CHAPTER 18 ACID-BASE EQUILIBRIA

FOLLOW-UP PROBLEMS

18.1A Plan: Examine the formulas and classify each as an acid or base. Strong acids are the hydrohalic acids HCl, HBr, and HI, and oxoacids in which the number of O atoms exceeds the number of ionizable protons by at least two. Other acids are weak acids. Strong bases are soluble oxides or hydroxides of the Group 1A(1) metals and Ca, Sr, and Ba in Group 2A(2). Other bases are weak bases.
Solution:
a) Chloric acid, HClO₃, is the stronger acid because acid strength increases as the number of O atoms in the acid increases.
b) Hydrochloric acid, HCl, is one of the strong hydrohalic acids whereas acetic acid, CH₃COOH, is a weak carboxylic acid.
c) Sodium hydroxide, NaOH, is a strong base because Na is a Group 1A(1) metal. Methylamine, CH₃NH₂, is an organic amine and, therefore, a weak base.

18.1B Plan: Examine the formulas and classify each as a strong acid, weak acid, strong base, or weak base. Strong acids are the hydrohalic acids HCl, HBr, and HI, and oxoacids in which the number of O atoms exceeds the number of ionizable protons by at least two. Other acids are weak acids. Strong bases are soluble oxides or hydroxides of the Group 1A(1) metals and Ca, Sr, and Ba in Group 2A(2). Other bases are weak bases.
Solution:
a) (CH₃)₃N is a weak base. It contains a nitrogen atom with a lone pair of electrons, which classifies it as a base; however, it is not one of the strong bases.
b) Hydroiodic acid, HI, is a strong acid (one of the strong acids listed above).
c) HBrO is a weak acid. It has an ionizable hydrogen, which makes it an acid. Specifically, it is an oxoacid, in which a polyatomic ion is the anion. In the case of this oxoacid, there is only one O atom for each ionizable hydrogen, so this is a weak acid. The reaction for the dissociation of this weak acid is:
\[ \text{HBrO}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{BrO}^-(aq) + \text{H}_3\text{O}^+(aq) \]
The corresponding equilibrium expression is:
\[ K_a = \frac{[\text{BrO}^-][\text{H}_3\text{O}^+]}{[\text{HBrO}]} \]
d) Ca(OH)₂ is a strong base (one of the strong bases listed above).

18.2A Plan: The product of [H₃O⁺] and [OH⁻] remains constant at 25°C because the value of \( K_w \) is constant at a given temperature. Use \( K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \) to solve for [H₃O⁺].
Solution:
Calculating [H₃O⁺]:
\[ [H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{6.7 \times 10^{-2}} = 1.4925 \times 10^{-13} = 1.5 \times 10^{-13} M \]
Since [OH⁻] > [H₃O⁺], the solution is basic.

18.2B Plan: The product of [H₃O⁺] and [OH⁻] remains constant at 25°C because the value of \( K_w \) is constant at a given temperature. Use \( K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \) to solve for [H₃O⁺].
Solution:
Calculating [OH⁻]:
\[ [OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-10}} = 5.5555 \times 10^{-5} = 5.6 \times 10^{-5} M \]
Since [OH⁻] > [H₃O⁺], the solution is basic.

18.3A Plan: NaOH is a strong base that dissociates completely in water. Subtract pH from 14.00 to find the pOH, and calculate inverse logs of pH and pOH to find [H₃O⁺] and [OH⁻], respectively.
18.3B Plan: HCl is a strong acid that dissociates completely in water. Subtract pH from 14.00 to find the pOH, and calculate inverse logs of pH and pOH to find $[H_3O^+]$ and $[OH^-]$, respectively.

**Solution:**

\[
\begin{align*}
\text{pH} + \text{pOH} &= 14.00 \\
pOH &= 14.00 - 2.28 = 11.72 \\
pH &= -\log [H_3O^+] \\
[H_3O^+] &= 10^{-pH} = 10^{-11.72} = 1.9055 \times 10^{-12} M \\
pOH &= -\log [OH^-] \\
[OH^-] &= 10^{-pOH} = 10^{-11.72} = 1.9055 \times 10^{-12} M
\end{align*}
\]
18.5B **Plan:** For a), write the reaction that shows the reaction of ammonia with water; for b), write a reaction between ammonia and HCl; for c), write the reaction between the ammonium ion and NaOH to produce ammonia.

**Solution:**

a) The following equation describes the dissolution of ammonia in water:

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

Ammonia is a known weak base, so it makes sense that it accepts a H⁺ from H₂O. The reaction arrow indicates that the equilibrium lies to the left because the question states, “you smell ammonia” (NH₄⁺ and OH⁻ are odorless). NH₄⁺ and OH⁻ are the stronger acid and base, so the reaction proceeds to the formation of the weaker acid and base.

b) The addition of excess HCl results in the following equation:

\[
\text{NH}_3(g) + \text{H}_3\text{O}^+(aq; \text{from HCl}) \rightleftharpoons \text{NH}_4^+(aq) + \text{H}_2\text{O}(l)
\]

HCl is a strong acid and is much stronger than NH₄⁺. Similarly, NH₃ is a stronger base than H₂O. The reaction proceeds to produce the weak acid and base, and thus the odor from NH₃ disappears.

c) The solution in (b) is mostly NH₄⁺ and H₂O. The addition of excess NaOH results in the following equation:

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

NH₄⁺ and OH⁻ are the stronger acid and base, respectively, and drive the reaction towards the formation of the weaker base and acid, NH₃(g) and H₂O, respectively. The reaction direction explains the return of the ammonia odor.

18.6A **Plan:** If HA is a stronger acid than HB, \(K_c > 1\) and more HA molecules will produce HB molecules. If HB is a stronger acid than HA, \(K_c < 1\) and more HB molecules will produce HA molecules.

**Solution:**

There are more HB molecules than there are HA molecules, so the equilibrium lies to the right and \(K_c > 1\). HA is the stronger acid.

18.6B **Plan:** Because HD is a stronger acid than HC, the reaction of HD and C⁻ will have \(K_c > 1\), and there should be more HC molecules than HD molecules at equilibrium.

**Solution:**

There are more green/white acid molecules in the solution than black/white acid molecules. Therefore, the green/white acid molecules represent HC, and the black/white acid molecules represent HD. The green spheres represent C⁻, and the black spheres represent D⁻. Because the reaction of the stronger acid HD with C⁻ will have \(K_c > 1\), the reverse reaction (HC + D⁻) will have \(K_c < 1\).

18.7A **Plan:** Write a balanced equation for the dissociation of NH₄⁺ in water. Using the given information, construct a reaction table that describes the initial and equilibrium concentrations. Construct an equilibrium expression and make assumptions where possible to simplify the calculations. Since the pH is known, \([H_3O^+]\) can be found; that value can be substituted into the equilibrium expression.

**Solution:**

\[
\begin{array}{c|c|c|c}
\text{Initial} & 0.2 \ M & \text{H}_2\text{O}(l) & \Rightarrow \text{H}_3\text{O}^+(aq) + \text{NH}_3(g) \\
\text{Change} & -x & +x & +x \\
\text{Equilibrium} & 0.2 - x & x & x \\
\end{array}
\]

The initial concentration of NH₄⁺ = 0.2 M because each mole of NH₄Cl completely dissociates to form one mole of NH₄⁺.

\[
x = [\text{H}_3\text{O}^+] = [\text{NH}_3] = 10^{-\text{pH}} = 10^{-5.0} = 1.0 \times 10^{-5} \ M
\]

\[
K_c = \left( \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} \right) = \frac{x^2}{(0.2 - x)} = \frac{(1.0 \times 10^{-5})(1.0 \times 10^{-5})}{(0.2 - 1.0 \times 10^{-5})} = 5 \times 10^{-10}
\]

18.7B **Plan:** Write a balanced equation for the dissociation of acrylic acid in water. Using the given information, construct a reaction table that describes the initial and equilibrium concentrations. Construct an equilibrium
expression. Since the pH is known, $[H_3O^+]$ can be found; that value can be used to find the equilibrium concentrations of all substances, which can then be substituted into the equilibrium expression to solve for the value of $K_a$.

**Solution:**

$$H_2C=CHCOOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2C=CHCOO^-(aq)$$

<table>
<thead>
<tr>
<th>Initial</th>
<th>$0.3 \text{ M}$</th>
<th>$0$</th>
<th>$0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change</td>
<td>$-x$</td>
<td>$+x$</td>
<td>$+x$</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>$0.3 - x$</td>
<td>$x$</td>
<td>$x$</td>
</tr>
</tbody>
</table>

According to the information given in the problem, pH at equilibrium = 2.43.

$[H_3O^+]_{eq} = 10^{-pH} = 10^{-2.43} = 3.7154 \times 10^{-3} = 3.7 \times 10^{-3} \text{ M} = x$

Thus, $[H_3O^+] = [H_2C=CHCOO^-] = 3.7 \times 10^{-3} \text{ M}$

$[H_2C=CHCOOH] = (0.30 - x) = (0.30 - 3.7 \times 10^{-3}) \text{ M} = 0.2963 \text{ M}$

$$K_a = \frac{[H_2C=CHCOO^-][H_3O^+]}{[H_2C=CHCOOH]}$$

$$K_a = \frac{(3.7 \times 10^{-3})(3.7 \times 10^{-3})}{(0.2963)} = 4.6203 \times 10^{-5} = 4.6 \times 10^{-5}$$

**18.8A Plan:** Write a balanced equation for the dissociation of HOCN in water. Using the given information, construct a table that describes the initial and equilibrium concentrations. Construct an equilibrium expression and solve the quadratic expression for $x$, the concentration of $H_3O^+$. Use the concentration of the hydronium ion to solve for pH.

**Solution:**

$$HOCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OCN^-(aq)$$

<table>
<thead>
<tr>
<th>Initial</th>
<th>$0.10 \text{ M}$</th>
<th>$0$</th>
<th>$0$</th>
</tr>
</thead>
<tbody>
<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>

$$K_a = 3.5 \times 10^{-4} = \frac{[OCN^-][H_3O^+]}{[HOCN]} = \frac{x^2}{(0.10 - x)}$$

In this example, the dissociation of HOCN is not negligible in comparison to the initial concentration. Therefore, the equilibrium expression is solved using the quadratic formula.

$$x^2 = 3.5 \times 10^{-4} (0.10 - x)$$

$$x^2 + 3.5 \times 10^{-4} x - 3.5 \times 10^{-5} = 0$$

$$a = 1 \quad b = 3.5 \times 10^{-4} \quad c = -3.5 \times 10^{-5}$$

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

$$x = \frac{-3.5 \times 10^{-4} \pm \sqrt{(3.5 \times 10^{-4})^2 - 4(1)(-3.5 \times 10^{-5})}}{2(1)}$$

$$x = 5.7436675 \times 10^{-3} \text{ M} H_3O^+$$

pH = $-\log [H_3O^+] = -\log [5.7436675 \times 10^{-3}] = 2.2408 = 2.24$

**18.8B Plan:** Write a balanced equation for the dissociation of $C_6H_5COOH$ in water. Using the given information, construct a table that describes the initial and equilibrium concentrations. Use $pK_a$ to solve for the value of $K_a$. Construct an equilibrium expression, use simplifying assumptions when possible to solve for $x$, the concentration of $H_3O^+$. Use the concentration of the hydronium ion to solve for pH.

**Solution:**

$$C_6H_5COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_5COO^- (aq)$$

<table>
<thead>
<tr>
<th>Initial</th>
<th>$0.25 \text{ M}$</th>
<th>$0$</th>
<th>$0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change</td>
<td>$-x$</td>
<td>$+x$</td>
<td>$+x$</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>$0.25 - x$</td>
<td>$x$</td>
<td>$x$</td>
</tr>
</tbody>
</table>
\[ K_a = 10^{-pK_a} = 10^{-4.20} = 6.3096 \times 10^{-5} = 6.3 \times 10^{-5} \]

\[ K_a = 6.3 \times 10^{-5} = \frac{[C_6H_5HCOO^-][H_3O^+]}{[C_6H_5COOH]} = \frac{(x)(x)}{(0.25 - x)} \]

Assume \( x \) is negligible so \( 0.25 - x \approx 0.25 \)

\[ \frac{(x)(x)}{(0.25)} = 6.3 \times 10^{-5} \]

\[ x^2 = (6.3 \times 10^{-5})(0.25); \ x = 3.9686 \times 10^{-3} = 4.0 \times 10^{-3} \]

Check the assumption by calculating the % error:

\[ \frac{4.0 \times 10^{-3}}{0.25} \times 100 = 1.6\% \text{ which is smaller than 5\%, so the assumption is valid.} \]

At equilibrium \( [H_3O^+]_{eq} = 4.0 \times 10^{-3} M \)

\[ pH = -\log [H_3O^+] = -\log [4.0 \times 10^{-3}] = 2.3979 = 2.40 \]

### 18.9A Plan:
Write the acid-dissociation reaction and the expression for \( K_a \). Set up a reaction table in which \( x \) = the concentration of the dissociated acid and also \( [\text{H}_3\text{O}^+] \). Use the expression for \( K_a \) to solve for \( x \), the concentration of cyanide ion at equilibrium. Then use the initial concentration of HCN and the equilibrium concentration of CN\(^-\) to find % dissociation.

#### Solution:

<table>
<thead>
<tr>
<th>Concentration</th>
<th>HCN(aq)</th>
<th>H(_2)O(l)</th>
<th>(\Delta)</th>
<th>H(_3)O(^+)(aq)</th>
<th>CN(^-)(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.75</td>
<td>–</td>
<td>+x</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>–x</td>
<td>+x</td>
<td>+x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.75 – x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ K_a = 6.2 \times 10^{-10} = \frac{[\text{CN}^-][\text{H}_3\text{O}^+]}{[\text{HCN}]} \]

\[ K_a = 6.2 \times 10^{-10} = \frac{[x][x]}{[0.75 - x]} \]

Assume \( x \) is small compared to 0.75.

\[ x = 2.1564 \times 10^{-5} = 2.2 \times 10^{-5} M \]

Check the assumption by calculating the % error:

\[ \frac{2.2 \times 10^{-5}}{0.75} \times 100 = 0.0029\% \text{ which is smaller than 5\%, so the assumption is valid.} \]

\[ \text{Percent HCN dissociated} = \frac{[\text{HCN}]_{dissoc}}{[\text{HCN}]_{init}} \times 100 \]

\[ \text{Percent HCN dissociated} = \frac{(2.2 \times 10^{-5})}{0.75} \times 100 = \text{0.0029}\% \]

### 18.9B Plan:
Write the acid-dissociation reaction and the expression for \( K_a \). Percent dissociation refers to the amount of the initial concentration of the acid that dissociates into ions. Use the percent dissociation to find the concentration of acid dissociated, which also equals \( [\text{H}_3\text{O}^+] \). HA will be used as the formula of the acid. Set up a reaction table in which \( x \) = the concentration of the dissociated acid and \( [\text{H}_3\text{O}^+] \). Substitute \( [\text{HA}], [\text{A}^-], \text{ and } [\text{H}_3\text{O}^+] \) into the expression for \( K_a \) to find the value of \( K_a \).

#### Solution:

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

\[ \text{Percent HA} = \frac{\text{dissociated acid}}{\text{initial acid}} \times 100 \]

\[ 3.16\% = \frac{x}{1.5 M} \times 100 \]

\[ [\text{Dissociated acid}] = x = 0.047 M \]

<table>
<thead>
<tr>
<th>Concentration</th>
<th>HA(aq)</th>
<th>H(_2)O(l)</th>
<th>(\Delta)</th>
<th>H(_3)O(^+)(aq)</th>
<th>A(^-(aq))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>1.5</td>
<td>–</td>
<td>+x</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>–x</td>
<td>+x</td>
<td>+x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>1.5 – x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Initial:**

<table>
<thead>
<tr>
<th></th>
<th>1.5</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
</table>

**Change:**

<table>
<thead>
<tr>
<th></th>
<th>–x</th>
<th>+x</th>
<th>+x</th>
</tr>
</thead>
</table>

**Equilibrium:**

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{(0.047)(0.047)}{(1.453)} = 1.5203 \times 10^{-3} = 1.5 \times 10^{-3}
\]

### 18.10A Plan:
Write the balanced equation and corresponding equilibrium expression for each dissociation reaction. Calculate the equilibrium concentrations of all species and convert \([\text{H}_3\text{O}^+]\) to pH. Find the equilibrium constant values from Appendix C, \(K_{a1} = 5.6 \times 10^{-2}\) and \(K_{a2} = 5.4 \times 10^{-5}\).

### Solution:

**HOOC–COOH(aq) + H_2O(l) \rightleftharpoons HOOC–COO^−(aq) + H_3O^+(aq)**

\[
K_{a1} = \frac{[\text{HC}_2\text{O}_4^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{C}_2\text{O}_4]} = 5.6 \times 10^{-2}
\]

**HOOC–COO^−(aq) + H_2O(l) \rightleftharpoons C_2O_4^2−(aq) + H_3O^+(aq)**

\[
K_{a2} = \frac{[\text{C}_2\text{O}_4^{2−}][\text{H}_3\text{O}^+]}{[\text{HOOC–COO}^-]} = 5.4 \times 10^{-5}
\]

**Assumptions:**

1) Since \(K_{a1} \gg K_{a2}\), the first dissociation produces almost all of the \(\text{H}_3\text{O}^+\), so \([\text{H}_3\text{O}^+]_{eq} = [\text{H}_3\text{O}^+]\) from \(\text{C}_2\text{H}_2\text{O}_4\).

