>
</table>

Substitute into the equilibrium-constant equation.

$$K_b = \frac{[HSO_4^-][OH^-]}{[SO_4^{2-}]} = \frac{(x)^2}{(0.0962 - x)} \approx \frac{(x)^2}{(0.0962)} = 9.09 \times 10^{-13}$$

$x = [OH^-] = 2.96 \times 10^{-7}$ M

$pOH = -\log [OH^-] = -\log (2.96 \times 10^{-7}) = 6.528$

$pH = 14.00 - 6.528 = 7.472 = 7.47$

17.103a. $[H_3O^+] \approx 0.100$ M

b. The 0.100-M $H_2SO_4$ ionizes to 0.100-M $H_3O^+$ and 0.100-M $HSO_4^-$. Assemble the usual table, and substitute into the $K_{a2}$ equilibrium-constant expression for $H_2SO_4$. Solve the resulting quadratic equation.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>$HSO_4^-$ + $H_2O$</th>
<th>$H_3O^+$ + $SO_4^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.100</td>
<td>0.100</td>
</tr>
<tr>
<td>Change</td>
<td>-$x$</td>
<td>$+x$</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.100 - $x$</td>
<td>0.100 + $x$</td>
</tr>
</tbody>
</table>

$x^2 + 0.111x - (1.10 \times 10^{-3}) = 0$

$$x = \frac{-0.111 \pm \sqrt{(0.111)^2 + 4(1.10 \times 10^{-3})}}{2}$$

$$= \frac{-0.111 \pm 0.1293}{2}$$

$$x = 9.154 \times 10^{-3}$$ M

$[H_3O^+] = 0.100 + x = 0.100 + 0.009154 = 0.109 = 0.11$ M
17.104a. \([H_3O^+] \cong 0.150 \text{ M}\)

b. The 0.150-M \(H_2SeO_4\) ionizes to 0.150-M \(H_3O^+\) and 0.150-M \(HSeO_4^-\). Assemble the usual table, and substitute into the \(K_{a2}\) equilibrium-constant expression for \(H_2SeO_4\). Solve the resulting quadratic equation.

Set up the table.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>(HSeO_4^-) + (H_2O)</th>
<th>(H_3O^+) + (SeO_4^{2-})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.150</td>
<td>0.150</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.150 - x</td>
<td>0.150 + x</td>
</tr>
</tbody>
</table>

\[x^2 + 0.162x - (1.80 \times 10^{-3}) = 0\]

\[x = \frac{-0.162 \pm \sqrt{(0.162)^2 + 4(1.8 \times 10^{-3})}}{2}\]

\[x = -0.162 \pm 0.1828\]

\[x = 1.04 \times 10^{-2}\]

\([H_3O^+] = 0.150 + 0.0104 = 0.1604 = 0.16 \text{ M}\)

17.105a. From the pH, calculate the \(H_3O^+\) ion concentration:

\([H_3O^+] = 10^{-pH} = 10^{-5.82} = 1.51 \times 10^{-6} \text{ M}\)

Use the table approach, giving the starting, change, and equilibrium concentrations.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>(CH_3NH_3^+) + (H_2O)</th>
<th>(CH_3NH_2^+) + (H_3O^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.10</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.10 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

From the hydronium ion concentration, \(x = 1.51 \times 10^{-6}\). Substituting into the equilibrium-constant expression gives

\[K_a = \frac{[CH_3NH_2][H_3O^+]}{[CH_3NH_3^+]^2} = \frac{(x)^2}{(0.10 - x)} \cong \frac{(1.51 \times 10^{-6})^2}{(0.10)} = 2.28 \times 10^{-11}\]

\[= 2.3 \times 10^{-11}\] (continued)
b. Now, use $K_w$ to calculate the value of $K_b$:

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{2.28 \times 10^{-11}} = 4.38 \times 10^{-4} = 4.4 \times 10^{-4}$$

c. The equilibrium concentration of $\text{CH}_3\text{NH}_3^+$ is approximately $0.450 \text{ mol/1.00 L} = 0.450 \text{ M}$. Use $[\text{CH}_3\text{NH}_3] \cong 0.250 \text{ M}$. For $K_a$, we get

$$K_a = \frac{[\text{CH}_3\text{NH}_2][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{NH}_3^+]} \cong \frac{(0.250)[\text{H}_3\text{O}^+]}{(0.450)} = 2.28 \times 10^{-11}$$

Solving for $[\text{H}_3\text{O}^+]$ gives

$$[\text{H}_3\text{O}^+] \cong \frac{(2.28 \times 10^{-11})(0.450)}{0.250} = 4.10 \times 10^{-11} \text{ M}$$

Thus, the pH is

$$\text{pH} = -\log (4.10 \times 10^{-11}) = 10.387 = 10.39$$

17.106a. From the pOH, calculate the $\text{OH}^-$ ion concentration:

$$[\text{OH}^-] = 10^{-p\text{OH}} = 10^{-5.31} = 4.90 \times 10^{-6} \text{ M}$$

Use the table approach, giving the starting, change, and equilibrium concentrations.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>$\text{C}_6\text{H}_5\text{COO}^-$</th>
<th>$\text{H}_2\text{O}$</th>
<th>$\text{C}_6\text{H}_5\text{COOH} + \text{OH}^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.15</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.15 - x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

From the hydroxide ion concentration, $x = 4.90 \times 10^{-6}$. Substituting into the equilibrium-constant expression gives

$$K_b = \frac{[\text{C}_6\text{H}_5\text{COOH}][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{COO}^-]} \cong \frac{(x)^2}{(0.15 - x)} \cong \frac{(4.90 \times 10^{-6})^2}{(0.15)} = 1.60 \times 10^{-10}$$

$$= 1.6 \times 10^{-10}$$

(continued)
b. Now, use $K_w$ to calculate the value of $K_a$:

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.60 \times 10^{-10}} = 6.25 \times 10^{-5} = 6.3 \times 10^{-5}$$

c. The reaction is:

$$C_6H_5COOH + H_2O \rightarrow C_6H_5COO^- + H_3O^+$$

From the pH, calculate the $H_3O^+$ and $C_6H_5COO^-$ ion concentrations:

$$[C_6H_5COO^-] = [H_3O^+] = 10^{-pH} = 10^{-2.83} = 1.48 \times 10^{-3} \text{ M}$$