2) Since \(K_{a1} (5.6 \times 10^{-2})\) is fairly large, solve the first equilibrium expression using the quadratic equation.

\[
x^2 + 5.6 \times 10^{-2} x - 8.4 \times 10^{-3} = 0
\]

\[
x = \frac{-5.6 \times 10^{-2} \pm \sqrt{(5.6 \times 10^{-2})^2 - 4(1)(-8.4 \times 10^{-3})}}{2(1)}
\]

\[
x = 0.067833 \ M \text{ H}_3\text{O}^+
\]

Therefore, \([\text{H}_3\text{O}^+] = [\text{HC}_2\text{O}_4^-] = 0.068 \ M\) and \(p\text{H} = -\log (0.067833) = 1.16856 = 1.17\). The oxalic acid concentration at equilibrium is \([\text{H}_2\text{C}_2\text{O}_4]_{\text{init}} - [\text{H}_2\text{C}_2\text{O}_4]_{\text{dissoc}} = 0.150 - 0.067833 = 0.82167 = 0.082 \ M\).

Solve for \([\text{C}_2\text{O}_4^{2−}]\) by rearranging the \(K_{a2}\) expression:

\[
[C_2O_4^{2−}] = \frac{K_{a2}[\text{HC}_2\text{O}_4^-]}{[\text{H}_3\text{O}^+]} = \frac{(5.4 \times 10^{-5})(0.067833)}{0.067833} = 5.4 \times 10^{-5} \ M
\]

### 18.10B Plan:
Write the balanced equation and corresponding equilibrium expression for each dissociation reaction. Calculate the equilibrium concentrations of all species and convert \([\text{H}_3\text{O}^+]\) to pH. Find the equilibrium constant values from Appendix C, \(K_{a1} = 4.5 \times 10^{-7}\) and \(K_{a2} = 4.7 \times 10^{-11}\).

### Solution:
\[
\text{H}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCO}_3^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})
\]
\[
K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 4.5 \times 10^{-7}
\]
\[
\text{HCO}_3^- (\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CO}_3^{2-}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})
\]
\[
K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 4.7 \times 10^{-11}
\]

Assumption:
1) Since \( K_{a1} \gg K_{a2} \), the first dissociation produces almost all of the \( \text{H}_3\text{O}^+ \), so \([\text{H}_3\text{O}^+]_{\text{eq}} = [\text{H}_3\text{O}^+] \) from \( \text{H}_2\text{CO}_3 \).
2) Because \( K_{a1} \) \((4.7 \times 10^{-7})\) is fairly small, \([\text{H}_2\text{CO}_3]\) \(\text{init} - x \approx [\text{H}_2\text{CO}_3]\)\(\text{init} \). Thus, \([\text{H}_2\text{CO}_3] = 0.075\ M - x \approx 0.075\ M \)

Solve the first equilibrium expression making the assumption that \( x \) is small.
\[
\begin{align*}
\text{Initial:} & \quad 0.075\ M \\
\text{Change:} & \quad -x \quad 0 \\
\text{Equilibrium:} & \quad 0.075 - x \quad +x \\
K_{a1} & = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{(x)(x)}{0.075 - x} \approx \frac{(x)(x)}{0.075} = 4.5 \times 10^{-7}
\end{align*}
\]
\[
x^2 = (0.075)(4.5 \times 10^{-7}); \quad x = 1.8371 \times 10^{-4} = 1.8 \times 10^{-4} \ M
\]

Check the assumption by calculating the % error:
\[
\frac{1.8 \times 10^{-4}}{0.075}(100) = 0.24\% \text{ which is smaller than 5\%, so the assumption is valid.}
\]

Therefore, \([\text{H}_3\text{O}^+] = [\text{HCO}_3^-] = 1.8 \times 10^{-4}\ \text{M} \) and \( \text{pH} = -\log (1.8 \times 10^{-4}) = 3.7447 \approx 3.74 \). The carbonic acid concentration at equilibrium is \([\text{H}_2\text{CO}_3]\)\(\text{init} - [\text{H}_2\text{CO}_3]\)\(\text{dissoc} = 0.075 - 1.8 \times 10^{-4} \approx 0.075\ M \)

18.11A Plan: Pyridine contains a nitrogen atom that accepts \( \text{H}^+ \) from water to form \( \text{OH}^- \) ions in aqueous solution. Write a balanced equation and equilibrium expression for the reaction, convert \( pK_b \) to \( K_b \), make simplifying assumptions (if valid), and solve for \( [\text{OH}^-] \). Calculate \( [\text{H}_3\text{O}^+] \) using \( [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \) and convert to \( \text{pH} \).

Solution:
\[
K_b = 10^{-pK_b} = 10^{-8.77} = 1.69824 \times 10^{-9}
\]
\[
\text{C}_5\text{H}_5\text{N}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_5\text{H}_5\text{NH}^+(aq) + \text{OH}^-(aq)
\]
\[
\begin{align*}
\text{Initial:} & \quad 0.10\ M \\
\text{Change:} & \quad -x \quad +x \\
\text{Equilibrium:} & \quad 0.10 - x \quad +x \\
K_b & = \frac{[\text{C}_5\text{H}_5\text{NH}^+][\text{OH}^-]}{[\text{C}_5\text{H}_5\text{N}]} = 1.69824 \times 10^{-9}
\end{align*}
\]

Assume that \( 0.10 - x \approx 0.10 \).
\[
K_b = \frac{[\text{C}_5\text{H}_5\text{NH}^+][\text{OH}^-]}{[\text{C}_5\text{H}_5\text{N}]} = \frac{x^2}{0.10} = 1.69824 \times 10^{-9}
\]
\[
x = 1.30316 \times 10^{-5} \approx 1.3 \times 10^{-5}\ M \quad [\text{OH}^-] = [\text{C}_5\text{H}_5\text{NH}^+]
\]

Since \( \frac{[\text{OH}^-]}{[\text{C}_5\text{H}_5\text{N}]}(100) = \frac{1.303265 \times 10^{-5}}{0.10}(100) = 0.01313 \) which < 5\%, the assumption that the dissociation of \( \text{C}_5\text{H}_5\text{N} \) is small is valid.
\[ [\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{1.303165 \times 10^{-5}} = 7.67362 \times 10^{-10} \text{ M} \]

\[ \text{pH} = -\log (7.67362 \times 10^{-10}) = 9.1149995 = 9.11 \]

(Since pyridine is a weak base, a pH > 7 is expected.)

18.11B Plan: Amphetamine contains a nitrogen atom that accepts H\(^+\) from water to form OH\(^-\) ions in aqueous solution. Write a balanced equation and equilibrium expression for the reaction, make simplifying assumptions (if valid), and solve for [OH\(^-\)]. Calculate [H\(_3\)O\(^+\)] using [H\(_3\)O\(^+\)][OH\(^-\)] = 1.0 \times 10^{-14} and convert to pH. In the information below, the symbol B will be used to represent the formula of amphetamine.

Solution:

\[
\begin{array}{ccc}
\text{B(aq)} & + & \text{H}_2\text{O(l)} \rightleftharpoons \text{BH}^+(aq) & + & \text{OH}^-(aq) \\
\text{Initial} & 0.075 \text{ M} & & 0 & \\
\text{Change} & -x & & +x & +x \\
\text{Equilibrium} & 0.075 - x & & x & x \\
\end{array}
\]

\[ K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} = 6.3 \times 10^{-5} \]

Assume that 0.075 - x \approx 0.075.

\[ K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} = \frac{x^2}{0.075} = 6.3 \times 10^{-5} \]

x = 0.0021737 = 2.2 \times 10^{-3} \text{ M} = [\text{OH}^-] = [\text{BH}^+] 

Check the assumption by calculating the % error:

\[ \frac{2.2 \times 10^{-3}}{0.075} \times 100 = 2.9\% \text{ which is smaller than 5\%, so the assumption is valid.} \]

\[ [\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1 \times 10^{-14}}{2.2 \times 10^{-3}} = 4.5 \times 10^{-12} \text{ M} \]

\[ \text{pH} = -\log (4.5 \times 10^{-12}) = 11.3424 = 11.35 \]

(Since amphetamine is a weak base, a pH > 7 is expected.)

18.12A Plan: The hypochlorite ion, ClO\(^-\), acts as a weak base in water. Write a balanced equation and equilibrium expression for this reaction. The \( K_b \) of ClO\(^-\) is calculated from the \( K_a \) of its conjugate acid, hypochlorous acid, HClO (from Appendix C, \( K_a = 2.9 \times 10^{-8} \)). Make simplifying assumptions (if valid), solve for [OH\(^-\)], convert to \[\text{H}_3\text{O}^+\] and calculate pH.

Solution:

\[
\begin{array}{ccc}
\text{ClO}^-\text{(aq)} & + & \text{H}_2\text{O(l)} \rightleftharpoons \text{HClO(aq)} & + & \text{OH}^-(aq) \\
\text{Initial} & 0.20 \text{ M} & & 0 & \\
\text{Change} & -x & & +x & +x \\
\text{Equilibrium} & 0.20 - x & & x & x \\
\end{array}
\]

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

\[ K_b = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{2.9 \times 10^{-8}} = 3.448276 \times 10^{-7} \]

Since \( K_b \) is very small, assume \( [\text{ClO}^-]_{eq} = 0.20 - x \approx 0.2. \)

\[ K_b = \frac{[\text{HClO}][\text{OH}^-]}{[\text{ClO}^-]} = \frac{x^2}{0.20} = 3.448276 \times 10^{-7} \]

x = 2.6261 \times 10^{-4} \text{ M}.

Therefore, \[ [\text{HClO}] = [\text{OH}^-] = 2.6 \times 10^{-4} \text{ M}. \]
Since \( \frac{[\text{OH}^-]}{[\text{ClO}^-]}(100) = \frac{2.6261\times10^{-4}}{0.20}(100) = 0.1313 \) which < 5\%, the assumption that the dissociation of \( \text{ClO}^- \) is small is valid.

\[ [\text{H}_3\text{O}^+] = \frac{1.0\times10^{-14}}{2.6261\times10^{-4}} = 3.8079\times10^{-11} \text{ M} \]

\[ \text{pH} = -\log(3.8079\times10^{-11}) = 10.4193 = 10.42 \]

(Since hypochlorite ion is a weak base, a pH > 7 is expected.)

18.12B Plan: The nitrite ion, \( \text{NO}_2^- \), acts as a weak base in water. Write a balanced equation and equilibrium expression for this reaction. The \( K_b \) of \( \text{NO}_2^- \) is calculated from the \( K_a \) of its conjugate acid, nitrous acid, \( \text{HNO}_2 \) (from Appendix C, \( K_a = 7.1\times10^{-4} \)). Make simplifying assumptions (if valid), solve for \([\text{OH}^-]\), convert to \([\text{H}_3\text{O}^+]\) and calculate pH.

Solution:

\[
\begin{array}{c|c|c|c}
\text{Initial} & 0.80 \text{ M} & 0 & 0 \\
\text{Change} & -x & +x & +x \\
\text{Equilibrium} & 0.80-x & x & x \\
\end{array}
\]

\[ K_b = \frac{[\text{HNO}_2][\text{OH}^-]}{[\text{NO}_2^-]} = 1.4 \times 10^{-11} \]

Since \( K_b \) is very small, assume \([\text{NO}_2^-]_{\text{eq}} = 0.80 - x \approx 0.8 \).

\[ K_b = \frac{[\text{HNO}_2][\text{OH}^-]}{[\text{NO}_2^-]} = \frac{x^2}{(0.80)} = 1.4 \times 10^{-11} \]

\[ x = 3.3 \times 10^{-6} \text{ M} \]

Check the assumption by calculating the % error:

\[ \frac{3.3 \times 10^{-6}}{0.80}(100) = 0.00041\% \text{ which is smaller than 5\%, so the assumption is valid.} \]

Therefore, \([\text{HNO}_2] = [\text{OH}^-] = 3.3 \times 10^{-6} \text{ M} \).

\[ [\text{H}_3\text{O}^+] = \frac{1\times10^{-14}}{3.3\times10^{-6}} = 3.0 \times 10^{-9} \text{ M} \]

\[ \text{pH} = -\log (3.0\times10^{-9}) = 8.5229 = 8.52 \]

Since nitrite ion is a weak base, a pH > 7 is expected.

18.13A Plan: Examine the cations and anions in each compound. If the cation is the cation of a strong base, the cation gives a neutral solution; the cation of a weak base gives an acidic solution. An anion of a strong acid gives a neutral solution while an anion of a weak acid is basic in solution.

Solution:

a) The ions are \( \text{K}^+ \) and \( \text{ClO}_2^- \); the \( \text{K}^+ \) is from the strong base KOH, and does not react with water. The \( \text{ClO}_2^- \) is from the weak acid HClO₂, so it reacts with water to produce \( \text{OH}^- \) ions. Since the base is strong and the acid is weak, the salt derived from this combination will produce a basic solution.

\( \text{K}^+ \) does not react with water.

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

b) The ions are \( \text{CH}_3\text{NH}_3^+ \) and \( \text{NO}_3^- \); \( \text{CH}_3\text{NH}_3^+ \) is derived from the weak base methylamine, \( \text{CH}_3\text{NH}_2 \). Nitrate ion, \( \text{NO}_3^- \), is derived from the strong acid \( \text{HNO}_3 \) (nitric acid). A salt derived from a weak base and strong acid produces an acidic solution.

\( \text{NO}_3^- \) does not react with water.

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

c) The ions are \( \text{Rb}^+ \) and \( \text{Br}^- \). Rubidium ion is derived from rubidium hydroxide, \( \text{RbOH} \), which is a strong base because \( \text{Rb} \) is a Group 1A(1) metal. Bromide ion is derived from hydrobromic acid, \( \text{HBr} \), a strong hydrohalic acid.
acid. Since both the base and acid are strong, the salt derived from this combination will produce a neutral solution.
Neither Rb⁺ nor Br⁻ react with water.

18.13B Plan: Examine the cations and anions in each compound. If the cation is the cation of a strong base, the cation gives a neutral solution; the cation of a weak base gives an acidic solution. An anion of a strong acid gives a neutral solution while an anion of a weak acid is basic in solution.

Solution:
a) The ions are Fe³⁺ and Br⁻. The Br⁻ is the anion of the strong acid HBr, so it does not react with water. The Fe³⁺ ion is small and highly charged, so the hydrated ion, Fe(H₂O)₆³⁺, reacts with water to produce H₃O⁺. Since the base is weak and the acid is strong, the salt derived from this combination will produce an acidic solution.

\[
\text{Br}^- \text{ does not react with water.}
\]

\[
\text{Fe(H}_2\text{O)}_6^{3+}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{Fe(H}_2\text{O)}_5\text{OH}^+ (aq) + \text{H}_3\text{O}^+ (aq)
\]

b) The ions are Ca²⁺ and NO₂⁻; the Ca²⁺ is from the strong base Ca(OH)₂, and does not react with water. The NO₂⁻ is from the weak acid HNO₂, so it reacts with water to produce OH⁻ ions. Since the base is strong and the acid is weak, the salt derived from this combination will produce a basic solution.

\[
\text{Ca}^2+ \text{ does not react with water.}
\]

\[
\text{NO}_2^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HNO}_2(aq) + \text{OH}^-(aq)
\]

c) The ions are C₆H₅NH₃⁺ and I⁻; C₆H₅NH₃⁺ is derived from the weak base aniline, C₆H₅NH₂. Iodide ion, I⁻, is derived from the strong acid HI (hydroiodic acid). A salt derived from a weak base and strong acid produces an acidic solution.

\[
\text{I}^- \text{ does not react with water.}
\]

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

18.14A Plan: Examine the cations and anions in each compound. If the cation is the cation of a strong base, the cation gives a neutral solution; the cation of a weak base gives an acidic solution. An anion of a strong acid gives a neutral solution while an anion of a weak acid is basic in solution.

Solution:
a) The two ions that comprise this salt are cupric ion, Cu²⁺, and acetate ion, CH₃COO⁻. Metal ions are acidic in water. Assume that the hydrated cation is Cu(H₂O)₆²⁺. The \( K_a \) is found in Appendix C.

\[
\text{Cu(H}_2\text{O)}_6^{2+}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{Cu(H}_2\text{O)}_5\text{OH}^+(aq) + \text{H}_3\text{O}^+(aq) \quad K_a = 3 \times 10^{-8}
\]

Acetate ion acts like a base in water. The \( K_b \) is calculated from the \( K_a \) of acetic acid (1.8x10⁻⁵):

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

\[
\text{CH}_3\text{COO}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{COOH}(aq) + \text{OH}^-(aq) \quad K_b = 5.6 \times 10^{-10}
\]

Cu(H₂O)₆²⁺ is a better proton donor than CH₃COO⁻ is a proton acceptor (i.e., \( K_a > K_b \)), so a solution of Cu(CH₃COO)₂ is acidic.

b) The two ions that comprise this salt are ammonium ion, NH₄⁺, and fluoride ion, F⁻. Ammonium ion is the acid of NH₃ with \( K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.76 \times 10^{-5}} = 5.7 \times 10^{-10} \).

\[
\text{NH}_4^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_3(aq) + \text{H}_3\text{O}^+(aq) \quad K_a = 5.7 \times 10^{-10}
\]

Fluoride ion is the base with \( K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}} = 1.5 \times 10^{-11} \).

\[
\text{F}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HF}(aq) + \text{OH}^-(aq) \quad K_b = 1.5 \times 10^{-11}
\]

Since \( K_a > K_b \), a solution of NH₄F is acidic.

c) The ions are K⁺ and HSO₃⁻; the K⁺ is from the strong base KOH, and does not react with water. The HSO₃⁻ can react as an acid:

\[
\text{HSO}_3^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{SO}_3^{2-}(aq) + \text{H}_3\text{O}^+(aq) \quad K_a = 6.5 \times 10^{-8}
\]

HSO₃⁻ can also react as a base. Its \( K_b \) value can be found by using the \( K_a \) of its conjugate acid, H₂SO₃.
\[
\text{HSO}_3^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{SO}_3(aq) + \text{OH}^-(aq) \quad K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-2}} = 7.1 \times 10^{-13}
\]

Since \(K_a > K_b\), a solution of KHSO₃ is **acidic**.

18.14B **Plan:** Examine the cations and anions in each compound. If the cation is the cation of a strong base, the cation gives a neutral solution; the cation of a weak base gives an acidic solution. An anion of a strong acid gives a neutral solution while an anion of a weak acid is basic in solution.

**Solution:**

a) The two ions that comprise this salt are sodium ion, \(\text{Na}^+\), and bicarbonate ion, \(\text{HCO}_3^-\). The \(\text{Na}^+\) is from the strong base NaOH, and does not react with water.

The \(\text{HCO}_3^-\) can react as an acid:

\[
\text{HCO}_3^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CO}_3^{2-}(aq) + \text{H}_3\text{O}^+(aq) \quad K_a = 4.7 \times 10^{-11}
\]

\(\text{HCO}_3^-\) can also react as a base. Its \(K_b\) value can be found by using the \(K_a\) of its conjugate acid, \(\text{H}_2\text{CO}_3\).

\[
\text{HCO}_3^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{CO}_3(aq) + \text{OH}^-(aq) \quad K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.5 \times 10^{-7}} = 2.2 \times 10^{-8}
\]

Since \(K_b > K_a\), a solution of NaHCO₃ is **basic**.

b) The two ions that comprise this salt are anilinium ion, \(\text{C}_6\text{H}_5\text{NH}_3^+\), and nitrite ion, \(\text{NO}_2^-\).

Anilinium ion is the acid of \(\text{C}_6\text{H}_5\text{NH}_2\) with \(K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{7.1 \times 10^{-3}} = 2.5 \times 10^{-5}\).

\[
\text{C}_6\text{H}_5\text{NH}_3^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_2(aq) + \text{H}_3\text{O}^+(aq) \quad K_a = 2.5 \times 10^{-5}
\]

Nitrite ion is the base with \(K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{2.5 \times 10^{-5}} = 4.0 \times 10^{-9}\).

\[
\text{NO}_2^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HNO}_2(aq) + \text{OH}^-(aq) \quad K_b = 1.4 \times 10^{-11}
\]

Since \(K_a > K_b\), a solution of \(\text{C}_6\text{H}_5\text{NH}_3\text{NO}_2\) is **acidic**.

c) The ions are \(\text{Na}^+\) and \(\text{H}_2\text{PO}_4^-\); the \(\text{Na}^+\) is from the strong base NaOH, and does not react with water. The \(\text{H}_2\text{PO}_4^-\) can react as an acid:

\[
\text{H}_2\text{PO}_4^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{PO}_4(aq) + \text{OH}^-(aq) \quad K_a = 6.3 \times 10^{-8}
\]

\(\text{H}_2\text{PO}_4^-\) can also react as a base. Its \(K_b\) value can be found by using the \(K_a\) of its conjugate acid, \(\text{H}_3\text{PO}_4\).

\[
\text{H}_2\text{PO}_4^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{PO}_4(aq) + \text{OH}^-(aq) \quad K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{7.2 \times 10^{-3}} = 1.4 \times 10^{-12}
\]

Since \(K_a > K_b\), a solution of NaH₂PO₄ is **acidic**.

18.15A **Plan:** A Lewis acid is an electron-pair acceptor while a Lewis base is an electron-pair donor.

**Solution:**

a)

\[
[\text{HO}_3^-(\text{aq}) + \text{OH}^-] \rightarrow \begin{array}{c}
\text{OH}^- \\
\text{HO}_3^-(\text{aq})
\end{array} 
\]

[trigonal planar] [tetrahedral]

Hydroxide ion, \(\text{OH}^-\), donates an electron pair and is the Lewis base; \(\text{Al(OH)}_3\) accepts the electron pair and is the Lewis acid. Note the change in geometry caused by the formation of the adduct.
Sulfur trioxide accepts the electron pair and is the Lewis acid. Water donates an electron pair and is the Lewis base.

c)

Co$^{3+}$ accepts six electron pairs and is the Lewis acid. Ammonia donates an electron pair and is the Lewis base.

18.15B Plan: A Lewis acid is an electron-pair acceptor while a Lewis base is an electron-pair donor.

Solution:
a) B(OH)$_3$ is the Lewis acid because it is accepting electron pairs from water, the Lewis base.
b) Cd$^{2+}$ accepts four electron pairs and is the Lewis acid. Each iodide ion donates an electron pair and is the Lewis base.
c) Each fluoride ion donates an electron pair to form a bond with boron in SiF$_6^{2-}$. The fluoride ion is the Lewis base and the boron tetrafluoride is the Lewis acid.

END–OF–CHAPTER PROBLEMS

18.1 The Arrhenius definition classifies substances as being acids or bases by their behavior in the solvent water.

18.2 All Arrhenius acids contain hydrogen and produce hydronium ion (H$_3$O$^+$) in aqueous solution. All Arrhenius bases contain an OH group and produce hydroxide ion (OH$^-$) in aqueous solution. Neutralization occurs when each H$_2$O$^+$ molecule combines with an OH$^-$ molecule to form two molecules of H$_2$O. Chemists found that the $\Delta H_{\text{rxn}}$ was independent of the combination of strong acid with strong base. In other words, the reaction of any strong base with any strong acid always produced 56 kJ/mol ($\Delta H = -56$ kJ/mol). This was consistent with Arrhenius’s hypothesis describing neutralization, because all other counter ions (those present from the dissociation of the strong acid and base) were spectators and did not participate in the overall reaction.

18.3 The Arrhenius acid-base definition is limited by the fact that it only classifies substances as an acid or base when dissolved in the single solvent water. The anhydrous neutralization of NH$_3$(g) and HCl(g) would not be included in the Arrhenius acid-base concept. In addition, it limits a base to a substance that contains OH in its formula. NH$_3$ does not contain OH in its formula but produces OH$^-$ ions in H$_2$O.

18.4 Strong acids and bases dissociate completely into their ions when dissolved in water. Weak acids only partially dissociate. The characteristic property of all weak acids is that a significant number of the acid molecules are not dissociated. For a strong acid, the concentration of hydronium ions produced by dissolving the acid is equal to the initial concentration of the undissociated acid. For a weak acid, the concentration of hydronium ions produced when the acid dissolves is less than the initial concentration of the acid.

18.5 Plan: Recall that an Arrhenius acid contains hydrogen and produces hydronium ion (H$_3$O$^+$) in aqueous solution.

Solution:
a) Water, H$_2$O, is an Arrhenius acid because it produces H$_3$O$^+$ ion in aqueous solution. Water is also an Arrhenius base because it produces the OH$^-$ ion as well.
b) Calcium hydroxide, Ca(OH)$_2$ is a base, not an acid.
c) Phosphorous acid, H$_3$PO$_3$, is a weak Arrhenius acid. It is weak because the number of O atoms equals the number of ionizable H atoms.
d) Hydroiodic acid, HI, is a strong Arrhenius acid.

18.6 Only (a) NaHSO$_4$

18.7 Plan: All Arrhenius bases contain an OH group and produce hydroxide ion (OH$^-$) in aqueous solution.
Solution:
Barium hydroxide, Ba(OH)$_2$, and potassium hydroxide, KOH, (b and d) are Arrhenius bases because they contain hydroxide ions and form OH$^-$ when dissolved in water. H$_3$AsO$_4$ and HClO, (a) and (c), are Arrhenius acids, not bases.

18.8 (b) H$_2$O is a very weak Arrhenius base.

18.9 Plan: $K_a$ is the equilibrium constant for an acid dissociation which has the generic equation

$\text{HA}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq)$. The $K_a$ expression is $\frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$. $[\text{H}_2\text{O}]$ is treated as a constant and omitted from the expression. Write the acid-dissociation reaction for each acid, following the generic equation, and then write the $K_a$ expression.
Solution:
a) \( \text{HCN}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CN}^-(aq) \)

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]}
\]
b) \( \text{HCO}_3^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CO}_3^{2-}(aq) \)

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}
\]
c) \( \text{HCOOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HCOO}^-(aq) \)

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]}
\]

18.10 a) \( \text{CH}_3\text{NH}_3^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CH}_3\text{NH}_2(aq) \)

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{NH}_2]}{[\text{CH}_3\text{NH}_3^+]}
\]
b) \( \text{HClO}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{ClO}^- (aq) \)

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{ClO}^-]}{[\text{HClO}]}
\]
c) \( \text{H}_2\text{S}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HS}^-(aq) \)

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{HS}^-]}{[\text{H}_2\text{S}]}
\]
18.11 Plan: $K_a$ is the equilibrium constant for an acid dissociation which has the generic equation

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

The $K_a$ expression is $\frac{[H_3O^+][A^-]}{[HA]}$. $[H_2O]$ is treated as a constant and omitted from the expression. Write the acid-dissociation reaction for each acid, following the generic equation, and then write the $K_a$ expression.

Solution:

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

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

b) $CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

c) $HBrO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + BrO_2^-(aq)$

$$K_a = \frac{[H_3O^+][BrO_2^-]}{[HBrO_2]}$$

18.12 a) $H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$

$$K_a = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]}$$

b) $H_3PO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_2^-(aq)$

$$K_a = \frac{[H_3O^+][H_2PO_2^-]}{[H_3PO_2]}$$

c) $HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$

$$K_a = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]}$$

18.13 Plan: $K_a$ values are listed in the Appendix. The larger the $K_a$ value, the stronger the acid. The $K_a$ value for hydroiodic acid, HI, is not shown because $K_a$ approaches infinity for strong acids and is not meaningful.

Solution:

HI is the strongest acid (it is one of the six strong acids), and acetic acid, $CH_3COOH$, is the weakest: $CH_3COOH < HF < HIO_3 < HI$

18.14 $HCl > HNO_2 > HClO > HCN$

18.15 Plan: Strong acids are the hydrohalic acids HCl, HBr, HI, and oxoacids in which the number of O atoms exceeds the number of ionizable protons by two or more; these include $HNO_3$, $H_2SO_4$, and $HClO_4$. All other acids are weak acids. Strong bases are metal hydroxides (or oxides) in which the metal is a Group 1A(1) metal or Ca, Sr, or Ba in Group 2A(2). Weak bases are NH$_3$ and amines.

Solution:

a) Arsenic acid, $H_3AsO_4$, is a weak acid. The number of O atoms is four, which exceeds the number of ionizable H atoms, three, by one. This identifies $H_3AsO_4$ as a weak acid.

b) Strontium hydroxide, Sr(OH)$_2$, is a strong base. Soluble compounds containing OH$^-$ ions are strong bases. Sr is a Group 2 metal.

c) HIO is a weak acid. The number of O atoms is one, which is equal to the number of ionizable H atoms identifying HIO as a weak acid.

d) Perchloric acid, $HClO_4$, is a strong acid. $HClO_4$ is one example of the type of strong acid in which the number of O atoms exceeds the number of ionizable H atoms by more than two.
18.16  a) weak base  b) strong base  c) strong acid  d) weak acid

18.17  Plan: Strong acids are the hydrohalic acids HCl, HBr, HI, and oxoacids in which the number of O atoms exceeds the number of ionizable protons by two or more; these include HNO₃, H₂SO₄, and HClO₄. All other acids are weak acids. Strong bases are metal hydroxides (or oxides) in which the metal is a Group 1A(1) metal or Ca, Sr, or Ba in Group 2A(2). Weak bases are NH₃ and amines.

Solution:
a) Rubidium hydroxide, RbOH, is a strong base because Rb is a Group 1A(1) metal.
b) Hydrobromic acid, HBr, is a strong acid, because it is one of the listed hydrohalic acids.
c) Hydrogen telluride, H₂Te, is a weak acid, because H is not bonded to an oxygen or halide.
d) Hypochlorous acid, HClO, is a weak acid. The number of O atoms is one, which is equal to the number of ionizable H atoms identifying HClO as a weak acid.

18.18  a) weak base  b) strong acid  c) weak acid  d) weak acid

18.19  Autoionization reactions occur when a proton (or, less frequently, another ion) is transferred from one molecule of the substance to another molecule of the same substance.

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

\[ \text{H}_2\text{SO}_4(l) + \text{H}_2\text{SO}_4(l) \rightleftharpoons \text{H}_3\text{SO}_4(\text{solvated}) + \text{HSO}_4^–(\text{solvated}) \]

18.20  \[ K_c = \frac{[\text{H}_3\text{O}^+] [\text{OH}–]}{[\text{H}_2\text{O}]} \]

[H₂O] is a constant and is included with the value of \( K_c \) to obtain \( K_w \):

\[ K_w = [\text{H}_3\text{O}^+]^2 X K_c = [\text{H}_3\text{O}^+]\text{[OH}–] \]

18.21  a) pH increases by a value of 1.

b) \([\text{H}_3\text{O}^+]\) increases by a factor of 1000.

18.22  Plan: The lower the concentration of hydronium \((\text{H}_3\text{O}^+)\) ions, the higher the pH. pH increases as \( K_a \) or the molarity of acid decreases. Recall that \( pK_a = -\log K_a \).

Solution:
a) At equal concentrations, the acid with the larger \( K_a \) will ionize to produce more hydronium ions than the acid with the smaller \( K_a \). The solution of an acid with the smaller \( K_a = 4 \times 10^{-7} \) has a lower \([\text{H}_3\text{O}^+]\) and higher pH.
b) \( pK_a \) is equal to \(-\log K_a \). The smaller the \( K_a \), the larger the \( pK_a \) is. So the acid with the larger \( pK_a \), 3.5, has a lower \([\text{H}_3\text{O}^+]\) and higher pH.
c) Lower concentration of the same acid means lower concentration of hydronium ions produced. The 0.01 M solution has a lower \([\text{H}_3\text{O}^+]\) and higher pH.
d) At the same concentration, strong acids dissociate to produce more hydronium ions than weak acids. The 0.1 M solution of a weak acid has a lower \([\text{H}_3\text{O}^+]\) and higher pH.
e) Bases produce \( \text{OH}– \) ions in solution, so the concentration of hydronium ion for a solution of a base solution is lower than that for a solution of an acid. The 0.01 \( M \) base solution has the higher pH.
f) \( \text{pOH} \) equals \(-\log \text{[OH}–]\). At 25°C, the equilibrium constant for water ionization, \( K_w \), equals \( 1 \times 10^{-14} \) so \( 14 = \text{pH} + \text{pOH} \). As \( \text{pOH} \) decreases, pH increases. The solution of \( \text{pOH} = 6.0 \) has the higher pH.

18.23  Plan: Part a) can be approached two ways. Because NaOH is a strong base, the \([\text{OH}–]\)\(_{\text{eq}}\) = [NaOH]\(_{\text{init}}\). One method involves calculating \([\text{H}_3\text{O}^+]\) using \( K_w = [\text{H}_3\text{O}^+]\text{[OH}–] \), then calculating pH from the relationship \( \text{pH} = -\log \text{[H}_3\text{O}^+] \). The other method involves calculating \( \text{pOH} \) and then using \( \text{pH} + \text{pOH} = 14.00 \) to calculate pH. Part b) also has two acceptable methods analogous to those in part a); only one method will be shown.

Solution:
a) First method:
\[ K_w = [\text{H}_3\text{O}^+]\text{[OH}–] \]
\[ [\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}–]} = \frac{1.0 \times 10^{-14}}{0.0111} = 9.0090 \times 10^{-13} \text{ M} \]
pH = –log [H₃O⁺] = –log (9.0090x10⁻¹³) = 12.04532 = 12.05

Second method:

pOH = –log [OH⁻] = –log (0.0111) = 1.954677

pH = 14.00 – pOH = 14.00 – 1.954677 = 12.04532 = 12.05

With a pH > 7, the solution is **basic**.

b) For a strong acid such as HCl:

[H₃O⁺] = [HCl] = 1.35x10⁻³ M

pH = –log (1.35x10⁻³) = 2.869666

pOH = 14.00 – 2.869666 = 11.130334 = 11.13

With a pH < 7, the solution is **acidic**.

18.24 a) pH = –log (0.0333) = 1.47756 = 1.478; **acidic**

b) pOH = –log (0.0347) = 1.45967 = 1.460; **basic**

18.25 **Plan:** HI is a strong acid, so [H₃O⁺] = [HI] and the pH can be calculated from the relationship pH = –log [H₃O⁺].

Ba(OH)₂ is a strong base, so [OH⁻] = 2 x [Ba(OH)₂] and pOH = –log [OH⁻].

**Solution:**

a) [H₃O⁺] = [HI] = 6.14x10⁻³ M,

pH = –log (6.14x10⁻³) = 2.211832 = 2.212. Solution is **acidic**.

b) [OH⁻] = 2 x [Ba(OH)₂] = 2(2.55 M) = 5.10 M
pOH = –log (5.10) = –0.70757 = –0.708. Solution is **basic**.

18.26 a) pOH = –log (7.52x10⁻⁴) = 3.12378

pH = 14.00 – 3.12378 = 10.87622 = 10.88 **basic**

b) pH = –log (1.59x10⁻³) = 2.79860

pOH = 14.00 – 2.79860 = 11.20140 = 11.20 **acidic**

18.27 **Plan:** The relationships are: pH = –log [H₃O⁺] and [H₃O⁺] = 10⁻ᵖH; pOH = –log [OH⁻] and [OH⁻] = 10⁻ᵖOH; and 14 = pH + pOH.