Use the value of $K_a$ to calculate the solubility of $C_6H_5COOH = y$.

$$K_a = \frac{[C_6H_5COO^-][H_3O^+]}{[C_6H_5COOH]} = \frac{(1.48 \times 10^{-3})^2}{y} = 6.25 \times 10^{-5}$$

Solving for $y$ gives the molar solubility

$$y = \frac{(1.48 \times 10^{-3})^2}{(6.25 \times 10^{-5})} = 0.0350 = 0.035 \text{ M}$$

17.107 a. True. Weak acids have small $K_a$ values, so most of the solute is present as undissociated molecules.

b. True. Weak acids have small $K_a$ values, so most of the solute is present as the molecule.

c. False. The hydroxide concentration equals the hydronium concentration only in neutral solutions.

d. False. If HA were a strong acid, the pH would be equal to two.

e. False. The $H_3O^+$ would be 0.010 if HA were a strong acid.

f. True. For every HA molecule that dissociates, one $H_3O^+$ is generated along with one $A^-$.

17.108 a. True. Approximately 1 percent or less of most weak bases react with water.

b. True. Very little base has reacted with water. For weak bases, most of the base is present as the molecule.

(continued)
c. False. This is a basic solution, so there will be very little $\text{H}_3\text{O}^+$.

d. False. If B were a strong base, the $[\text{OH}^-]$ would be equal to 0.10 M.

e. True. $\text{B} + \text{H}_2\text{O} \rightarrow \text{BH}^+ + \text{OH}^-$

f. False. Most B is present as B, so little $\text{OH}^-$ is produced upon addition of the base to water.

17.109 a. At the equivalence point, moles of acid equal moles of base. Thus,

$$\text{moles acid} = 0.115 \text{ mol/L} \times 0.03383 \text{ L} = 3.890 \times 10^{-3}$$

The molar mass is

$$\text{Molar mass} = \frac{0.288 \text{ g}}{3.890 \times 10^{-3} \text{ mol}} = 74.04 \text{ g/mol}$$

b. At the 50 percent titration point, $\text{pH} = \text{pK}_a$. Since the pH measurement wasn't made, it is necessary to obtain an $[\text{A}^-]/[\text{HA}]$ ratio. The ratio can be in terms of moles, percent, mL, or M because the units end up canceling out. First, use the pH to obtain the $\text{H}_3\text{O}^+$ ion concentration. Express the other concentrations in mL for convenience.

$$[\text{H}_3\text{O}^+] = 10^{-4.92} = 1.20 \times 10^{-5} \text{ M}$$

$$\text{HA}_a \approx 33.83 \text{ mL}$$

$$[\text{HA}] = 33.83 \text{ mL} - 17.54 \text{ mL} = 16.29 \text{ mL}$$

$$[\text{A}^-] = [\text{OH}^-] = 17.54 \text{ mL}$$

$$K_a = [\text{H}_3\text{O}^+] \times \frac{[\text{A}^-]}{[\text{HA}]} = 1.20 \times 10^{-5} \text{ M} \times \frac{17.54 \text{ mL}}{16.29 \text{ mL}} = 1.29 \times 10^{-5}$$

$$= 1.3 \times 10^{-5}$$

17.110 a. At the equivalence point, moles of base equal moles of acid. Thus

$$\text{moles base} = 0.135 \text{ mol/L} \times 0.03924 \text{ L} = 5.297 \times 10^{-3}$$

The molar mass is

$$\text{Molar mass} = \frac{0.239 \text{ g}}{5.297 \times 10^{-3} \text{ mol}} = 45.11 \text{ g/mol}$$

(continued)
b. At the 50 percent titration point, pK\(_b\) = pOH. Since the pH measurement wasn't made, it is necessary to obtain a [HB\(^+\)]/[B] ratio. The ratio can be in terms of moles, percent, mL, or M because the units end up canceling out. First, use the pH to obtain the OH\(^-\) ion concentration. Express the other concentrations in mL for convenience.

\[
pOH = 14.00 - 10.73 = 3.27
\]

\[
[OH^-] = 10^{-3.27} = 5.370 \times 10^{-4}
\]

\[
B_0 \cong 39.24 \text{ mL}
\]

\[
[B] \cong 39.24 - 18.35 = 20.89 \text{ mL}
\]

\[
[HB^+] \cong [H_3O^+] = 18.35 \text{ mL}
\]

\[
K_b = [OH^-] \times \frac{[HB^+][OH^-]}{[B]} = 5.370 \times 10^{-4} \times \frac{18.35 \text{ mL}}{20.89 \text{ mL}} = 4.72 \times 10^{-4}
\]

\[
= 4.7 \times 10^{-4}
\]

17.111a. Initial pH: Use the table approach, and give the starting, change, and equilibrium concentrations.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>NH(_3) + H(_2)O</th>
<th>NH(_4^+) + OH(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.10</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.10 - x</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

Substituting into the equilibrium-constant expression gives

\[
K_b = \frac{[NH_4^+][OH^-]}{[OH^-]} = \frac{(x)^2}{(0.10 - x)} \equiv \frac{(x)^2}{(0.10)} = 1.8 \times 10^{-5}
\]

Rearranging and solving for x gives

\[
x = [OH^-] = \sqrt{(0.10)(1.8 \times 10^{-5})} = 1.34 \times 10^{-3} \text{ M}
\]

\[
pOH = - \log (1.34 \times 10^{-3}) = 2.873
\]

\[
pH = 14 - pOH = 14 - 2.873 = 11.127 = 11.13
\]

(continued)
30 percent titration point: Express the concentrations as percents for convenience.

\[ [\text{NH}_3] \approx 70\% \text{ and } [\text{NH}_4^+] \approx 30\% \]

Plug into the equilibrium-constant expression.

\[ K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(30\%)(x)}{(70\%)} = 1.8 \times 10^{-5} \]