**Solution:**

a) [H₃O⁺] = 10⁻ᵖH = 10⁻⁹.85 = 1.4125375x10⁻¹⁰ = 1.4x10⁻¹⁰ M H₃O⁺
pOH = 14.00 – pH = 14.00 – 9.85 = 4.15

[OH⁻] = 10⁻ᵖOH = 10⁻⁴.15 = 7.0794578x10⁻⁵ = 7.1x10⁻⁵ M OH⁻

b) pH = 14.00 – pOH = 14.00 – 9.43 = 4.57

[H₃O⁺] = 10⁻ᵖH = 10⁻⁴.57 = 2.691535x10⁻⁵ = 2.7x10⁻⁵ M H₃O⁺

[OH⁻] = 10⁻ᵖOH = 10⁻⁹.43 = 3.7153523x10⁻¹⁰ = 3.7x10⁻¹⁰ M OH⁻

18.28 a) [H₂O⁺] = 10⁻ᵖH = 10⁻³.47 = 3.38844x10⁻⁴ = 3.4x10⁻⁴ M H₂O⁺
pOH = 14.00 – pH = 14.00 – 3.47 = 10.53

[OH⁻] = 10⁻ᵖOH = 10⁻¹⁰.53 = 2.951209x10⁻¹¹ = 3.0x10⁻¹¹ M OH⁻

b) pH = 14.00 – pOH = 14.00 – 4.33 = 9.67

[H₂O⁺] = 10⁻ᵖH = 10⁻⁹.67 = 2.13796x10⁻¹⁰ = 2.1x10⁻¹⁰ M H₂O⁺

[OH⁻] = 10⁻ᵖOH = 10⁻⁴.33 = 4.67735x10⁻⁵ = 4.7x10⁻⁵ M OH⁻

18.29 **Plan:** The relationships are: pH = –log [H₂O⁺] and [H₂O⁺] = 10⁻ᵖH; pOH = –log [OH⁻] and [OH⁻] = 10⁻ᵖOH; and 14 = pH + pOH.

**Solution:**

a) [H₂O⁺] = 10⁻ᵖH = 10⁻⁸.97 = 1.69824x10⁻⁵ = 1.7x10⁻⁵ M H₂O⁺
pOH = 14.00 – pH = 14.00 – 4.77 = 9.23

[OH⁻] = 10⁻ᵖOH = 10⁻⁹.23 = 5.8884x10⁻¹⁰ = 5.9x10⁻¹⁰ M OH⁻

b) pH = 14.00 – pOH = 14.00 – 5.65 = 8.35

[H₂O⁺] = 10⁻ᵖH = 10⁻⁸.35 = 4.46684x10⁻⁹ = 4.5x10⁻⁹ M H₂O⁺

[OH⁻] = 10⁻ᵖOH = 10⁻⁵.65 = 2.23872x10⁻⁶ = 2.2x10⁻⁶ M OH⁻

18.30 a) [H₂O⁺] = 10⁻ᵖH = 10⁻⁸.97 = 1.071519x10⁻⁹ = 1.1x10⁻⁹ M H₂O⁺
\[ \text{pOH} = 14.00 - \text{pH} = 14.00 - 8.97 = 5.03 \]

\[ [\text{OH}^-] = 10^{-\text{pOH}} = 10^{-5.03} = 9.3325 \times 10^{-6} \, M \, \text{OH}^- \]

b) \[ \text{pH} = 14.00 - \text{pOH} = 14.00 - 11.27 = 2.73 \]

\[ [\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-2.73} = 1.862087 \times 10^{-3} = 1.9 \times 10^{-3} \, M \, \text{H}_3\text{O}^+ \]

\[ [\text{OH}^-] = 10^{-\text{pOH}} = 10^{-11.27} = 5.3703 \times 10^{-12} = 5.4 \times 10^{-12} \, M \, \text{OH}^- \]

18.31 Plan: The pH is increasing, so the solution is becoming more basic. Therefore, \text{OH}^- ion is added to increase the pH. Since one mole of \text{H}_3\text{O}^+ will react with one mole of \text{OH}^-, the difference in \[ [\text{H}_3\text{O}^+] \] would be equal to the \[ [\text{OH}^-] \] added. Use the relationship \[ [\text{H}_3\text{O}^+] = 10^{-\text{pH}} \] to find \[ [\text{H}_3\text{O}^+] \] at each pH.

Solution:

\[ [\text{H}_3\text{O}^+] = 10^{-3.15} = 7.07946 \times 10^{-4} \, M \, \text{H}_3\text{O}^+ \]

\[ [\text{H}_3\text{O}^+] = 10^{-3.65} = 2.23872 \times 10^{-4} \, M \, \text{H}_3\text{O}^+ \]

Add (7.07946 \times 10^{-4} M \text{H}_3\text{O}^+ - 2.23872 \times 10^{-4} M \text{H}_3\text{O}^+) = 4.84074 \times 10^{-4} = 4.8 \times 10^{-4} \text{ mol of OH}^- \text{ per liter} \]

18.32 The pH is decreasing so the solution is becoming more acidic. Therefore, \text{H}_3\text{O}^+ ion is added to decrease the pH.

\[ [\text{H}_3\text{O}^+] = 10^{-5.33} = 4.67735 \times 10^{-10} \, M \, \text{H}_3\text{O}^+ \]

\[ [\text{H}_3\text{O}^+] = 10^{-9.07} = 8.51138 \times 10^{-10} \, M \, \text{H}_3\text{O}^+ \]

Add (8.51138 \times 10^{-10} M \text{H}_3\text{O}^+ - 4.67735 \times 10^{-10} M \text{H}_3\text{O}^+) = 3.83403 \times 10^{-10} = 3.8 \times 10^{-10} \text{ mol of H}_3\text{O}^+ \text{ per liter} \]

18.33 Plan: The pH is increasing, so the solution is becoming more basic. Therefore, \text{OH}^- ion is added to increase the pH. Since one mole of \text{H}_3\text{O}^+ will react with one mole of \text{OH}^-, the difference in \[ [\text{H}_3\text{O}^+] \] would be equal to the \[ [\text{OH}^-] \] added. Use the relationship \[ [\text{H}_3\text{O}^+] = 10^{-\text{pH}} \] to find \[ [\text{H}_3\text{O}^+] \] at each pH.

Solution:

\[ [\text{H}_3\text{O}^+] = 10^{-4.52} = 3.01995 \times 10^{-5} \, M \, \text{H}_3\text{O}^+ \]

\[ [\text{H}_3\text{O}^+] = 10^{-5.25} = 5.623413 \times 10^{-6} \, M \, \text{H}_3\text{O}^+ \]

Moles of \text{OH}^- = \frac{2.4576 \times 10^{-5} \text{ mol}}{5.6 \text{ L}} = 1.3763 \times 10^{-4} \, \text{ mol of OH}^- \]

18.34 The pH is decreasing so the solution is becoming more acidic. Therefore, \text{H}_3\text{O}^+ ion is added to decrease the pH.

\[ [\text{H}_3\text{O}^+] = 10^{-8.92} = 1.20226 \times 10^{-9} \, M \, \text{H}_3\text{O}^+ \]

\[ [\text{H}_3\text{O}^+] = 10^{-6.33} = 4.67735 \times 10^{-7} \, M \, \text{H}_3\text{O}^+ \]

Add (4.67735 \times 10^{-10} M \text{H}_3\text{O}^+ - 1.20226 \times 10^{-9} M \text{H}_3\text{O}^+) (87.5 mL)(10^{-3} \text{ L/1 mL}) = 4.08216 \times 10^{-8} = 4.1 \times 10^{-8} \text{ mol of H}_3\text{O}^+ \]

18.35 Scene A has a pH of 4.8.

\[ [\text{H}_3\text{O}^+] = 10^{-4.8} = 1.58489 \times 10^{-5} \, M \, \text{H}_3\text{O}^+ \]

Scene B:

\[ [\text{H}_3\text{O}^+] = \left( \frac{25 \text{ spheres}}{2 \text{ spheres}} \right) \times 1.58489 \times 10^{-5} \, \text{M} \, \text{H}_3\text{O}^+ \]

\[ \text{pH} = -\log [\text{H}_3\text{O}^+] = -\log [1.98 \times 10^{-4}] = 3.7 \]

18.36 Plan: Apply Le Chatelier’s principle in part a). In part b), given that the pH is 6.80, \[ [\text{H}_3\text{O}^+] \] can be calculated using the relationship \[ [\text{H}_3\text{O}^+] = 10^{-\text{pH}} \]. The problem specifies that the solution is neutral (pure water), meaning \[ [\text{H}_3\text{O}^+] = [\text{OH}^-] \]. A new \( K_w \) can then be calculated.

Solution:

a) Heat is absorbed in an endothermic process: \( 2\text{H}_2\text{O}(l) + \text{heat} \rightarrow \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq) \). As the temperature increases, the reaction shifts to the formation of products. Since the products are in the numerator of the \( K_w \) expression, rising temperature increases the value of \( K_w \).

b) \[ [\text{H}_3\text{O}^+] = 10^{-6.80} = 1.58489 \times 10^{-7} \, M \, \text{H}_3\text{O}^+ \]

\[ [\text{H}_3\text{O}^+] = 1.6 \times 10^{-7} \, M \, [\text{H}_3\text{O}^+] = [\text{OH}^-] \]

\[ K_w = [\text{H}_3\text{O}^+]\text{[OH}^-] = (1.58489 \times 10^{-7})(1.58489 \times 10^{-7}) = 2.511876 \times 10^{-14} = 2.5 \times 10^{-14} \]

For a neutral solution: \text{pOH} = 6.80
The Brønsted-Lowry theory defines acids as proton donors and bases as proton acceptors, while the Arrhenius definition looks at acids as containing ionizable H atoms and at bases as containing hydroxide ions. In both definitions, an acid produces hydronium ions and a base produces hydroxide ions when added to water. Ammonia, NH₃, and carbonate ion, CO₃²⁻, are two Brønsted-Lowry bases that are not Arrhenius bases because they do not contain hydroxide ions. Brønsted-Lowry acids must contain an ionizable H atom in order to be proton donors, so a Brønsted-Lowry acid that is not an Arrhenius acid cannot be identified. (Other examples are also acceptable.)

Every acid has a conjugate base, and every base has a conjugate acid. The acid has one more H and one more positive charge than the base from which it was formed.

a) Acid-base reactions are proton transfer processes. Thus, the proton will be transferred from the stronger acid to the stronger base to form the weaker acid and weaker base.

\[ \text{HB(aq)} + \text{A}^- (\text{aq}) \rightarrow \text{HA(aq)} + \text{B}^- (\text{aq}) \]

The spontaneous direction of a Brønsted-Lowry acid-base reaction is that the stronger acid will transfer a proton to the stronger base to produce the weaker acid and base. Thus at equilibrium there should be relatively more of weaker acid and base present than there will be of the stronger acid and base. Since there is more HA and B⁻ in sample and less HB and A⁻, \( \text{HB} \) must be the stronger acid and \( \text{A}^- \) must be the stronger base.

An amphoteric substance can act as either an acid or a base. In the presence of a strong base (OH⁻), the dihydrogen phosphate ion acts like an acid by donating hydrogen:

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

In the presence of a strong acid (HCl), the dihydrogen phosphate ion acts like a base by accepting hydrogen:

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

Plan: \( K_a \) is the equilibrium constant for an acid dissociation which has the generic equation

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

The \( K_a \) expression is

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

and omitted from the expression. Write the acid-dissociation reaction for each acid, following the generic equation, and then write the \( K_a \) expression.

Solution:

a) When phosphoric acid is dissolved in water, a proton is donated to the water and dihydrogen phosphate ions are generated.

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

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

b) Benzoic acid is an organic acid and has only one proton to donate from the carboxylic acid group. The H atoms bonded to the benzene ring are not acidic hydrogens.

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

\[ K_a = \frac{[\text{C}_6\text{H}_5\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{C}_6\text{H}_5\text{COOH}]} \]

c) Hydrogen sulfate ion donates a proton to water and forms the sulfate ion.

\[ \text{HSO}_4^- (\text{aq}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{SO}_4^{2-} (\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \]

\[ K_a = \frac{[\text{SO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{HSO}_4^-]} \]

a) Formic acid, an organic acid, has only one proton to donate from the carboxylic acid group. The remaining H atom, bonded to the carbon, is not an acidic hydrogen.

\[ \text{HCOOH(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{HCOO}^- (\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \]
K_a = \left[ \frac{\text{H}_3\text{O}^+ \cdot \text{HCOO}^-}{\text{HCOOH}} \right]

b) When chloric acid is dissolved in water, a proton is donated to the water and chlorate ions are generated.

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

K_a = \left[ \frac{\text{H}_3\text{O}^+ \cdot \text{ClO}_3^-}{\text{HClO}_3} \right]

c) The dihydrogen arsenate ion donates a proton to water and forms the hydrogen arsenate ion.

\[
\text{H}_2\text{AsO}_4^- (aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HAsO}_4^{2-} (aq) + \text{H}_3\text{O}^+(aq)
\]

K_a = \left[ \frac{\text{H}_3\text{O}^+ \cdot \text{HAsO}_4^{2-}}{\text{H}_2\text{AsO}_4^-} \right]

8.43 Plan: To derive the conjugate base, remove one H from the acid and decrease the charge by 1 (acids donate H^+). Since each formula in this problem is neutral, the conjugate base will have a charge of –1.

Solution:

a) Cl^–
b) HCO_3^–
c) OH^–

8.44 a) PO_4^{3–}
b) NH_3
c) S^{2–}

8.45 Plan: To derive the conjugate acid, add an H and increase the charge by 1 (bases accept H^+).

Solution:

a) NH_4^+
b) NH_3
c) C_{10}H_{14}N_2H^+

8.46 a) OH^–
b) HSO_4^–
c) H_3O^\square

8.47 Plan: The acid donates the proton to form its conjugate base; the base accepts a proton to form its conjugate acid.

Solution:

a) HCl + H_2O \rightleftharpoons \text{Cl}^- + \text{H}_3\text{O}^+

Conjugate acid-base pairs: HCl/Cl^- and H_2O/H_2O

b) HClO_4 + H_2SO_4 \rightleftharpoons \text{ClO}_4^- + \text{H}_3\text{SO}_4^+

Conjugate acid-base pairs: HClO_4/ClO_4^- and H_3SO_4^-/H_2SO_4

Note: Perchloric acid is able to protonate another strong acid, H_2SO_4, because perchloric acid is a stronger acid. (HClO_4’s oxygen atoms exceed its hydrogen atoms by one more than H_2SO_4.)

c) HPO_4^{2–} + H_2SO_4 \rightleftharpoons H_2PO_4^- + HSO_4

Conjugate acid-base pairs: H_2SO_4/HSO_4^- and H_3PO_4/HPO_4^{2–}

8.48 a) NH_3 + HNO_3 \rightleftharpoons NH_4^+ + NO_3^–

Conjugate pairs: HNO_3/NO_3^-; NH_4^+/NH_3

b) O^{2–} + H_2O \rightleftharpoons \text{OH}^- + \text{OH}^–

Conjugate pairs: OH^-/O^{2–}; H_2O/OH^–

c) NH_4^+ + BrO_3\rightleftharpoons NH_3 + HBrO_3

Conjugate pairs: NH_4^+/NH_3; HBrO_3/BrO_3

8.49 Plan: The acid donates the proton to form its conjugate base; the base accepts a proton to form its conjugate acid.

Solution:
a) $\text{NH}_3 + \text{H}_3\text{PO}_4 \rightleftharpoons \text{NH}_4^+ + \text{H}_2\text{PO}_4^-$

Conjugate acid-base pairs: $\text{H}_3\text{PO}_4/\text{H}_2\text{PO}_4^-$; $\text{NH}_4^+/\text{NH}_3$

b) $\text{CH}_3\text{O}^- + \text{NH}_3 \rightleftharpoons \text{CH}_3\text{OH} + \text{NH}_2^-$

Conjugate acid-base pairs: $\text{NH}_3/\text{NH}_2^-; \text{CH}_3\text{OH}/\text{CH}_3\text{O}^-$

c) $\text{HPO}_4^{2-} + \text{HSO}_4^- \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{SO}_4^{2-}$

Conjugate acid-base pairs: $\text{HSO}_4^-/\text{SO}_4^{2-}; \text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$

18.50 a) $\text{NH}_4^+ + \text{CN}^- \rightleftharpoons \text{NH}_3 + \text{HCN}$

Conjugate acid-base pairs: $\text{NH}_3/\text{NH}_2^-; \text{HCN/CN}^-$

b) $\text{H}_2\text{O} + \text{HS}^- \rightleftharpoons \text{OH}^- + \text{H}_2\text{S}$

Conjugate acid-base pairs: $\text{H}_2\text{O}/\text{OH}^-; \text{H}_2\text{S}/\text{HS}^-$

c) $\text{HSO}_3^- + \text{CH}_3\text{NH}_2 \rightleftharpoons \text{SO}_3^{2-} + \text{CH}_3\text{NH}_3^+$

Conjugate acid-base pairs: $\text{HSO}_3^-/\text{SO}_3^{2-}; \text{CH}_3\text{NH}_3^+/\text{CH}_3\text{NH}_2$

18.51 Plan: Write total ionic equations (show all soluble ionic substances as dissociated into ions) and then remove the spectator ions to write the net ionic equations. The (aq) subscript denotes that each species is soluble and dissociates in water. The acid donates the proton to form its conjugate base; the base accepts a proton to form its conjugate acid.