Solving for \( x \) gives

\[ x = [\text{OH}^-] = 1.8 \times 10^{-5} \times \frac{70\%}{30\%} = 4.20 \times 10^{-5} \text{ M} \]

\[ \text{pOH} = -\log (4.20 \times 10^{-5}) = 4.377 \]

\[ \text{pH} = 14 - \text{pOH} = 14 - 4.377 = 9.623 = 9.6 \]

50 percent titration point:

\[ [\text{NH}_4^+] = [\text{NH}_3] \]

\[ K_b = [\text{OH}^-] = 1.8 \times 10^{-5} \text{ M} \]

\[ \text{pOH} = -\log (1.8 \times 10^{-5}) = 4.744 \]

\[ \text{pH} = 14 - \text{pOH} = 14 - 4.744 = 9.26 \]

100 percent titration point:

The \( \text{NH}_4\text{Cl} \) that is produced has undergone a two-fold dilution.

\[ [\text{NH}_4^+] = 0.0500 \text{ M} \]

Use the table approach, and give the starting, change, and equilibrium concentrations.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>\text{NH}_4^+</th>
<th>\text{H}_2\text{O} &amp; \boxplus \boxminus</th>
<th>\text{NH}_3</th>
<th>\text{H}_3\text{O}^+</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.0500</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.0500 - x</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

(continued)
Now, use $K_w$ to calculate the value of $K_a$:

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.55 \times 10^{-10}$$

Plug into the equilibrium-constant expression.

$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{(x)^2}{(0.0500 - x)} \cong \frac{(x)^2}{(0.0500)} = 5.55 \times 10^{-10}$$

Solving for $x$ gives

$$x = [\text{H}_3\text{O}^+] = \sqrt{0.0500 \times \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}} = 5.27 \times 10^{-6} \text{ M}$$

$$\text{pH} = -\log (5.27 \times 10^{-6}) = 5.278 = 5.28$$

b. The solution is acidic because the $\text{NH}_4^+$ ion reacts with water to produce acid. Ammonium chloride is the salt of a weak base and a strong acid.

17.112  a. Initial pH: Use the table approach, and give the starting, change, and equilibrium concentrations. Here, $A^- = \text{CH}_3\text{CH}_2\text{COO}^-$.  

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HA + H$_2$O</th>
<th>H$_3$O$^+$ + A$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.15</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.15 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

Substituting into the equilibrium-constant expression gives

$$K_a = \frac{[\text{H}_3\text{O}^+][A^-]}{[\text{HA}]} = \frac{(x)^2}{(0.15 - x)} \cong \frac{(x)^2}{(0.15)} = 1.3 \times 10^{-5}$$

Rearranging and solving for $x$ gives

$$x = [\text{H}_3\text{O}^+] = \sqrt{(0.15)(1.3 \times 10^{-5})} = 1.40 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log (1.40 \times 10^{-3}) = 2.853 = 2.85$$

(continued)
50 percent titration point:

\[ [\text{H}_3\text{O}^+] = [\text{A}^-] = K_a = 1.3 \times 10^{-5} \text{ M} \]

\[ \text{pH} = -\log (1.3 \times 10^{-5}) = 4.886 = 4.89 \]

60 percent titration point: Express the concentrations as percents for convenience.

\[ [\text{HA}] \approx 40\% \text{ and } [\text{A}^-] \approx 60\% \]

Plug into the equilibrium-constant expression.

\[ K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \approx \frac{(60\%)(x)}{(40\%)} = 1.3 \times 10^{-5} \]

Solving for \( x \) gives

\[ x = [\text{H}_3\text{O}^+] = 1.3 \times 10^{-5} \times \frac{40\%}{60\%} = 8.67 \times 10^{-6} \text{ M} \]

\[ \text{pH} = -\log (8.67 \times 10^{-6}) = 5.062 = 5.06 \]

100 percent titration point:

The salt produced has undergone a two-fold dilution.

\[ [\text{A}^-] = 0.0750 \text{ M} \]

Use the table approach, and give the starting, change, and equilibrium concentrations.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>A(^-) + H(_2)O</th>
<th>HA + OH(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.0750</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.0750 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

Now, use \( K_w \) to calculate the value of \( K_b \):

\[ K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.3 \times 10^{-5}} = 7.69 \times 10^{-10} \]

(continued)
Plug into the equilibrium-constant expression.

\[ K_b = \frac{[HA][OH^-]}{[A^-]} = \frac{x^2}{0.0750 - x} \approx \frac{x^2}{0.0750} = 7.69 \times 10^{-10} \]

Solving for \( x \) gives

\[ x = [OH^-] = \sqrt{0.0750 \times 7.69 \times 10^{-10}} = 7.59 \times 10^{-6} \text{ M} \]

\[ \text{pOH} = - \log (7.59 \times 10^{-6}) = 5.120 \]

\[ \text{pH} = 14 - \text{pOH} = 14 - 5.120 = 8.880 = 8.88 \]

b. The solution is basic because the propionate ion reacts with water to produce \( \text{OH}^- \). Potassium propionate is the salt of a weak acid and a strong base.

17.113a. Select the conjugate pair that has a \( pK_a \) value closest to a pH of 2.88.

\( pK_a (\text{H}_2\text{C}_2\text{O}_4) = 1.25 \)

\( pK_a (\text{H}_3\text{PO}_4) = 2.16 \)

\( pK_a (\text{HCOOH}) = 3.77 \)

Therefore, the best pair is \( \text{H}_3\text{PO}_4 \) and \( \text{H}_2\text{PO}_4^- \).

b. Using the Henderson-Hasselbalch equation,

\[ \text{pH} = pK_a + \log \frac{[A^-]}{[HA]} \]

\[ 2.88 = 2.16 + \log \frac{[A^-]}{[HA]} \]

\[ \log \frac{[A^-]}{[HA]} = 0.72 \]

\[ \frac{[A^-]}{[HA]} = 10^{0.72} = 5.24 \]