Solution:

a) $\text{Na}^+$(aq) + $\text{OH}^-(aq) + \text{Na}^+$(aq) + $\text{H}_2\text{PO}_4^-(aq) \rightleftharpoons \text{H}_2\text{O}(l) + 2\text{Na}^+$(aq) + $\text{HPO}_4^{2-}$(aq)

Net: $\text{OH}^-(aq) + \text{H}_2\text{PO}_4^-(aq) \rightleftharpoons \text{H}_2\text{O}(l) + \text{HPO}_4^{2-}$(aq)

Conjugate acid-base pairs: $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ and $\text{H}_2\text{O}/\text{OH}^-$

b) $\text{K}^+$(aq) + $\text{HSO}_4^-(aq) + 2\text{K}^+$(aq) + $\text{CO}_3^{2-}$(aq) $\rightleftharpoons 2\text{K}^+$(aq) + $\text{SO}_4^{2-}$(aq) + $\text{K}^+$(aq) + $\text{HCO}_3^-$

Net: $\text{HSO}_4^-(aq) + \text{CO}_3^{2-}$(aq) $\rightleftharpoons \text{SO}_4^{2-}$(aq) + $\text{HCO}_3^-$

Conjugate acid-base pairs: $\text{H}_2\text{O}_4^-/\text{SO}_4^{2-}$ and $\text{HCO}_3^-/\text{CO}_3^{2-}$

18.52 a) $\text{H}_2\text{O}^-(aq) + \text{CO}_3^{2-}$(aq) $\rightleftharpoons \text{HCO}_3^-(aq) + \text{H}_2\text{O}(l)$

Conjugate acid-base pairs: $\text{H}_2\text{O}^-/\text{H}_2\text{O}; \text{HCO}_3^-/\text{CO}_3^{2-}$

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

Conjugate acid-base pairs: $\text{NH}_4^+/\text{NH}_3; \text{H}_2\text{O}/\text{OH}^-$

18.53 Plan: The two possible reactions involve reacting the acid from one conjugate pair with the base from the other conjugate pair. The reaction that favors the products ($K_c > 1$) is the one in which the stronger acid produces the weaker acid. The reaction that favors reactants ($K_c < 1$) is the reaction in which the weaker acid produces the stronger acid.

Solution:
The conjugate pairs are $\text{H}_2\text{S}$ (acid)/$\text{HS}^-$ (base) and $\text{HCl}$ (acid)/$\text{Cl}^-$ (base). Two reactions are possible:

(1) $\text{HS}^- + \text{HCl} \rightleftharpoons \text{H}_2\text{S} + \text{Cl}^-$ and (2) $\text{H}_2\text{S} + \text{Cl}^- \rightleftharpoons \text{HS}^- + \text{HCl}$

The first reaction is the reverse of the second. HCl is a strong acid and $\text{H}_2\text{S}$ a weak acid. Reaction (1) with the stronger acid producing the weaker acid favors products and $K_c > 1$. Reaction (2) with the weaker acid forming the stronger acid favors the reactants and $K_c < 1$.

18.54 $K_c > 1$: $\text{HNO}_3 + \text{F}^- \rightleftharpoons \text{NO}_3^- + \text{HF}$

$K_c < 1$: $\text{NO}_3^- + \text{HF} \rightleftharpoons \text{HNO}_3 + \text{F}^-$
Plan: An acid-base reaction that favors the products ($K_c > 1$) is one in which the stronger acid produces the weaker acid. Use the figure to decide which of the two acids is the stronger acid.

Solution:

a) $\text{HCl} + \text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{Cl}^-$

strong acid     stronger base       weak acid     weaker base

HCl is ranked above NH$_4^+$ in the list of conjugate acid-base pair strength and is the stronger acid. NH$_3$ is ranked above Cl$^-$ and is the stronger base. NH$_3$ is shown as a “stronger” base because it is stronger than Cl$^-$, but is not considered a “strong” base. The reaction proceeds toward the production of the weaker acid and base, i.e., the reaction as written proceeds to the right and $K_c > 1$. The stronger acid is more likely to donate a proton than the weaker acid.

b) $\text{H}_2\text{SO}_3 + \text{NH}_3 \rightleftharpoons \text{HSO}_3^- + \text{NH}_4^+$

stronger acid stronger base weaker base weaker acid

H$_2$SO$_3$ is ranked above NH$_4^+$ and is the stronger acid. NH$_3$ is a stronger base than HSO$_3^-$. The reaction proceeds toward the production of the weaker acid and base, i.e., the reaction as written proceeds to the right and $K_c > 1$.

18.56 Neither a or b have $K_c > 1$.

18.57 Plan: An acid-base reaction that favors the reactants ($K_c < 1$) is one in which the weaker acid produces the stronger acid. Use the figure to decide which of the two acids is the weaker acid.

Solution:

a) $\text{NH}_4^+ + \text{HPO}_4^{2-} \rightleftharpoons \text{NH}_3 + \text{H}_2\text{PO}_4^-$

weaker acid weaker base stronger base stronger acid

$K_c < 1$ The reaction proceeds toward the production of the weaker acid and base, i.e., the reaction as written proceeds to the left.

b) $\text{HSO}_3^- + \text{HS}^- \rightleftharpoons \text{H}_2\text{SO}_3 + \text{S}^{2-}$

weaker base weaker acid stronger acid stronger base

$K_c < 1$ The reaction proceeds toward the production of the weaker acid and base, i.e., the reaction as written proceeds to the left.

18.58 a) $K_c < 1$ b) $K_c > 1$

18.59 a) The concentration of a strong acid is very different before and after dissociation since a strong acid exhibits 100% dissociation. After dissociation, the concentration of the strong acid approaches 0, or [HA] $\approx 0$.

b) A weak acid dissociates to a very small extent ($<100\%$), so the acid concentration after dissociation is nearly the same as before dissociation.

c) Same as b), but the percent, or extent, of dissociation is greater than in b).

d) Same as a)

18.60 No, HCl and CH$_3$COOH are never of equal strength because HCl is a strong acid with $K_a > 1$ and CH$_3$COOH is a weak acid with $K_a < 1$. The $K_a$ of the acid, not the concentration of H$_3$O$^+$ in a solution of the acid, determines the strength of the acid.

18.61 Plan: We are given the percent dissociation of the original HA solution ($33\%$), and we know that the percent dissociation increases as the acid is diluted. Thus, we calculate the percent dissociation of each diluted sample and see which is greater than $33\%$. To determine percent dissociation, we use the following formula:

$$\text{Percent HA dissociated} = \frac{[\text{HA}]_{\text{dissoc}}}{[\text{HA}]_{\text{init}}} \times 100$$

with $[\text{HA}]_{\text{dissoc}}$ equal to the number of H$_3$O$^+$ (or A$^-$) ions and $[\text{HA}]_{\text{init}}$ equal to the number of HA plus the number of H$_3$O$^+$ (or A$^-$).

Solution:

Calculating the percent dissociation of each diluted solution:

Solution 1. Percent dissociation = $[4/(5+4)] \times 100 = 44\%$

Solution 2. Percent dissociation = $[2/(7 + 2)] \times 100 = 22\%$

Solution 3. Percent dissociation = $[3/(6 + 3)] \times 100 = 33\%$

Therefore, scene 1 represents the diluted solution.
18.62 Water will add approximately $10^{-7}$ M to the $H_3O^+$ concentration. (The value will be slightly lower than for pure water.)

a) $CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$

$0.10 - x \quad x \quad x$

$K_a = 1.8 \times 10^{-5} = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$

$K_a = 1.8 \times 10^{-5} = \frac{(x)(x)}{(0.1 - x)}$

Assume $x$ is small compared to 0.1 so $0.1 - x = 0.1$.

$K_a = 1.8 \times 10^{-5} = \frac{(x)(x)}{(0.1)}$

$x = 1.3416 \times 10^{-3} M$

Since the $H_3O^+$ concentration from $CH_3COOH$ is many times greater than that from $H_2O$, $[H_3O^+] = [CH_3COO^-]$.

b) The extremely low $CH_3COOH$ concentration means the $H_3O^+$ concentration from $CH_3COOH$ is near that from $H_2O$. Thus $[H_3O^+] = [CH_3COO^-]$.

c) $CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$

$CH_3COONa(aq) \rightarrow CH_3COO^-(aq) + Na^+(aq)$

$K_a = 1.8 \times 10^{-5} = \frac{(x)(0.1 + x)}{(0.1 - x)}$

Assume $x$ is small compared to 0.1.

$x = [H_3O^+] = 1.8 \times 10^{-5}$

$[CH_3COO^-] = 0.1 + x = 0.1 M$

Thus, $[CH_3COO^-] > [H_3O^+]$

18.63 The higher the negative charge on a species, the more difficult it is to remove a positively charged $H^+$ ion.

18.64 Plan: Write the acid-dissociation reaction and the expression for $K_a$. Set up a reaction table and substitute the given value of $[H_3O^+]$ for $x$; solve for $K_a$.

Solution:
Butanoic acid dissociates according to the following equation:

$CH_3CH_2CH_2COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CH_2CH_2COO^-(aq)$

Initial: $0.15 \quad 0 \quad 0$

Change: $-x \quad +x \quad +x$

Equilibrium: $0.15 - x \quad x \quad x$

According to the information given in the problem, $[H_3O^+]_{eq} = 1.51 \times 10^{-3} M = x$

Thus, $[H_3O^+] = [CH_3CH_2CH_2COO^-] = 1.51 \times 10^{-3} M$

$[CH_3CH_2CH_2COOH] = (0.15 - x) = (0.15 - 1.51 \times 10^{-3}) M = 0.14849 M$

$K_a = \frac{[H_3O^+][CH_3CH_2CH_2COO^-]}{[CH_3CH_2CH_2COOH]}$

$K_a = \frac{(1.51 \times 10^{-3})(1.51 \times 10^{-3})}{0.14849} = 1.53552 \times 10^{-5} = 1.5 \times 10^{-5}$

18.65 Any weak acid dissociates according to the following equation:

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

$[H_3O^+] = 10^{-9.0} = 10^{-4.88} = 1.31826 \times 10^{-5} M$

Thus, $[H_3O^+] = [A^-] = 1.31826 \times 10^{-5} M$, and $[HA] = (0.035 - 1.31826 \times 10^{-5}) = 0.03499 M$

$K_a = \frac{[H_3O^+][A^-]}{[HA]}$
\[ K_a = \frac{\left(1.31826 \times 10^{-5}\right)\left(1.31826 \times 10^{-5}\right)}{0.03499} = 4.967 \times 10^{-9} = 5.0 \times 10^{-9} \]

18.66  **Plan:** Write the acid-dissociation reaction and the expression for \( K_a \). Set up a reaction table in which \( x \) = the concentration of the dissociated HNO\(_2\) and also \([H_3O^+]\). Use the expression for \( K_a \) to solve for \( x \) ([H\(_3\)O\(^+\)]).

**Solution:**
For a solution of a weak acid, the acid-dissociation equilibrium determines the concentrations of the weak acid, its conjugate base and H\(_3\)O\(^+\). The acid-dissociation reaction for HNO\(_2\) is:

\[
\text{Concentration } \begin{array}{c}
\text{HNO}_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)
\end{array}
\]

**Initial**

\[
\begin{array}{c|c|c|c}
\text{HNO}_2(aq) & \text{H}_2O(l) & \text{H}_3O^+(aq) & \text{NO}_2^-(aq) \\
\hline
0.60 & 0 & 0 & 0 \\
\end{array}
\]

**Change**

\[
\begin{array}{c|c|c|c}
-x & +x & +x & \\
\end{array}
\]

**Equilibrium**

\[
\begin{array}{c|c|c|c}
\text{HNO}_2(aq) & \text{H}_2O(l) & \text{H}_3O^+(aq) & \text{NO}_2^-(aq) \\
\hline
0.60 - x & x & x &  \\
\end{array}
\]

(The H\(_3\)O\(^+\) contribution from water has been neglected.)

\[
K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]} = 7.1 \times 10^{-4}
\]

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

Assume \( x \) is small compared to 0.60: \( 0.60 - x = 0.60 \)

\[x = 0.020639767\]

Check assumption that \( x \) is small compared to 0.60:

\[
\frac{0.020639767}{0.60}(100) = 3.4\% \text{ error, so the assumption is valid.}
\]

\[[H_3O^+] = [NO_2^-] = 2.1 \times 10^{-2} M\]

The concentration of hydroxide ion is related to concentration of hydronium ion through the equilibrium for water:

\[
2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \text{ with } K_w = 1.0 \times 10^{-14}
\]

\[
[OH^-] = \frac{1.0 \times 10^{-14}}{0.020639767} = 4.84502 \times 10^{-13} = 4.8 \times 10^{-13} M OH^-
\]

18.67  **For a solution of a weak acid, the acid-dissociation equilibrium determines the concentrations of the weak acid, its conjugate base and H\(_3\)O\(^+\).** The acid-dissociation reaction for HF is:

\[
\text{Concentration } \begin{array}{c}
\text{HF}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)
\end{array}
\]

**Initial**

\[
\begin{array}{c|c|c|c}
\text{HF}(aq) & \text{H}_2O(l) & \text{H}_3O^+(aq) & \text{F}^-(aq) \\
\hline
0.75 & 0 & 0 & 0 \\
\end{array}
\]

**Change**

\[
\begin{array}{c|c|c|c}
-x & +x & +x & \\
\end{array}
\]

**Equilibrium**

\[
\begin{array}{c|c|c|c}
\text{HF}(aq) & \text{H}_2O(l) & \text{H}_3O^+(aq) & \text{F}^-(aq) \\
\hline
0.75 - x & x & x &  \\
\end{array}
\]

(The H\(_3\)O\(^+\) contribution from water has been neglected.)

\[
K_a = 6.8 \times 10^{-4} = \frac{[H_3O^+][F^-]}{[HF]} \]

\[K_a = 6.8 \times 10^{-4} = \frac{(x)(x)}{(0.75 - x)} \]

Assume \( x \) is small compared to 0.75:

\[x = 0.02258\]

Check assumption: \( (0.02258/0.75) \times 100\% = 3\% \text{ error, so the assumption is valid.} \]

\[[H_3O^+] = [F^-] = 2.3 \times 10^{-2} M\]

\[[OH^-] = \frac{1.0 \times 10^{-14} \times 0.02258}{4.42869796 \times 10^{-13}} = 4.4 \times 10^{-13} M OH^-\]

18.68  **Plan:** Write the acid-dissociation reaction and the expression for \( K_a \). Set up a reaction table in which \( x \) = the
concentration of the dissociated acid and also $[H_3O^+]$. Use the expression for $K_a$ to solve for $x$ ($[H_3O^+]$). $K_a$ is found from the $pK_a$ by using the relationship $K_a = 10^{-pK_a}$.

**Solution:**

$K_a = 10^{-pK_a} = 10^{-2.87} = 1.34896 \times 10^{-3}$

<table>
<thead>
<tr>
<th>Concentration</th>
<th>$\text{ClCH}_2\text{COOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{ClCH}_2\text{COO}^-(aq)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>1.25</td>
</tr>
<tr>
<td>Change</td>
<td>$-x$</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>$1.25 - x$</td>
</tr>
</tbody>
</table>

$x = 0.04106337$

Check assumption that $x$ is small compared to 1.25: $\frac{0.04106337}{1.25} \times 100 = 3.3\%$. The assumption is good.

$[H_3O^+] = [\text{ClCH}_2\text{COO}^-] = 0.041 \text{ M}$

$[\text{ClCH}_2\text{COOH}] = 1.25 - 0.04106337 = 1.20894 = 1.21 \text{ M}$

$pH = -\log [H_3O^+] = -\log (0.04106337) = 1.3865 = 1.39$

---

Write a balanced chemical equation and equilibrium expression for the dissociation of hypochlorous acid and convert $pK_a$ to $K_a$.

$K_a = 10^{-pK_a} = 10^{-7.54} = 2.88403 \times 10^{-8}$

$\text{HClO}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{ClO}^-(aq)$

$x = 5.75902 \times 10^{-5}$

Check assumption: $(5.75902 \times 10^{-5}/0.115) \times 100 = 0.05\%$. The assumption is good.

$[H_3O^+] = [\text{ClO}^-] = 5.8 \times 10^{-5} \text{ M}$

$[\text{HClO}] = 0.115 - 5.75902 \times 10^{-5} = 0.11494 = 0.115 \text{ M}$

$pH = -\log [H_3O^+] = -\log (5.75902 \times 10^{-5}) = 4.2397 = 4.24$

---

**Plan:** Write the acid-dissociation reaction and the expression for $K_a$. Percent dissociation refers to the amount of the initial concentration of the acid that dissociates into ions. Use the percent dissociation to find the concentration of acid dissociated, which also equals $[H_3O^+]$. HA will be used as the formula of the acid. Set up a reaction table in which $x = \text{the concentration of the dissociated acid and } [H_3O^+]$. pH and $[OH^-]$ are determined from $[H_3O^+]$. Substitute $[HA]$, $[A^-]$, and $[H_3O^+]$ into the expression for $K_a$ to find the value of $K_a$.

**Solution:**

a) $\text{HA}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + A^-(aq)$

Percent HA = \( \frac{\text{dissociated acid}}{\text{initial acid}} \times 100\)
3.0% = \frac{x}{0.20} (100)
[Dissociated acid] = x = 6.0 \times 10^{-3} M
Concentration HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)
Initial: 0.20 0 0
Change: -x +x +x
Equilibrium: 0.20 – x x x
[Dissociated acid] = x = [A^-] = [H_3O^+] = 6.0 \times 10^{-3} M
pH = -\log [H_3O^+] = -\log (6.0 \times 10^{-3}) = 2.22185 = 2.22
K_w = 1.0 \times 10^{-14} = [H_3O^+][OH^-]
[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{6.0 \times 10^{-3}} = 1.666667 \times 10^{-12} = 1.7 \times 10^{-12} M
pOH = -\log [OH^-] = -\log (1.666667 \times 10^{-12}) = 11.7782 = 11.78

b) In the equilibrium expression, substitute the concentrations above and calculate $K_a$.

$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{(6.0 \times 10^{-3})(6.0 \times 10^{-3})}{(0.20 – 6.0 \times 10^{-3})} = 1.8567 \times 10^{-4} = 1.9 \times 10^{-4}$

18.71 Percent dissociation refers to the amount of the initial concentration of the acid that dissociates into ions. Use the percent dissociation to find the concentration of acid dissociated. HA will be used as the formula of the acid.

a) The concentration of acid dissociated is equal to the equilibrium concentrations of $A^-$ and $H_3O^+$. Then, pH and [OH^-] are determined from $[H_3O^+]$.

Percent HA dissociated = \frac{\text{dissociated acid}}{\text{initial acid}} (100)

12.5% = \frac{x}{0.735} (100)
[Dissociated acid] = 9.1875 \times 10^{-2} M
HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)
0.735 – x x x
[Dissociated acid] = x = [H_3O^+] = 9.19 \times 10^{-2} M
pH = -\log [H_3O^+] = -\log (9.1875 \times 10^{-2}) = 1.03680 = 1.037
[OH^-] = \frac{K_w}{[H_3O^+]} (9.1875 \times 10^{-2}) = 1.0884 \times 10^{-13} = 1.1 \times 10^{-13} M
pOH = -\log [OH^-] = -\log (1.0884 \times 10^{-13}) = 12.963197 = 12.963

b) In the equilibrium expression, substitute the concentrations above and calculate $K_a$.

$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{(9.1875 \times 10^{-2})(9.1875 \times 10^{-2})}{(0.735 - 9.1875 \times 10^{-2})} = 1.3125 \times 10^{-2} = 1.31 \times 10^{-2}$

18.72 Plan: Write the acid-dissociation reaction and the expression for $K_a$. Calculate the molarity of HX by dividing moles by volume. Convert pH to $[H_3O^+]$, set up a reaction table in which x = the concentration of the dissociated acid and also $[H_3O^+]$, and substitute into the equilibrium expression to find $K_a$.

Concentration (M) of HX = \frac{0.250 \text{ mol}}{655 \text{ mL}} \left( \frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) = 0.381679 M
Concentration HX(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + X^-(aq)
Initial: 0.381679 0 0
Change: -x +x +x
Equilibrium: 0.381679 – x x x
$[H_3O^+] = 10^{-pH} = 10^{-3.54} = 2.88403 \times 10^{-4} M = x$
Thus, $[H_3O^+] = [X^-] = 2.88403 \times 10^{-4} M$, and $[HX] = (0.381679 - 2.88403 \times 10^{-4}) M$
\[ K_a = \frac{[H_3O^+][X^-]}{[HX]} = \frac{(2.88403 \times 10^{-4})(2.88403 \times 10^{-4})}{(0.381679 - 2.88403 \times 10^{-4})} = 2.18087 \times 10^{-7} = 2.2 \times 10^{-7} \]

18.73 Calculate the molarity of HY by dividing moles by volume. Convert pH to \([H_3O^+]\) and substitute into the equilibrium expression.

\[
\text{Concentration of HY} = \frac{4.85 \times 10^{-3}}{0.095} = 0.0510526 M
\]

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

\[ 0.0510526 - x \quad x \quad x \]

\[ [H_3O^+] = 10^{-pH} = 10^{-2.68} = 2.08926 \times 10^{-3} M = x \]

Thus, \([H_3O^+] = [Y^-] = 2.08926 \times 10^{-3} M\) and \([HY] = (0.0510526 - 2.08926 \times 10^{-3}) M\)

\[ K_a = \frac{[H_3O^+][Y^-]}{[HY]} = \frac{(2.08926 \times 10^{-3})(2.08926 \times 10^{-3})}{(0.0510526 - 2.08926 \times 10^{-3})} = 8.91516 \times 10^{-5} = 8.9 \times 10^{-5} \]

18.74 Plan: Write the acid-dissociation reaction and the expression for \(K_a\). Set up a reaction table in which \(x\) = the concentration of the dissociated acid and also \([H_3O^+]\). Use the expression for \(K_a\) to solve for \(x\) (\([H_3O^+]\)). OH\(^-\) and then pOH can be found from \([H_3O^+]\).

**Solution:**

a) Concentration \(\text{HZ(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{Z}^-(aq)\)

\[
\begin{array}{c|c|c|c}
\text{Initial} & 0.075 & 0 & 0 \\
\text{Change} & -x & +x & +x \\
\text{Equilibrium} & 0.075 - x & x & x \\
\end{array}
\]

(\(\text{H}_3\text{O}^+\) contribution from water has been neglected.)

\[ K_a = 2.55 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+][\text{Z}^-]}{[\text{HZ}]} \]

\[ K_a = 2.55 \times 10^{-4} = \frac{(x)(x)}{(0.075 - x)} \quad \text{Assume } x \text{ is small compared to 0.075.} \]

\[ K_a = 2.55 \times 10^{-4} = \frac{(x)(x)}{(0.075)} \]

\([\text{H}_3\text{O}^+] = x = 4.3732 \times 10^{-3} \)

Check assumption that \(x\) is small compared to 0.075:

\[ \frac{4.3732 \times 10^{-3}}{0.075} \times 100 = 6\% \text{ error, so the assumption is not valid.} \]

Since the error is greater than 5%, it is not acceptable to assume \(x\) is small compared to 0.075, and it is necessary to use the quadratic equation.

\[ K_a = 2.55 \times 10^{-4} = \frac{(x)(x)}{(0.075 - x)} \]

\[ x^2 + 2.55 \times 10^{-4} x - 1.9125 \times 10^{-5} = 0 \]

\[ a = 1 \quad b = 2.55 \times 10^{-4} \quad c = -1.9125 \times 10^{-5} \]

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

\[ x = \frac{-2.55 \times 10^{-4} \pm \sqrt{(2.55 \times 10^{-4})^2 - 4(1)(-1.9125 \times 10^{-5})}}{2(1)} \]

\[ x = 0.00425 \text{ or } -0.00453 \]
pH = –log [H\textsubscript{3}O\textsuperscript{+}] = –log (0.00425) = 2.3716 = 2.37

b) Concentration HZ(aq) + H\textsubscript{2}O(l) ⇄ H\textsubscript{3}O\textsuperscript{+}(aq) + Z\textsuperscript{−}(aq)

<table>
<thead>
<tr>
<th>Initial</th>
<th>0.045</th>
<th>—</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change</td>
<td>–x</td>
<td>+x</td>
<td>+x</td>
<td>—</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.045 – x</td>
<td>x</td>
<td>x</td>
<td>—</td>
</tr>
</tbody>
</table>

(The H\textsubscript{3}O\textsuperscript{+} contribution from water has been neglected.)

\[ K_a = 2.55 \times 10^{-4} = \frac{[H\textsubscript{3}O\textsuperscript{+}][Z\textsuperscript{−}]}{[HZ]} \]

Assume x is small compared to 0.45.

\[ K_a = 2.55 \times 10^{-4} = \frac{(x)(x)}{(0.045 – x)} \]

\[ K_a = 2.55 \times 10^{-4} = \frac{(x)(x)}{0.045} \]

\[ [H\textsubscript{3}O\textsuperscript{+}] = x = 3.3875 \times 10^{-3} \]

Check assumption that x is small compared to 0.45:

\[ \frac{3.3875 \times 10^{-3}}{0.045} \times 100 = 7.5\% \text{ error, so the assumption is not valid.} \]

Since the error is greater than 5%, it is not acceptable to assume x is small compared to 0.045, and it is necessary to use the quadratic equation.

\[ K_a = 2.55 \times 10^{-4} = \frac{(x)(x)}{0.045 – x} \]

\[ x^2 = (2.55 \times 10^{-4})(0.045 – x) = 1.1475 \times 10^{-5} – 2.55 \times 10^{-4} x \]

\[ x^2 + 2.55 \times 10^{-4} x – 1.1475 \times 10^{-5} = 0 \]

\[ a = 1 \quad b = 2.55 \times 10^{-4} \quad c = -1.1475 \times 10^{-5} \]

\[ x = \frac{-b \pm \sqrt{b^2 – 4ac}}{2a} \]

\[ x = \frac{-2.55 \times 10^{-4} \pm \sqrt{(2.55 \times 10^{-4})^2 – 4(1)(-1.1475 \times 10^{-5})}}{2(1)} \]

\[ x = 3.26238 \times 10^{-3} \text{ M H}\textsubscript{3}O\textsuperscript{+} \]

\[ [OH\textsuperscript{−}] = \frac{K_w}{[H\textsubscript{3}O\textsuperscript{+}]} = \frac{1.0 \times 10^{-14}}{3.26238 \times 10^{-3}} = 3.0652468 \times 10^{-12} \text{ M} \]

\[ \text{pOH} = –\log [OH\textsuperscript{−}] = –\log (3.0652468 \times 10^{-12}) = 11.51353 = 11.51 \]

18.75 Calculate \( K_a \) from \( pK_a \).

\( K_a = 10^{-pK_a} = 10^{-4.89} = 1.28825 \times 10^{-5} \)

a) Begin with a reaction table, and then use the \( K_a \) expression as in earlier problems.

<table>
<thead>
<tr>
<th>Initial</th>
<th>0.035</th>
<th>—</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change</td>
<td>–x</td>
<td>+x</td>
<td>+x</td>
<td>—</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.035 – x</td>
<td>x</td>
<td>x</td>
<td>—</td>
</tr>
</tbody>
</table>

(The H\textsubscript{3}O\textsuperscript{+} contribution from water has been neglected.)

\[ K_a = 1.28825 \times 10^{-5} = \frac{[H\textsubscript{3}O\textsuperscript{+}][Q\textsuperscript{−}]}{[HQ]} \]

Assume x is small compared to 0.035.
\[ K_a = 1.28825 \times 10^{-5} = \frac{(x)(x)}{(0.035)} \]

\[[H_3O^+] = x = 6.71482 \times 10^{-4} M\]

Check assumption: \((6.71482 \times 10^{-4}/0.035) \times 100% = 2%\) error, so the assumption is valid.

\[ [H_3O^+] = 6.7 \times 10^{-4} M \]

b) Concentration \(HQ(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Q(aq)\)

Initial 0.65 — 0 0
Change \(-x\) \(+x\) \(+x\)
Equilibrium 0.65 – \(x\) \(x\) \(x\)

(The \(H_3O^+\) contribution from water has been neglected.)

\[ K_a = 1.28825 \times 10^{-5} = \frac{[H_3O^+][Q^-]}{[HQ]} \]

\[ K_a = 1.28825 \times 10^{-5} = \frac{(x)(x)}{(0.65 - x)} \]

Assume \(x\) is small compared to 0.65.

\[ K_a = 1.28825 \times 10^{-5} = \frac{(x)(x)}{(0.65)} \]

\[[H_3O^+] = x = 2.89372 \times 10^{-3} M\]

Check assumption: \((2.89372 \times 10^{-3}/0.65) \times 100% = 0.4%\) error, so the assumption is valid.

\[ [OH^-] = K_w/[H_3O^+] = (1.0 \times 10^{-14})/(2.89372 \times 10^{-3}) = 3.4558 \times 10^{-12} = 3.5 \times 10^{-12} M \]

18.76 Plan: Write the acid-dissociation reaction and the expression for \(K_a\). Set up a reaction table in which \(x\) = the concentration of the dissociated acid and also \([H_3O^+]\). Use the expression for \(K_a\) to solve for \(x\) ([H_3O^+]), \(OH^-\) and then \(pOH\) can be found from \([H_3O^+]\).

Solution:

a) Concentration \(HY(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Y^-(aq)\)

Initial 0.175 — 0 0
Change \(-x\) \(+x\) \(+x\)
Equilibrium 0.175 – \(x\) \(x\) \(x\)

(The \(H_3O^+\) contribution from water has been neglected.)

\[ K_a = 1.50 \times 10^{-4} = \frac{[H_3O^+][Y^-]}{[HY]} \]

\[ K_a = 1.50 \times 10^{-4} = \frac{(x)(x)}{(0.175 - x)} \]

Assume \(x\) is small compared to 0.175.

\[ K_a = 1.50 \times 10^{-4} = \frac{(x)(x)}{(0.175)} \]

\[[H_3O^+] = x = 5.1235 \times 10^{-3} M\]

Check assumption that \(x\) is small compared to 0.175:

\[
\frac{5.1235 \times 10^{-3}}{0.175} \times 100 = 3\% \text{ error, so the assumption is valid.}
\]

\[ \text{pH} = -\log[H_3O^+] = -\log(5.1235 \times 10^{-3}) = 2.29043 = 2.290\]

b) Concentration \(HX(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + X^-(aq)\)

Initial 0.175 — 0 0
Change \(-x\) \(+x\) \(+x\)
Equilibrium 0.175 – \(x\) \(x\) \(x\)

(The \(H_3O^+\) contribution from water has been neglected.)

\[ K_a = 2.00 \times 10^{-2} = \frac{[H_3O^+][X^-]}{[HX]} \]
\[ K_a = 2.00 \times 10^{-2} = \frac{(x)(x)}{(0.175 - x)} \]

Assume \( x \) is small compared to 0.175.

\[ K_a = 2.00 \times 10^{-2} = \frac{(x)(x)}{(0.175)} \]

\[ [H_3O^+] = x = 5.9161 \times 10^{-2} \ M \]

Check assumption that \( x \) is small compared to 0.175:

\[ \frac{5.9161 \times 10^{-2}}{0.175} \times 100 = 34\% \text{ error, so the assumption is not valid.} \]

Since the error is greater than 5\%, it is not acceptable to assume \( x \) is small compared to 0.175, and it is necessary to use the quadratic equation.

\[ K_a = 2.00 \times 10^{-2} = \frac{(x)(x)}{(0.175 - x)} \]

\[ x^2 = (2.00 \times 10^{-2})(0.175 - x) = 0.0035 - 2.00 \times 10^{-2} x \]

\[ x^2 + 2.00 \times 10^{-2} x - 0.0035 = 0 \]

\[ a = 1 \quad b = 2.00 \times 10^{-2} \quad c = -0.0035 \]

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

\[ x = \frac{-2.00 \times 10^{-2} \pm \sqrt{(2.00 \times 10^{-2})^2 - 4(1)(-0.0035)}}{2(1)} \]

\[ x = 5.00 \times 10^{-2} \ M H_3O^+ \]

\[ [OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{5.00 \times 10^{-2}} = 2.00 \times 10^{-13} \ M \]

\[ pOH = -\log [OH^-] = -\log (2.00 \times 10^{-13}) = 12.69897 = 12.699 \]

18.77 a) Begin with a reaction table, then use the \( K_a \) expression as in earlier problems.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>HCN(aq)</th>
<th>H_2O(l)</th>
<th>H_3O^+(aq)</th>
<th>CN^-(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.55</td>
<td>—</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>0.55 – x</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

(The H_3O^+ contribution from water has been neglected.)

\[ K_a = 6.2 \times 10^{-10} = \frac{[H_3O^+][CN^-]}{[HCN]} \]

\[ K_a = 6.2 \times 10^{-10} = \frac{(x)(x)}{(0.55 - x)} \]

Assume \( x \) is small compared to 0.55.

\[ K_a = 6.2 \times 10^{-10} = \frac{(x)(x)}{(0.55)} \]

\[ [H_3O^+] = x = 1.84662 \times 10^{-5} \ M \]

Check assumption: \((1.84662 \times 10^{-5}/0.55) \times 100\% = 0.0034\% \text{ error, so the assumption is valid.} \]

\[ pH = -\log [H_3O^+] = -\log (1.84662 \times 10^{-5}) = 4.7336 = 4.73 \]

b) Begin this part like part a).

<table>
<thead>
<tr>
<th>Concentration</th>
<th>HIO_3(aq)</th>
<th>H_2O(l)</th>
<th>H_3O^+(aq)</th>
<th>IO_3^- (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.044</td>
<td>—</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>0.044 – x</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

(The H_3O^+ contribution from water has been neglected.)
\[ K_a = 0.16 = \frac{[\text{H}_3\text{O}^+][\text{IO}_3^-]}{[\text{HIO}_3]} \]

\[ K_a = 0.16 = \frac{[x][x]}{(0.044 - x)} \quad \text{Assume } x \text{ is small compared to 0.044.} \]

\[ K_a = 0.16 = \frac{[x][x]}{(0.044)} \]

\[[\text{H}_3\text{O}^+] = x = 8.3905 \times 10^{-2} \]

Check assumption: \((8.3905 \times 10^{-2}/0.044) \times 100\% = 191\%\) error, so the assumption is not valid.

Since the error is greater than 5\%, it is not acceptable to assume \(x\) is small compared to 0.044, and it is necessary to use the quadratic equation.

\[ x^2 = (0.16)(0.044 - x) = 0.00704 - 0.16x \]

\[ x^2 + 0.16x - 0.00704 = 0 \]

\[ a = 1 \quad b = 0.16 \quad c = -0.00704 \]

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

\[ x = \frac{-0.16 \pm \sqrt{(0.16)^2 - 4(1)(-0.00704)}}{2(1)} \]

\[ x = 0.03593 \quad M \text{H}_3\text{O}^+ \]

\[ [\text{OH}^-] = K_w[\text{H}_3\text{O}^+] = (1.0 \times 10^{-14})/(0.03593) = 2.78 \times 10^{-13} \quad M \]

\[ \text{pOH} = -\log [\text{OH}^-] = -\log (2.78 \times 10^{-13}) = 12.56 \]

18.78 Plan: Write the acid-dissociation reaction and the expression for \(K_a\). Set up a reaction table in which \(x\) is the concentration of the dissociated acid and also \([\text{H}_3\text{O}^+]\). Use the expression for \(K_a\) to solve for \(x\), the concentration of benzoate ion at equilibrium. Then use the initial concentration of benzoic acid and the equilibrium concentration of benzoate to find % dissociation.