(continued)
Therefore, 5.24 times more conjugate base is needed than acid. Since the starting concentrations of \( \text{H}_3\text{PO}_4 \) (HA) and \( \text{H}_2\text{PO}_4^- \) (A\(^-\)) are the same, the volume of A\(^-\) needed is 5.24 times the volume of HA needed. For 50 mL of buffer, this is

\[
50 \text{ mL} = \text{vol HA} + \text{vol A}^- = \text{vol HA} + 5.24 \text{ vol HA} = 6.24 \text{ vol HA}
\]

Therefore, the volume of 0.10 M \( \text{H}_3\text{PO}_4 \) required is

\[
\frac{50 \text{ mL}}{6.24} = 8.01 \text{ mL} = 8 \text{ mL}
\]

The volume of 0.10 M \( \text{H}_2\text{PO}_4^- \) required is

\[
50 \text{ mL} - 8.01 \text{ mL} = 42.0 \text{ mL} = 42 \text{ mL}
\]

17.114a. Select the conjugate pair that has a pK\(_a\) value closest to a pH of 6.96.

\[
pK_a (\text{NH}_4^+) = 9.25
\]

\[
pK_a (\text{H}_2\text{CO}_3) = 6.37
\]

\[
pK_a (\text{H}_2\text{PO}_4^-) = 7.21
\]

Therefore, the best pair is \( \text{H}_2\text{PO}_4^- \) and \( \text{HPO}_4^{2-} \).

b. Using the Henderson-Hasselbalch equation,

\[
\text{pH} = pK_a + \log \frac{[A^-]}{[HA]}
\]

\[
6.96 = 7.21 + \log \frac{[A^-]}{[HA]}
\]

\[
\log \frac{[A^-]}{[HA]} = -0.25
\]

\[
\frac{[A^-]}{[HA]} = 10^{-0.25} = 0.562
\]

Therefore, 0.562 times more conjugate base is needed than acid. Since the starting concentrations of \( \text{H}_2\text{PO}_4^- \) (HA) and \( \text{HPO}_4^{2-} \) (A\(^-\)) are the same, the volume of A\(^-\) needed is 5.24 times the volume of HA needed. For 100 mL of buffer, this is

\[
100 \text{ mL} = \text{vol HA} + \text{vol A}^- = \text{vol HA} + 0.562 \text{ vol HA} = 1.562 \text{ vol HA}
\]

(continued)
Therefore, the volume of 0.10 M H$_2$PO$_4^-$ required is

\[
\text{vol H}_2\text{PO}_4^- = \frac{100 \text{ mL}}{1.562} = 64.02 \text{ mL} = 64 \text{ mL}
\]

The volume of 0.10 M HPO$_4^{2-}$ required is

\[
100 \text{ mL} - 64.02 \text{ mL} = 35.98 \text{ mL} = 36 \text{ mL}
\]

17.115a. At the equivalence point, moles of base equal moles of acid. Therefore,

\[
M_{\text{NH}_2\text{OH}} \times 25.0 \text{ mL} = 0.150 \text{ M} \times 35.8 \text{ mL}
\]

\[
M_{\text{NH}_2\text{OH}} = \frac{0.150 \text{ M} \times 35.8 \text{ mL}}{25.0 \text{ mL}} = 0.2148 = 0.215
\]

b. Concentration of NH$_3$OH$^+$ at the equivalence point is

\[
[\text{NH}_3\text{OH}^+] = \frac{(25.0 \text{ mL})(0.215 \text{ M})}{25.0 \text{ mL} + 35.8 \text{ mL}} = 0.08840 \text{ M}
\]

\[
K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.1 \times 10^{-8}} = 9.09 \times 10^{-7}
\]

Use the table approach, and give the starting, change, and equilibrium concentrations.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>NH$_3$OH$^+$</th>
<th>H$_2$O</th>
<th>NH$_2$OH</th>
<th>H$_3$O$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.08840</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
<td>0</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.08840 - x</td>
<td>x</td>
<td>x</td>
<td>0</td>
</tr>
</tbody>
</table>

Substituting into the equilibrium-constant expression gives

\[
K_a = \frac{[\text{NH}_2\text{OH}][\text{H}_3\text{O}^+]}{[\text{NH}_3\text{OH}^+]} = \frac{(x)^2}{(0.08840 - x)} \approx \frac{(x)^2}{(0.08840)} = 9.09 \times 10^{-7}
\]

Rearranging and solving for x gives

\[
x = [\text{H}_3\text{O}^+] = \sqrt{(0.08840)(9.09 \times 10^{-7})} = 2.83 \times 10^{-4} \text{ M}
\]

\[
pH = -\log (2.84 \times 10^{-4}) = 3.547 = 3.55
\]

(continued)
c. You need an indicator to change pH around pH of 3 to 4. Therefore, the appropriate indicator is bromophenol blue. Select an indicator that changes color around the equivalence point.

17.116a. At the equivalence point, moles of base equal moles of acid. The molar mass of NaHCO$_3$ is 84.01 g/mol. Therefore,

$$\text{mol base} = \frac{\text{mol acid}}{84.01 \text{ g NaHCO}_3} \times 1 \text{ mol NaHCO}_3$$

$$= 6.690 \times 10^{-3} \text{ mol}$$

The molarity of the base is

$$M_{\text{NaOH}} = \frac{6.690 \times 10^{-3} \text{ mol}}{0.04236 \text{ L}} = 0.1579 = 0.158 \text{ M}$$

b. The concentration of CO$_3^{2-}$ at the equivalence point is

$$[\text{CO}_3^{2-}] = \frac{6.690 \times 10^{-3} \text{ mol}}{0.02500 \text{ L} + 0.04236 \text{ L}} = 0.09932 \text{ M}$$

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.8 \times 10^{-11}} = 2.08 \times 10^{-4}$$

Use the table approach, and give the starting, change, and equilibrium concentrations.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>CO$_3^{2-}$</th>
<th>H$_2$O</th>
<th>HCO$_3^-$</th>
<th>OH$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.09932</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.09932 - x</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

Substituting into the equilibrium-constant expression gives

$$K_b = \frac{[\text{HCO}_3^-][\text{OH}^-]}{[\text{CO}_3^{2-}]} = \frac{x^2}{0.09932 - x} \approx \frac{x^2}{0.09932} = 2.08 \times 10^{-4}$$