Solution:

<table>
<thead>
<tr>
<th>Concentration</th>
<th>(\text{C}_6\text{H}_5\text{COOH}(aq))</th>
<th>(\text{H}_2\text{O}(l))</th>
<th>(\Leftrightarrow)</th>
<th>(\text{H}_3\text{O}^+(aq))</th>
<th>(\text{C}_6\text{H}_5\text{COO}^-(aq))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.55</td>
<td>0</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>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.55 - x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ K_a = 6.3 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]} \]

\[ K_a = 6.3 \times 10^{-5} = \frac{[x][x]}{(0.55 - x)} \quad \text{Assume } x \text{ is small compared to 0.55.} \]

\[ K_a = 6.3 \times 10^{-5} = \frac{[x][x]}{(0.55)} \]

\[ x = 5.8864 \times 10^{-3} \quad M \]

\[ \text{Percent C}_6\text{H}_5\text{COOH dissociated} = \frac{[\text{C}_6\text{H}_5\text{COOH}]_{\text{dissociated}}}{[\text{C}_6\text{H}_5\text{COOH}]_{\text{initial}}} \]

\[ \text{Percent C}_6\text{H}_5\text{COOH dissociated} = \frac{5.8864 \times 10^{-3} \quad M}{0.55 \quad M} \times 100 = 1.07025 = 1.1\% \]
First, find the concentration of acetate ion at equilibrium. Then use the initial concentration of acetic acid and equilibrium concentration of acetate to find % dissociation.

Concentration $\text{CH}_3\text{COOH(aq)}$ $+ \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CH}_3\text{COO}^-(aq)$

<table>
<thead>
<tr>
<th></th>
<th>Initial</th>
<th>Change</th>
<th>Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3\text{COOH}$</td>
<td>0.050</td>
<td>$-x$</td>
<td>0.050 $-x$</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td></td>
<td>$+x$</td>
<td>$x$</td>
</tr>
<tr>
<td>$\text{CH}_3\text{COO}^-$</td>
<td>0</td>
<td></td>
<td>$x$</td>
</tr>
</tbody>
</table>

$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$

Assume $x$ is small compared to 0.050.

$x = 9.48683 \times 10^{-5} \text{ M}$

Percent $\text{CH}_3\text{COOH}$ dissociated $= \frac{[\text{CH}_3\text{COOH}]_{\text{dissociated}}}{[\text{CH}_3\text{COOH}]_{\text{initial}}} \times 100$

Percent $\text{CH}_3\text{COOH}$ dissociated $= \frac{9.48683 \times 10^{-4}}{0.050} \times (100) = 1.897367 = 1.9\%$

Plan: Write balanced chemical equations and corresponding equilibrium expressions for dissociation of hydrosulfuric acid, $\text{H}_2\text{S}$, and $\text{HS}^-$.

Since $K_{a1} \gg K_{a2}$, assume that almost all of the $\text{H}_3\text{O}^+$ comes from the first dissociation. Set up reaction tables in which $x$ = the concentration of dissociated acid and $[\text{H}_3\text{O}^+]$.

Solution:

$\text{H}_2\text{S(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HS}^-(aq)$

$K_{a1} = 9 \times 10^{-8} = \frac{[\text{H}_3\text{O}^+][\text{HS}^-]}{[\text{H}_2\text{S}]}$

Assume $x$ is small compared to 0.10.

$x = 9.48683 \times 10^{-5}$

$[\text{H}_3\text{O}^+][\text{HS}^-] = x = 9 \times 10^{-8} \text{ M}$

$pH = -\log [\text{H}_3\text{O}^+] = -\log (9.48683 \times 10^{-5}) = 4.022878 = 4.0$

$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{9.48683 \times 10^{-5}} = 1.05409 \times 10^{-10} = 1 \times 10^{-10} \text{ M}$

$pOH = -\log [\text{OH}^-] = -\log (1.05409 \times 10^{-10}) = 9.9771 = 10.0$

$[\text{H}_2\text{S}] = 0.10 - x = 0.10 - 9.48683 \times 10^{-5} = 0.099905 = 0.10 \text{ M}$

Concentration is limited to one significant figure because $K_a$ is given to only one significant figure. The pH is given to what appears to be two significant figures because the number before the decimal point (4) represents the exponent and the number after the decimal point represents the significant figures in the concentration.
Calculate $[S^{2-}]$ by using the $K_{a2}$ expression and assuming that $[HS^{-}]$ and $[H_{3}O^{+}]$ come mostly from the first dissociation. This new calculation will have a new $x$ value.

Concentration

<table>
<thead>
<tr>
<th></th>
<th>$HS^{-}(aq)$</th>
<th>$+H_{2}O(l)$</th>
<th>$H_{3}O^{+}(aq)$</th>
<th>$+S^{2-}(aq)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>$9.48683 \times 10^{-5}$</td>
<td>$-$</td>
<td>$9.48683 \times 10^{-5}$</td>
<td>$0$</td>
</tr>
<tr>
<td>Change</td>
<td>$-$</td>
<td>$+x$</td>
<td>$-$</td>
<td>$+x$</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>$9.48683 \times 10^{-5} - x$</td>
<td>$9.48683 \times 10^{-5} + x$</td>
<td>$x$</td>
<td></td>
</tr>
</tbody>
</table>

$K_{a2} = 1 \times 10^{-17} = \frac{[H_{3}O^{+}][S^{2-}]}{[HS^{-}]}$

Assume $x$ is small compared to $9.48683 \times 10^{-5}$.

The small value of $x$ means that it is not necessary to recalculate the $[H_{3}O^{+}]$ and $[HS^{-}]$ values.

18.81 Write balanced chemical equations and corresponding equilibrium expressions for dissociation of malonic acid ($H_{2}C_{3}H_{2}O_{4}$).

$K_{a1} = 1.4 \times 10^{-3} = \frac{[H_{3}O^{+}][HC_{3}H_{2}O_{4}^{-}]}{[H_{2}C_{3}H_{2}O_{4}]}$  
$K_{a2} = 2.0 \times 10^{-6} = \frac{[H_{3}O^{+}][C_{3}H_{2}O_{4}^{2-}]}{[HC_{3}H_{2}O_{4}^{-}]}$

Since $K_{a1} >> K_{a2}$, assume that almost all of the $H_{3}O^{+}$ comes from the first dissociation.

$K_{a1} = 1.4 \times 10^{-3} = \frac{[H_{3}O^{+}][HC_{3}H_{2}O_{4}^{-}]}{[H_{2}C_{3}H_{2}O_{4}]}$

$x = \frac{(0.200 - x)(x)}{(0.200)}$  
Assume $x$ is small compared to 0.200.

$x = 0.016733$

Check assumption: $(0.016733/0.200) \times 100\% = 8\%$ error, so the assumption is not valid. Since the error is greater than 5%, it is not acceptable to assume $x$ is small compared to 0.200, and it is necessary to use the quadratic equation.

$x^{2} = 2.8 \times 10^{-4} - 1.4 \times 10^{-3} x$

$x^{2} + 1.4 \times 10^{-3} x - 2.8 \times 10^{-4} = 0$

$a = 1 \quad b = 1.4 \times 10^{-3} \quad c = -2.8 \times 10^{-4}$

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

$x = \frac{-1.4 \times 10^{-3} \pm \sqrt{(1.4 \times 10^{-3})^{2} - 4(1)(-2.8 \times 10^{-4})}}{2(1)}$

$x = 1.6048 \times 10^{-2}$

$[H_{3}O^{+}] = [HC_{3}H_{2}O_{4}^{-}] = x = 1.6 \times 10^{-2} M$

$pH = -\log [H_{3}O^{+}] = -\log (1.6048 \times 10^{-2}) = 1.79458 = 1.79$
\[ [\text{OH}^-] = K_w/[\text{H}_3\text{O}^+] = (1.0 \times 10^{-14})/(1.6048 \times 10^{-2}) = 6.23131 \times 10^{-13} = 6.2 \times 10^{-13} \text{ M} \]

\[ \text{pOH} = -\log [\text{OH}^-] = -\log (6.23131 \times 10^{-13}) = 12.2054 = 12.21 \]

\[ [\text{H}_2\text{C}_3\text{H}_2\text{O}_4] = (0.200 - 1.6048 \times 10^{-2}) \text{ M} = 0.183952 = 0.18 \text{ M} \]

Concentration is limited to two significant figures because \( K_a \) is given to only two significant figures. The pH is given to what appears to be three significant figures because the number before the decimal point (1) represents the exponent and the number after the decimal point represents the significant figures in the concentration.

Calculate \([\text{C}_3\text{H}_2\text{O}_4^{2-}]\) by using the \( K_{a2} \) expression and assuming that \([\text{HC}_3\text{H}_2\text{O}_4^-]\) and \([\text{H}_3\text{O}^+]\) come mostly from the first dissociation. This new calculation will have a new \( x \) value.

\[
\begin{align*}
\text{HC}_3\text{H}_2\text{O}_4^- (aq) & \;+\; \text{H}_2\text{O}(l) \;\rightleftharpoons\; \text{H}_2\text{O}^+(aq) \;+\; \text{C}_3\text{H}_2\text{O}_4^{2-} (aq) \\
1.6048 \times 10^{-2} - x & \;=\; \frac{[\text{H}_2\text{O}^+][\text{C}_3\text{H}_2\text{O}_4^{2-}]}{[\text{HC}_3\text{H}_2\text{O}_4^-]} \\
K_{a2} & = 2.0 \times 10^{-6} = \frac{[\text{H}_2\text{O}^+][\text{C}_3\text{H}_2\text{O}_4^{2-}]}{[\text{HC}_3\text{H}_2\text{O}_4^-]} \\
K_{a2} & = 2.0 \times 10^{-6} = \frac{(1.6048 \times 10^{-2} + x)(x)}{(1.6048 \times 10^{-2} - x)} \quad \text{Assume } x \text{ is small compared to } 1.6048 \times 10^{-2}. \\
K_{a2} & = 2.0 \times 10^{-6} = \frac{(1.6048 \times 10^{-2})(x)}{(1.6048 \times 10^{-2})} \\
x & = [\text{C}_3\text{H}_2\text{O}_4^{2-}] = 2.0 \times 10^{-5} = 2.0 \times 10^{-5} \text{ M}
\end{align*}
\]

18.82 Write balanced chemical equations and corresponding equilibrium expressions for dissociation of aspirin (HC₉H₇O₄).

\[
\text{HC}_9\text{H}_7\text{O}_4(aq) \;+\; \text{H}_2\text{O}(l) \;\rightleftharpoons\; \text{H}_2\text{O}^+(aq) \;+\; \text{C}_9\text{H}_7\text{O}_4^-(aq)
\]

\[
0.018 - x \;=\; \frac{[\text{H}_2\text{O}^+][\text{C}_9\text{H}_7\text{O}_4^-]}{[\text{HC}_9\text{H}_7\text{O}_4]} \\
K_a & = 3.6 \times 10^{-4} = \frac{[\text{H}_2\text{O}^+][\text{C}_9\text{H}_7\text{O}_4^-]}{[\text{HC}_9\text{H}_7\text{O}_4]} \\
K_a & = 3.6 \times 10^{-4} = \frac{(x)(x)}{(0.018 - x)} \quad \text{Assume } x \text{ is small compared to } 0.018. \\
K_a & = 3.6 \times 10^{-4} = \frac{(x)(x)}{(0.018)} \\
[\text{H}_2\text{O}^+] & = x = 2.54558 \times 10^{-3}
\]

Check assumption: (2.54558 \times 10^{-3}/0.018) \times 100\% = 14\% error, so the assumption is not valid. Since the error is greater than 5\%, it is not acceptable to assume \( x \) is small compared to 0.018, and it is necessary to use the quadratic equation.

\[
\begin{align*}
x^2 & = (3.6 \times 10^{-4})(0.018 - x) = 6.48 \times 10^{-6} - 3.6 \times 10^{-4} x \\
x^2 + 3.6 \times 10^{-4} x - 6.48 \times 10^{-6} = 0 \\
a & = 1 \quad b = 3.6 \times 10^{-4} \quad c = -6.48 \times 10^{-6} \\
x & = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \\
x & = \frac{-3.6 \times 10^{-4} \pm \sqrt{(3.6 \times 10^{-4})^2 - 4(1)(-6.48 \times 10^{-6})}}{2(1)} \\
x & = 2.37194 \times 10^{-3} \text{ M} \text{ H}_2\text{O}^+ \\
\text{pH} & = -\log [\text{H}_2\text{O}^+] = -\log (2.37194 \times 10^{-3}) = 2.624896 = 2.62
\end{align*}
\]

18.83 Plan: Write the acid-dissociation reaction and the expression for \( K_a \). Set up a reaction table in which \( x \) = the concentration of the dissociated acid and also \([\text{H}_3\text{O}^+]\). Use the expression for \( K_a \) to solve for \( x \), the concentration of formate ion at equilibrium. Then use the initial concentration of formic acid and the equilibrium concentration of formate to find \% dissociation.
Solution:

\[
\text{Concentration: } HCOOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCOO^-(aq)
\]

<table>
<thead>
<tr>
<th></th>
<th>Initial</th>
<th>Change</th>
<th>Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCOOH(aq)</td>
<td>0.75</td>
<td>–x</td>
<td>0.75 – x</td>
</tr>
<tr>
<td>H_2O(l)</td>
<td>0</td>
<td>+x</td>
<td>x</td>
</tr>
<tr>
<td>HCOO^-(aq)</td>
<td>0</td>
<td>+x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[
K = 1.8 \times 10^{-4} = \frac{[H_3O^+][HCOO^-]}{[HCOOH]}
\]

\[
K = 1.8 \times 10^{-4} = \frac{(x)(x)}{(0.75 - x)} \quad \text{Assume x is small compared to 0.75.}
\]

\[
x = 1.161895 \times 10^{-2}
\]

\[
\text{Percent HCOOH dissociated} = \frac{[\text{HCOOH}]_{\text{dissociated}}}{[\text{HCOOH}]_{\text{initial}}} \cdot 100
\]

\[
\text{Percent HCOOH dissociated} = \frac{1.161895 \times 10^{-2} M}{0.75 M} \cdot 100 = 1.54919 = 1.5\%
\]

18.84 Electronegativity increases left to right across a period. As the nonmetal becomes more electronegative, the acidity of the binary hydride increases. The electronegative nonmetal attracts the electrons more strongly in the polar bond, shifting the electron density away from H⁺ and making the H⁺ more easily transferred to a surrounding water molecule to make H₃O⁺.

18.85 As the nonmetal increases in size, its bond to hydrogen becomes longer and weaker, so that H⁺ is more easily lost, and a stronger acid results.

18.86 There is an inverse relationship between the strength of the bond to the acidic proton and the strength of the acid. A weak bond means the hydrogen ion is more easily lost, and hence the acid is stronger.

18.87 The two factors that explain the greater acid strength of HClO₄ are:
1) Chlorine is more electronegative than iodine, so chlorine more strongly attracts the electrons in the bond with oxygen. This makes the H in HClO₄ less tightly held by the oxygen than the H in HIO.
2) Perchloric acid has more oxygen atoms than HIO, which leads to a greater shift in electron density from the hydrogen atom to the oxygen atoms making the H in HClO₄ more susceptible to transfer to a base.

18.88 Plan: For oxyacids, acid strength increases with increasing number of oxygen atoms and increasing electronegativity of the nonmetal in the acid. For binary acids, acid strength increases with increasing electronegativity across a row and increases with increasing size of the nonmetal down a column.

Solution:

a) Selenic acid, H₂SeO₄, is the stronger acid because it contains more oxygen atoms.

b) Phosphoric acid, H₃PO₄, is the stronger acid because P is more electronegative than As.

c) Hydrotelluric acid, H₂Te, is the stronger acid because Te is larger than S and so the Te–H bond is weaker.

18.89 a) H₂Se
b) H₃SO₄
   c) H₂SO₃

18.90 Plan: For oxyacids, acid strength increases with increasing number of oxygen atoms and increasing electronegativity of the nonmetal in the acid. For binary acids, acid strength increases with increasing electronegativity across a row and increases with increasing size of the nonmetal in a column.

Solution:

a) H₂Se, hydrogen selenide, is a stronger acid than H₃As, arsenic hydride, because Se is more electronegative than As.

b) B(OH)₃, boric acid also written as H₃BO₃, is a stronger acid than Al(OH)₃, aluminum hydroxide, because boron is more electronegative than aluminum.
c) HBrO₂, bromous acid, is a stronger acid than HBrO, hypobromous acid, because there are more oxygen atoms in HBrO₂ than in HBrO.

18.91 a) HBr   b) H₃AsO₄   c) HNO₂

18.92 Plan: Acidity increases as the value of $K_a$ increases. Determine the ion formed from each salt and compare the corresponding $K_a$ values from Appendix C.

Solution:
a) Copper(II) bromide, CuBr₂, contains Cu²⁺ ion with $K_a = 3 \times 10^{-8}$. Aluminum bromide, AlBr₃, contains Al³⁺ ion with $K_a = 1 \times 10^{-5}$. The concentrations of Cu²⁺ and Al³⁺ are equal, but the $K_a$ of AlBr₃ is almost three orders of magnitude greater. Therefore, 0.5 M AlBr₃ is the stronger acid and would have the lower pH.
b) Zinc chloride, ZnCl₂, contains the Zn²⁺ ion with $K_a = 1 \times 10^{-9}$. Tin(II) chloride, SnCl₂, contains the Sn²⁺ ion with $K_a = 4 \times 10^{-7}$. Since both solutions have the same concentration, and $K_a$ (Sn²⁺) > $K_a$ (Zn²⁺), 0.3 M SnCl₂ is the stronger acid and would have the lower pH.

18.93 a) FeCl₃   b) BeCl₂

18.94 Plan: A higher pH (more basic solution) results when an acid has a smaller $K_a$ (from the Appendix). Determine the ion formed from each salt and compare the corresponding $K_a$ values from Appendix C.