Rearranging and solving for $x$ gives

$$x = [\text{OH}^-] = \sqrt{(0.09932)(2.08 \times 10^{-4})} = 4.55 \times 10^{-3} \text{ M}$$

(continued)
\[
pH = 14 - \text{pOH} = 14 - 2.342 = 11.66 \\
c. Alizarin yellow R. It changes color around the equivalence point.
\]

17.117 a. \( \text{H}_3\text{O}^+(\text{aq}) + \text{NH}_3(\text{aq}) \rightarrow \text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \)

b. \( \text{NH}_4^+(\text{aq}) + \text{OH}^- (\text{aq}) \rightarrow \text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \)

c. Initial:
\[
\text{mol NH}_3 = 1.0 \text{ mol/L} \times 0.100 \text{ L} = 0.100 \text{ = 0.10 mol} \\
\text{mol NH}_4^+ = 0.50 \text{ mol/L} \times 0.100 \text{ L} \times \frac{2 \text{ mol NH}_4^+}{1 \text{ mol (NH}_4)_2\text{SO}_4} = 0.100 = 0.10 \text{ mol}
\]

After addition of HCl: The HCl is completely consumed by producing 0.0100 mol of \( \text{NH}_4^+ \). The amount of \( \text{NH}_3 \) is decreased by 0.0100 mol.
\[
\text{mol HCl added} = 1.00 \text{ mol/L} \times 0.0100 \text{ L} = 0.0100 \text{ mol} \\
\text{mol NH}_3 = 0.100 - 0.01000 = 0.090 = 0.09 \text{ mol} \\
\text{mol NH}_4^+ = 0.100 + 0.01000 = 0.110 = 0.11 \text{ mol}
\]
The reaction is:
\[
\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^- 
\]
Substituting into the equilibrium-constant expression gives
\[
K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(0.110)[\text{OH}^-]}{(0.090)} = 1.8 \times 10^{-5}
\]
Rearranging and solving for [OH\(^-\)] gives
\[
[\text{OH}^-] = 1.8 \times 10^{-5} \times \frac{0.090}{0.110} = 1.47 \times 10^{-5} \text{ M}
\]
\[
p\text{OH} = - \log (1.47 \times 10^{-5}) = 4.83 \\
p\text{H} = 14 - p\text{OH} = 14 - 4.83 = 9.17 = 9.2
\]
d. This is a buffer system, so the ratio of \( \text{NH}_4^+/\text{NH}_3 \) has not changed very much.
17.118 a. Use the table approach, and give the starting, change, and equilibrium concentrations. The initial concentration of formic acid (HCOOH) is 0.150 mol/0.425 L = 0.3529 M.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>HCOOH + H₂O ⇌ H₃O⁺ + HCOO⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting</td>
<td>0.3529</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
</tr>
<tr>
<td></td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.3529 - x</td>
</tr>
</tbody>
</table>

Substituting into the equilibrium-constant expression gives

$$K_a = \frac{[HCOO^-][H_3O^+]}{[HCOOH]} = \frac{(x)^2}{(0.3529 - x)} \approx \frac{(0.3529)^2}{(0.3529)} = 1.7 \times 10^{-4}$$

Rearranging and solving for x gives

$$x = [H_3O^+] = [HCOO^-] = \sqrt{(0.3529)(1.7 \times 10^{-4})} = 7.74 \times 10^{-3} = 7.7 \times 10^{-3} M$$

b. To decrease the HCOO⁻ concentration by a factor of ten, the concentration must be reduced to 7.74 x 10⁻⁴ M. The change in equilibrium is

$$HCOOH(aq) + H_2O(l) ⇌ H_3O^+(aq) + HCOO^-(aq)$$

Assume the changes in concentration are small, so [HCOOH] ≈ 0.3529 M. Substitute into the rearranged equilibrium-constant equation.

$$[H_3O^+] = \frac{[HCOOH]K_a}{[HCOO^-]} = \frac{(0.3529)(1.7 \times 10^{-4})}{7.74 \times 10^{-4}} = 0.0775 = 0.078 M$$

$$0.0775 M \times 425 mL = 2.00 M \times V$$

$$V = 16.4 = 16 mL$$

c. This is the common ion effect. An increase in the H₃O⁺ concentration shifts the equilibrium so the percent dissociation of HCOOH is decreased.
17.119a. From the pH \( [\text{H}_3\text{O}^+] = 10^{-7.44} = 3.63 \times 10^{-8} \) M. The reaction is
\[
\text{H}_2\text{PO}_4^-(aq) + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HPO}_4^{2-}(aq) \quad K_{a_2} = 6.2 \times 10^{-8}
\]

\[
K_{a_2} = \frac{[\text{HPO}_4^{2-}] [\text{H}_3\text{O}^+]}{[\text{H}_2\text{PO}_4^-]}
\]

Rearranging gives
\[
\frac{[\text{H}_2\text{PO}_4^-]}{[\text{HPO}_4^{2-}]} = \frac{[\text{H}_3\text{O}^+]}{K_{a_2}} = \frac{3.63 \times 10^{-8}}{6.2 \times 10^{-8}} = \frac{0.5855}{1} = 0.59 \text{ to 1}
\]

Or, using the Henderson-Hasselbalch equation
\[
\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}
\]

\[7.44 = 7.21 + \log \frac{[\text{base}]}{[\text{acid}]}
\]

\[
\log \frac{[\text{base}]}{[\text{acid}]} = 0.23
\]

\[
\frac{[\text{base}]}{[\text{acid}]} = 10^{0.23} = 1.71
\]

You must invert each side. The result is
\[
\frac{[\text{acid}]}{[\text{base}]} = \frac{1}{1.71} = \frac{0.5857}{1} = 0.59 \text{ to 1}
\]

b. \( [\text{H}_3\text{O}^+] = K_{a_2} = \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}
\]

If \( \text{HPO}_4^{2-} = 1.00 \text{ mol} \), then when 25 percent of it is converted into \( \text{H}_2\text{PO}_4^- \), 0.75 mol remain, and \( \text{H}_2\text{PO}_4^- \) becomes \( 0.586 + 0.25 = 0.836 \text{ mol} \). Therefore,
\[
[\text{H}_3\text{O}^+] = 6.2 \times 10^{-8} \times \frac{0.836}{0.75} = 6.91 \times 10^{-8}
\]

\[
\text{pH} = - \log (6.91 \times 10^{-8}) = 7.161 = 7.16
\]

(continued)
c. Assume H$_2$PO$_4^-$ = 0.586 mol. Then, H$_2$PO$_4^-$ remaining = 0.586 - (0.15 x 0.586) 
\[= 0.85 \times 0.586 = 0.498 \text{ mol left}\]
The moles of HPO$_4^{2-}$ = 1.00 + (0.15 x 0.586) = 1.088 mol.

\[[H_3O^+] = 6.2 \times 10^{-8} \times \frac{0.498}{1.088} = 2.84 \times 10^{-8} \text{ M}\]

\[\text{pH} = - \log (2.84 \times 10^{-8}) = 7.547 = 7.55\]

17.120a. From the pH, [H$_3$O$^+$] = $10^{-7.42} = 3.80 \times 10^{-8}$ M. The reaction is

H$_2$CO$_3$(aq) + H$_2$O(l) $\rightarrow$ H$_3$O$^+$ (aq) + HCO$_3^-$ (aq) \hspace{1cm} K_a = 4.3 \times 10^{-7}

\[K_a = \frac{[HCO_3^-][H_3O^+]}{[H_2CO_3]}\]

Rearranging gives

\[\frac{[H_2CO_3]}{[HCO_3^-]} = \frac{[H_3O^+]}{K_a} = \frac{3.80 \times 10^{-8}}{4.3 \times 10^{-7}} = \frac{0.0884}{1} = 0.088 \text{ to 1}\]

Or, using the Henderson-Hasselbalch equation

\[\text{pH} = pK_a + \log \frac{[\text{base}]}{[\text{acid}]}\]

7.42 = 6.367 + log \[\frac{[\text{base}]}{[\text{acid}]}\]

\[\log \frac{[\text{base}]}{[\text{acid}]} = 1.053\]

\[\frac{[\text{base}]}{[\text{acid}]} = 10^{1.053} = 11.30\]

You must invert each side. The result is

\[\frac{[\text{acid}]}{[\text{base}]} = \frac{1}{11.30} = \frac{0.0885}{1} = 0.089 \text{ to 1}\]

(continued)
b. If HCO₃⁻ = 1.00 mol, then when 15 percent of it is converted into H₂CO₃, 0.85 mol remain, and H₂CO₃ becomes 0.0884 + 0.15 = 0.238 mol. Therefore,

\[ [H_3O^+] = 4.3 \times 10^{-7} \times \frac{0.238}{0.85} = 1.20 \times 10^{-7} \text{ M} \]

pH = - log (1.20 \times 10^{-7}) = 6.920 = 6.92

c. Assume H₂CO₃ = 0.0884 mol. Then, HCO₃⁻ = 0.0884 - 0.25 \times 0.0884

= 0.75 \times 0.0884 = 0.0663 \text{ mol left}

The moles of HCO₃⁻ = 1.000 + 0.25 \times 0.0884 = 1.0221 mol.

\[ [H_3O^+] = 4.3 \times 10^{-7} \times \frac{0.0663}{1.0221} = 2.79 \times 10^{-8} \text{ M} \]

\[ \text{pH} = - \log (2.79 \times 10^{-8}) = 7.547 = 7.55 \]

17.121a. H₂A + H₂O ⇄ H₃O⁺ + HA⁻ \quad K_{a₁}

HA⁻ + H₂O ⇄ H₃O⁺ + A²⁻ \quad K_{a₂}

H₂A + 2 H₂O ⇄ 2 H₃O⁺ + A²⁻, \quad K = K_{a₁} \times K_{a₂}

b. H₂A >> H₃O⁺ = HA⁻ >> A²⁻

c. H₂A + H₂O ⇄ H₃O⁺ + HA⁻ \quad K_{a₁} = 1.0 \times 10^{-3}

0.0250 - x 

K_{a₁} = \frac{[HA^-][H₃O^+]}{[H₂A]} = \frac{(x)^2}{(0.0250 - x)} = 1.0 \times 10^{-3}

Rearranging into a quadratic equation and solving for x gives

\[ x^2 + (1.0 \times 10^{-3})x + (-2.50 \times 10^{-5}) = 0 \]

\[ x = \frac{-(1.0 \times 10^{-3}) \pm \sqrt{(1.0 \times 10^{-3})^2 - 4(1)(-2.50 \times 10^{-5})}}{2} \]

x = [H₃O⁺] = [HA⁻] = 4.52 \times 10^{-3} = 4.5 \times 10^{-3} \text{ M}

\[ \text{pH} = - \log (4.52 \times 10^{-3}) = 2.344 = 2.34 \]

\[ [H₂A] = 0.0250 - x = 0.0250 - 4.52 \times 10^{-3} = 0.02048 = 0.0205 \text{ M} \]

(continued)
d. \[ \text{HA}^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^{2-} \quad K_{a_2} = 4.6 \times 10^{-5} \]

\[ 4.52 \times 10^{-3} - y = 4.52 \times 10^{-3} + y \]

Assume \( y \) is small compared to \( 4.52 \times 10^{-3} \) M. Substitute into the rearranged equilibrium-constant equation to get

\[ [\text{A}^{2-}] = \frac{[\text{HA}^-]K_{a_2}}{[\text{H}_3\text{O}^+]} = \frac{(4.52 \times 10^{-3})(4.6 \times 10^{-5})}{(4.52 \times 10^{-3})} = 4.6 \times 10^{-5} \text{ M} \]

17.122a. \[ \text{H}_2\text{A} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HA}^- \quad K_{a_1} \]

\[ \text{HA}^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^{2-} \quad K_{a_2} \]

\[ \text{H}_2\text{A} + 2 \text{H}_2\text{O} \rightleftharpoons 2 \text{H}_3\text{O}^+ + \text{A}^{2-}, \quad K = K_{a_1} x K_{a_2} \]

b. \( \text{H}_2\text{A} \gg \text{H}_3\text{O}^+ = \text{HA}^- \gg \text{A}^{2-} \)

c. \[ \text{H}_2\text{A} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HA}^- \quad K_{a_1} = 4.0 \times 10^{-4} \]

\[ 0.0100 - x \quad x \quad x \]

Substitute into the equilibrium-constant equation to get

\[ K_{a_1} = \frac{[\text{HA}^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{A}]} = \frac{(x)^2}{(0.0100 - x)} = 4.0 \times 10^{-4} \]

Rearranging into a quadratic equation and solving for \( x \) gives

\[ x^2 + (4.0 \times 10^{-4})x + (-4.00 \times 10^{-6}) = 0 \]

\[ x = \frac{- (4.0 \times 10^{-4}) \pm \sqrt{(4.0 \times 10^{-4})^2 - (4)(1)(-4.00 \times 10^{-6})}}{2} \]

\[ x = [\text{H}_3\text{O}^+] = [\text{HA}] = 1.81 \times 10^{-3} = 1.8 \times 10^{-3} \text{ M} \]

\[ \text{pH} = - \log (1.81 \times 10^{-3}) = 2.742 = 2.74 \]

\[ [\text{H}_2\text{A}] = 0.0100 - x = 0.0100 - 1.81 \times 10^{-3} = 0.00819 = 0.0082 \text{ M} \]

(continued)
d. $\text{HA}^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^{2-}$ \hspace{1cm} $K_{a_2} = 9.0 \times 10^{-6}$

$1.81 \times 10^{-3} - y \hspace{1cm} 1.81 \times 10^3 + y \hspace{1cm} y$

Assume $y$ is small compared to $1.81 \times 10^{-3}$ M. Substitute into the rearranged equilibrium-constant equation to get

$$[A^{2-}] = \frac{[\text{HA}^-]K_{a_2}}{[\text{H}_3\text{O}^+]} = \frac{(1.81 \times 10^{-3})(9.0 \times 10^{-6})}{(1.81 \times 10^{-3})} = 9.0 \times 10^{-6} \text{ M}$$

17.123a. From the pH, $[\text{H}_3\text{O}^+] = 10^{-4.45} = 3.55 \times 10^{-5} \text{ M}$. The NaCH$_3$COO is generated by the acid-base reaction, resulting in the formation of a buffer solution. The reaction is

$$\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^- \hspace{1cm} K_a = 1.7 \times 10^{-5}$$

$0.15 - x \hspace{1cm} x \hspace{1cm} x$

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

Rearranging gives

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

$$\frac{x}{0.15 - x} = \frac{1.7 \times 10^{-5}}{3.55 \times 10^{-5}}$$

Solving for $x$ gives $x = 0.0486 \text{ mol}$. Therefore, the molar concentration is

$$[\text{CH}_3\text{COO}^-] = 0.0486 \text{ mol}/0.375 \text{ L} = 0.1296 = 0.13 \text{ M}$$

b. moles OH$^- = \text{ moles CH}_3\text{COO}^-$

$$0.0486 \text{ mol} = 0.25 \text{ M} \times V_{\text{NaOH}}$$

$$V_{\text{NaOH}} = 0.0486 \text{ mol}/0.25 \text{ M} = 0.194 = 0.19 \text{ L} = (1.9 \times 10^2 \text{ mL})$$

c. The volume of the original acid is $V = 0.375 \text{ L} - 0.194 \text{ L} = 0.181 \text{ L}$. Therefore, the concentration of the original acid is

$$[\text{CH}_3\text{COOH}] = 0.15 \text{ mol}/0.181 \text{ L} = 0.829 = 0.83 \text{ M}$$
17.124 a. From the pH, \([H_3O^+] = 10^{-4.56} = 2.75 \times 10^{-5}\) M. The CH₃COOH is generated by the acid-base reaction, resulting in the formation of a buffer solution. The reaction is

\[
\text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+ \xrightleftharpoons{} \text{H}_2\text{O} + \text{CH}_3\text{COOH} \quad K_a = 1.7 \times 10^{-5}
\]

Rearranging gives

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

Solving for \(x\) gives \(x = 0.0618\) mol. Therefore, the molar concentration is

\[
[\text{CH}_3\text{COO}^-] = 0.0618 \text{ mol}/0.650 \text{ L} = 0.0951 = 0.095 \text{ M}
\]

b. moles of HCl equal moles of CH₃COOH

\[
0.0618 \text{ mol} = 0.15 \text{ M} \times V_{\text{NaOH}}
\]

\[
V_{\text{NaOH}} = \frac{0.0618 \text{ mol}}{0.15 \text{ M}} = 0.412 = 0.41 \text{ L}
\]

c. The volume of the original acid is \(V = 0.650 \text{ L} - 0.412 \text{ L} = 0.238 \text{ L}\). Therefore, the concentration of the original acid is

\[
[\text{CH}_3\text{COOH}] = 0.10 \text{ mol}/0.238 \text{ L} = 0.420 = 0.42 \text{ M}
\]
17.125 Use the pH to calculate \([H_3O^+]\), and then use the \(K_a\) of 1.7 x 10\(^{-5}\) and the \(K_a\) expression to calculate the molarity of acetic acid (HAc), assuming ionization is negligible. Convert molarity to mass percentage using the formula weight of 60.05 g/mol of HAc.

\[
[H_3O^+] = \text{antilog} (-2.45) = 3.548 \times 10^{-3} \text{ M}
\]

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the \(x\) and the \((0.003548 \text{ M})\) terms into the expression:

\[
K_a = \frac{[H_3O^+][Ac^-]}{[HAc]} \cong \frac{(0.003548)^2}{(x)}
\]

Solve the equation for \(x\), assuming 0.003548 is much smaller than \(x\).

\[
x = (0.003548)^2 \div (1.7 \times 10^{-5}) \cong [HAc] \cong 0.7404 \text{ M}
\]

\((0.7404 \text{ mol HAc/L}) \times (60.05 \text{ g/mol}) \times (1 \text{ L/1090 g})(100\%)
\]

\[= 4.078 \cong 4.1 \text{ percent HAc}\]

17.126 Use the pH to calculate \([OH^-]\), and then use the \(K_b\) of 1.8 x 10\(^{-5}\) and the \(K_b\) expression to calculate the molarity of ammonia (NH\(_3\)), assuming ionization is negligible. Convert molarity to mass percentage using the formula weight of 17.03 g/mol of NH\(_3\).

\[
[OH^-] = \text{antilog} [- (14.00 - 11.87)] = 7.413 \times 10^{-3} \text{ M}
\]

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the \(x\) and the \((0.007413 \text{ M})\) terms into the expression:

\[
K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} \cong \frac{(0.007413)^2}{(x)} = 1.8 \times 10^{-5}
\]

Solve the equation for \(x\), assuming 0.007413 is much smaller than \(x\).

\[
x = (0.007413)^2 \div (1.8 \times 10^{-5}) \cong [NH_3] = 3.053 \text{ M}
\]

\((3.053 \text{ mol NH}_3/\text{L}) \times (17.03 \text{ g/mol}) \times (1 \text{ L/1000 g}) \times 100\%
\]

\[= 5.199 \cong 5.2 \text{ percent NH}_3\]
17.127 Find the \([\text{H}_3\text{O}^+]\) and \([\text{C}_2\text{H}_3\text{O}_2^-]\) by solving for the approximate \([\text{H}_3\text{O}^+]\), noting \(x\) is much smaller than the starting 0.92 M of acetic acid. The usual table is used but is not shown; only the final setup for \([\text{H}_3\text{O}^+]\) is shown. Use \(K_f = 1.858 \degree\text{C/m}\) for the constant for water.

\[
[\text{H}_3\text{O}^+] = [\text{C}_2\text{H}_3\text{O}_2^-] = (1.7 \times 10^{-5} \times 0.92)^{1/2} = 0.003954 \text{ M}
\]

Total molarity of acid + ions = 0.92 + 0.003954 = 0.9239

Molality = \(m = 0.9239 \text{ mol} \div (1.000 \text{ L} \times 0.953 \text{ kg H}_2\text{O/L}) = 0.9695 \text{ m}\)

Freezing point = \(-\Delta T_f = -K_f c_m = (-1.858 \degree\text{C/m}) \times 0.9695 \text{ m} = -1.801 = -1.8 \degree\text{C}\)

17.128 Find the \([\text{NH}_4^+]\) and \([\text{OH}^-]\) by solving for the approximate \([\text{OH}^-]\), noting \(x\) is much smaller than the starting 0.87 M of ammonia. The usual table is used but is not shown; only the final setup for \([\text{OH}^-]\) is shown. Use \(K_f = 1.858 \degree\text{C/m}\) for the constant for water.

\[
[\text{NH}_4^+] = [\text{OH}^-] = (1.8 \times 10^{-5} \times 0.87)^{1/2} = 0.003957 \text{ M}
\]

Total molarity of base and ions = 0.87 + 0.003957 = 0.8739 M

\(\text{kg NH}_3/\text{L} = 0.87 \text{ mol/L} \times 0.017 \text{ kg/mol} = 0.0148 \text{ kg NH}_3/\text{L}\)

\(\text{kg H}_2\text{O/L} = 0.992 \text{ kg soln/L} - 0.0148 \text{ kg NH}_3/\text{L} = 0.977 \text{ kg H}_2\text{O/L}\)

Molality = \(m = 0.8739 \text{ mol} \div (1.000 \text{ L} \times 0.977 \text{ kg solv/L}) = 0.8944 \text{ m}\)

Freezing point = \(-\Delta T_f = -K_f c_m = (-1.858 \degree\text{C/m}) \times 0.8944 \text{ m} = -1.662 = -1.7 \degree\text{C}\)

17.129 The \([\text{H}_3\text{O}^+]\) = -antilog (-4.35) = 4.46 \times 10^{-5} \text{ M}. Note that 0.465 L of 0.0941 M NaOH will produce 0.043756 mol of acetate, \(\text{Ac}^-\) ion. Rearranging the \(K_a\) expression for acetic acid (HAc) and \(\text{Ac}^-\) and canceling the volume in the mol/L of each, you obtain:

\[
\frac{[\text{HAc}]}{[\text{Ac}^-]} = \frac{[\text{H}^+]}{K_a} = \frac{4.46 \times 10^{-5}}{1.7 \times 10^{-5}} = \frac{2.63}{1.00} \approx \frac{x \text{ mol HAc}}{0.043756 \text{ mol Ac}^-}
\]

\(x = 0.1149 \text{ mol HAc}\)

Total mol HAc added = 0.1149 + 0.043756 = 0.1587 mol HAc

Mol/L of pure HAc = 1049 g HAc/L \times (1 \text{ mol HAc/60.05 g}) = 17.467 mol/L

L of pure HAc needed = 0.1587 mol HAc \times (L/17.467 mol) = 0.00908 L (9.1 mL)
17.130 The $[\text{H}_3\text{O}^+] = \text{antilog} (-3.50) = 3.16 \times 10^{-4}$ M. Note that 0.325 L of 0.0857 M NaOH will produce 0.027852 mol of formate, $\text{Fo}^-$, ion. Rearranging the $K_a$ expression for formic acid (HFo) and $\text{Fo}^-$ and canceling the volume in the mol/L of each, you obtain:

$$\frac{[\text{HFo}]}{[\text{Fo}^-]} = \frac{[H^+]}{K_a} = \frac{3.16 \times 10^{-4}}{1.7 \times 10^{-4}} = \frac{1.858}{1.00} \cong \frac{x \text{ mol HFo}}{0.027852 \text{ mol Fo}^-}$$

$$x = 0.05175 \text{ mol HFo}$$

Total mol HFo added = 0.05175 + 0.027852 = 0.079602 mol HFo

Mol/L of pure HFo = 1220 g HFo/L $\times$ (1 mol HFo/46.027 g) = 26.506 mol/L

L of pure HFo needed = 0.079602 mol HAc $\times$ (L/26.506 mol) = 0.00300 L (3.0 mL)