Solution:
a) The Ni(NO₃)₂ solution has a higher pH than the Co(NO₃)₂ solution because $K_a$ of Ni²⁺ (1x10⁻¹⁰) is smaller than the $K_a$ of Co²⁺ (2x10⁻¹⁰). Note that nitrate ion is the conjugate base of a strong acid and therefore does not influence the pH of the solution.
b) The Al(NO₃)₃ solution has a higher pH than the Cr(NO₃)₂ solution because $K_a$ of Al³⁺ (1x10⁻⁵) is smaller than the $K_a$ of Cr³⁺ (1x10⁻⁵).

18.95 a) NaCl   b) Co(NO₃)₂

18.96 All Brønsted-Lowry bases contain at least one lone pair of electrons. This lone pair binds with an H⁺ and allows the base to act as a proton-acceptor.

18.97 The negative charge and lone pair of the anion in many cases is able to extract a proton from water forming OH⁻ ions. Non-basic anions are from strong acids and include I⁻, NO₃⁻, Cl⁻, ClO₄⁻.

18.98 a) The species present are: CH₃COOH(aq), CH₃COO⁻(aq), H₃O⁺(aq), and OH⁻(aq).
b) CH₃COOH(aq) + H₂O(l) ⇌ H₃O⁺(aq) + CH₃COO⁻(aq)
   The solution is acidic because H₃O⁺ ions are formed.
   CH₃COO⁻(aq) + H₂O(l) ⇌ OH⁻(aq) + CH₃COOH(aq)
   The solution is basic because OH⁻ ions are formed.

18.99 Plan: $K_b$ is the equilibrium constant for a base dissociation which has the generic equation

\[ B(aq) + H₂O(l) ⇌ BH⁺(aq) + OH⁻(aq) \]

The $K_b$ expression is

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

and omitted from the expression. Write the base-dissociation reaction for each base, showing the base accepting a proton from water, and then write the $K_b$ expression.

Solution:
a) C₃H₅N(aq) + H₂O(l) ⇌ C₃H₅NH⁺(aq) + OH⁻(aq)
   
   \[ K_b = \frac{\text{[C₃H₅NH}^+\text{][OH}^-\text{]} }{\text{[C₃H₅N]}} \]

b) CO₃²⁻(aq) + H₂O(l) ⇌ HCO₃⁻(aq) + OH⁻(aq)
   
   \[ K_b = \frac{\text{[HCO₃}^-\text{][OH}^-\text{]} }{\text{[CO₃²⁻]} \} } \]
The bicarbonate can then also dissociate as a base, but this occurs to an insignificant amount in a solution of carbonate ions.

18.100  a) \( C_6H_5COO^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + C_6H_5COOH(aq) \)

\[ K_b = \frac{[C_6H_5COOH][OH^-]}{[C_6H_5COO^-]} \]

b) \( (CH_3)_2N(aq) + H_2O(l) \rightleftharpoons OH^- (aq) + (CH_3)_3NH^+(aq) \)

\[ K_b = \frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_2N]} \]

18.101  **Plan:** \( K_b \) is the equilibrium constant for a base dissociation which has the generic equation

\[ B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^- (aq) \].  The \( K_b \) expression is \[ \frac{[BH^+][OH^-]}{[B]} \].  \([H_2O]\) is treated as a constant and omitted from the expression.  Write the base-dissociation reaction for each base, showing the base accepting a proton from water, and then write the \( K_b \) expression.

**Solution:**

a) \( HONH_2(aq) + H_2O(l) \rightleftharpoons OH^- (aq) + HONH_3^+(aq) \)

\[ K_b = \frac{[HONH_3^+][OH^-]}{[HONH_2]} \]

b) \( HPO_4^{2-} (aq) + H_2O(l) \rightleftharpoons H_2PO_4^- (aq) + OH^- (aq) \)

\[ K_b = \frac{[H_2PO_4^-][OH^-]}{[HPO_4^{2-}]} \]

18.102  a) \( (NH_2)_2C=NH(aq) + H_2O(l) \rightleftharpoons OH^- (aq) + (NH_2)_2C=NH_2^-(aq) \)

\[ K_b = \frac{[(NH_2)_2C=NH^+][OH^-]}{[(NH_2)_2C=NH]} \]

b) \( HCC^- (aq) + H_2O(l) \rightleftharpoons OH^- (aq) + HCCH(aq) \)

\[ K_b = \frac{[HCCH][OH^-]}{[HCC^-]} \]

18.103  **Plan:** Write the balanced equation for the base reaction and the expression for \( K_b \).  Set up a reaction table in which \( x = \) the concentration of reacted base and also \( [OH^-] \).  Use the expression for \( K_b \) to solve for \( x, [OH^-] \), and then calculate \( [H_3O^+] \) and pH.

**Solution:**

The formula of dimethylamine has two methyl (CH\(_3\)) groups attached to a nitrogen:

\[
\cdot \quad \begin{array}{c}
\text{CH}_3
\
\text{N}
\
\text{H}
\end{array}
\]

\[
\text{CH}_3
\]

The nitrogen has a lone pair of electrons that will accept the proton from water in the base-dissociation reaction:

The value for the dissociation constant is from Appendix C.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>((\text{CH}_3)_2\text{NH}(aq) + H_2O(l) \rightleftharpoons \text{OH}^- (aq) + (\text{CH}_3)_2\text{NH}_2^-(aq))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.070 0 0</td>
</tr>
<tr>
<td>Change</td>
<td>(-x) (+x) (+x)</td>
</tr>
</tbody>
</table>
Equilibrium 0.070 – x  

Kb = 5.9x10^{-4} = \left[ \frac{\left( \text{CH}_3 \text{NH}_2^+ \right) \left[ \text{OH}^- \right]}{\left( \text{CH}_3 \text{NH} \right)} \right] 

Kb = 5.9x10^{-4} = \frac{\left[ \text{x} \right] \left[ \text{x} \right]}{\left[ 0.070 - \text{x} \right]}

Assume 0.070 – x = 0.070

5.9x10^{-4} = \frac{\left[ \text{x} \right] \left[ \text{x} \right]}{\left[ 0.070 \right]}

x = 6.4265x10^{-3} M

Check assumption that x is small compared to 0.070:

\frac{6.4265x10^{-3}}{0.070} \times 100 = 9\% error, so the assumption is not valid.

The problem will need to be solved as a quadratic.

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

x = \frac{-5.9x10^{-4} \pm \sqrt{(5.9x10^{-4})^2 - 4 \times (1)(-4.13x10^{-5})}}{2(1)} = 6.13827x10^{-3} M \text{OH}^–

\left[ \text{H}_3\text{O}^+ \right] = \frac{K_w}{\left[ \text{OH}^- \right]} = \frac{1.0x10^{-14}}{6.13827x10^{-3}} = 1.629124x10^{-12} M \text{H}_3\text{O}^+

\text{pH} = -\log \left[ \text{H}_3\text{O}^+ \right] = -\log \left( 1.629124x10^{-12} \right) = 11.7880 = \textbf{11.79}

18.104 \quad (\text{CH}_3\text{CH}_2)\text{NH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^–(aq) + (\text{CH}_3\text{CH}_2)\text{NH}_2^+ (aq)

0.12 – x  

Kb = 8.6x10^{-4} = \left[ \frac{\left( \text{CH}_3\text{CH}_2 \text{NH}_2^+ \right) \left[ \text{OH}^- \right]}{\left( \text{CH}_3\text{CH}_2 \text{NH} \right)} \right] 

Kb = 8.6x10^{-4} = \frac{\left[ \text{x} \right] \left[ \text{x} \right]}{\left[ 0.12 - \text{x} \right]}

Assume x is small compared to 0.12.

Kb = 8.6x10^{-4} = \frac{\left[ \text{x} \right] \left[ \text{x} \right]}{\left[ 0.12 \right]}

x = 0.0101587

Check assumption: (0.0101587/0.12) x 100\% = 8\% error, so the assumption is not valid.

Since the error is greater than 5\%, it is not acceptable to assume x is small compared to 0.12, and it is necessary to use the quadratic equation.

x^2 = (8.6x10^{-4})(0.12 – x) = 1.032x10^{-4} – 8.6x10^{-4} x

x^2 + 8.6x10^{-4} x – 1.032x10^{-4} = 0

a = 1 \quad b = 8.6x10^{-4} \quad c = -1.032x10^{-4}

x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}
18.105 Plan: Write the balanced equation for the base reaction and the expression for $K_b$. Set up a reaction table in which $x$ = the concentration of reacted base and also $[OH^-]$. Use the expression for $K_b$ to solve for $x$, $[OH^-]$, and then calculate $[H_3O^+]$ and pH.

Solution:

Concentration: $\text{HOCH}_2\text{CH}_2\text{NH}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + \text{HOCH}_2\text{CH}_2\text{NH}_3^+(aq)$

Initial: $0.25$ $0$ $0$

Change: $-x$ $+x$ $+x$

Equilibrium: $0.25 - x$ $x$ $x$

$K_b = 3.2 \times 10^{-5} = \frac{[\text{HOCH}_2\text{CH}_2\text{NH}_3^+][\text{OH}^-]}{[\text{HOCH}_2\text{CH}_2\text{NH}_2]}$

Assume $x$ is small compared to $0.25$.

$x = 2.8284 \times 10^{-3} \text{ M OH}^-

Check assumption that $x$ is small compared to $0.25$: 

$x = \frac{2.8284 \times 10^{-3}}{0.25} \times 100% = 1%$ error, so the assumption is valid.

$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{2.8284 \times 10^{-3}} = 3.53568 \times 10^{-12} \text{ M H}_3\text{O}^+$

$pH = -\log [\text{H}_3\text{O}^+] = -\log (3.53568 \times 10^{-12}) = 11.4515 = 11.45$

18.106 Plan: The $K_b$ of a conjugate base is related to the $K_a$ of the conjugate acid through the equation $K_w = K_a x K_b$.

Solution:

a) Acetate ion, $\text{CH}_3\text{COO}^-$, is the conjugate base of acetic acid, $\text{CH}_3\text{COOH}$.

$K_w = K_a x K_b$
\[
K_b \text{ of } \text{CH}_3\text{COO}^- = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.5556 \times 10^{-10} = 5.6 \times 10^{-10}
\]

b) Anilinium ion is the conjugate acid of the weak base aniline, \(C_6H_5\text{NH}_2\).

\[
K_a \text{ of } C_6H_5\text{NH}_3^+ = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.0 \times 10^{-10}} = 2.5 \times 10^{-5}
\]

18.108

a) Benzoate ion, \(C_6H_5\text{COO}^-\), is the conjugate base of benzoic acid, \(C_6H_5\text{COOH}\). The \(K_b\) for benzoate ion is related to the \(K_a\) for benzoic acid through the equation

\[
K_w = K_a \times K_b
\]

\[
K_b \text{ of } C_6H_5\text{COO}^- = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.3 \times 10^{-5}} = 1.58730 \times 10^{-10} = 1.6 \times 10^{-10}
\]

b) The 2-hydroxyethylammonium ion is the conjugate acid of 2-hydroxyethylamine so the \(pK_a\) for 2-hydroxyethylammonium ion is related to the \(pK_b\) of 2-hydroxyethylamine by the relationship

\[
pK_a = 14.00 + pK_b
\]

\[
pK_a = 14.00 + 4.49 = 9.51
\]

18.109

Plan: The \(K_b\) of a conjugate base is related to the \(K_a\) of the conjugate acid through the equation

\[
K_w = K_a \times K_b
\]

Solution:

a) \(\text{HClO}_2\) is the conjugate acid of chlorite ion, \(\text{ClO}_2^-\).

\[
K_b \text{ of } \text{ClO}_2^- = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.1 \times 10^{-2}} = 9.0909 \times 10^{-13}
\]

\[
pK_b = –\log (9.0909 \times 10^{-13}) = 12.04139 = 12.04
\]

b) \((\text{CH}_3\text{CH}_2)_2\text{NH}\) is the conjugate base of \((\text{CH}_3\text{CH}_2)_2\text{NH}_2^+\).

\[
K_a \text{ of } (\text{CH}_3\text{CH}_2)_2\text{NH}_2^+ = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{5.9 \times 10^{-4}} = 1.694915 \times 10^{-11}
\]

\[
pK_a = –\log (1.694915 \times 10^{-11}) = 10.77085 = 10.77
\]

18.110

a) The \(K_a\) of nitrous acid, \(\text{HNO}_2\), is reported in Appendix C. \(\text{HNO}_2\) is the conjugate acid of nitrite ion, \(\text{NO}_2^-\).

The \(K_b\) for nitrite ion is related to the \(K_a\) for nitrous acid through the equation

\[
K_w = K_a \times K_b
\]

\[
K_b \text{ of } \text{NO}_2^- = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{7.1 \times 10^{-4}} = 1.4084507 \times 10^{-11}
\]

\[
pK_b = –\log (1.4084507 \times 10^{-11}) = 10.851258 = 10.85
\]

b) The \(K_b\) of hydrazine, \(\text{H}_2\text{NNH}_2\), is reported in the problem. Hydrazine is the conjugate base of \(\text{H}_2\text{N–NH}_3^+\).

The \(K_a\) for \(\text{H}_2\text{N–NH}_3^+\) is related to the \(K_b\) for \(\text{H}_2\text{NNH}_2\) through the equation

\[
K_w = K_a \times K_b
\]

\[
K_a \text{ of } \text{H}_2\text{N–NH}_3^+ = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{8.5 \times 10^{-7}} = 1.17647 \times 10^{-8}
\]

\[
pK_a = –\log (1.17647 \times 10^{-8}) = 7.9294 = 7.93
\]

18.111

Plan: In part a), potassium cyanide, when placed in water, dissociates into potassium ions, \(K^+\), and cyanide ions, \(\text{CN}^-\). Potassium ion is the conjugate acid of a strong base, \(\text{KOH}\), so \(K^+\) does not react with water. Cyanide ion is the conjugate base of a weak acid, \(\text{HCN}\), so it does react with a base-dissociation reaction. To find the pH first set up a reaction table and use \(K_b\) for \(\text{CN}^-\) to calculate \([\text{OH}^-]\). Find the \(K_b\) for \(\text{CN}^-\) from the equation

\[
K_w = K_a \times K_b
\]

Chloride ion is the conjugate base of a strong acid so it will not influence the pH of the solution.

Triethylammonium ion is the conjugate acid of a weak base, so an acid-dissociation reaction determines the pH of the solution. To find the pH first set up a reaction table and use \(K_a\) for \((\text{CH}_3\text{CH}_2)_2\text{NH}^+\) to calculate \([\text{H}_3\text{O}^+]\). Find the \(K_a\) for \((\text{CH}_3\text{CH}_2)_2\text{NH}^-\) from the equation

\[
K_w = K_a \times K_b
\]
Solution:

a) CN\(^{-}\)\((aq) + H_{2}O(l) \rightleftharpoons HCN(aq) + OH^{-}(aq)\)

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>CN(^{-})((aq) + H_{2}O(l) \rightleftharpoons HCN(aq) + OH^{-}(aq))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.150 -x +x +x</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.150 -x +x +x</td>
</tr>
</tbody>
</table>

Equilibrium constant \(K_b\) for CN\(^{-}\):

\[
K_b = \frac{[HCN][OH^-]}{[CN^-]} = 1.612903 \times 10^{-5}
\]

Assume \(x\) is small compared to 0.150.

\[
x = 1.555 \times 10^{-3} M\ OH^{-}
\]

Check assumption that \(x\) is small compared to 0.150:

\[
\frac{1.555 \times 10^{-3}}{0.150}(100) = 1\%\ error,\ so\ the\ assumption\ is\ valid.
\]

\[
[H_3O^+] = K_w \cdot \frac{[OH^-]}{[H_2O]} = \frac{1.0 \times 10^{-14}}{1.555 \times 10^{-3}} = 6.430868 \times 10^{-12} M\ H_3O^+
\]

\[
pH = -\log [H_3O^+] = -\log (6.430868 \times 10^{-12}) = 11.19173 = 11.19
\]

b) \((CH_3CH_2)_3NH^+(aq) + H_2O(l) \rightleftharpoons (CH_3CH_2)_3N(aq) + H_3O^+(aq)\)

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>((CH_3CH_2)_3NH^+(aq) + H_2O(l) \rightleftharpoons (CH_3CH_2)_3N(aq) + H_3O^+(aq))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.40 -x +x +x</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.40 -x +x +x</td>
</tr>
</tbody>
</table>

Equilibrium constant \(K_a\) for \((CH_3CH_2)_3NH^+\):

\[
K_a = \frac{[H_3O^+][C(CH_3CH_2)_3N]}{[(CH_3CH_2)_3NH^+]} = 1.9230769 \times 10^{-11}
\]

Assume \(x\) is small compared to 0.40.

\[
x = 0.40 \times 2.7735 \times 10^{-6} M\ H_3O^+
\]

Check assumption that \(x\) is small compared to 0.40:

\[
\frac{2.7735 \times 10^{-6}(100)}{0.40} = 0.0007\%\ error,\ so\ the\ assumption\ is\ valid.
\]

\[
pH = -\log [H_3O^+] = -\log (2.7735 \times 10^{-6}) = 5.55697 = 5.56
\]

18.112 a) Sodium phenolate, when placed in water, dissociates into sodium ions, \(Na^+\), and phenolate ions, \(C_{6}H_{5}O^-\).

Sodium ion is the conjugate acid of a strong base, \(NaOH\), so \(Na^+\) does not react with water. Phenolate ion is the conjugate base of a weak acid, \(C_{6}H_{5}OH\), so it does react with the base-dissociation reaction:
C₆H₅O⁻(aq) + H₂O(l) ⇌ C₆H₅OH(aq) + OH⁻(aq)

To find the pH first set up a reaction table and use $K_b$ for C₆H₅O⁻ to calculate [OH⁻].

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>Initial</th>
<th>Change</th>
<th>Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₅O⁻(aq)</td>
<td>0.100</td>
<td>–x</td>
<td>0.100 – x</td>
</tr>
<tr>
<td>H₂O(l)</td>
<td>0</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>C₆H₅OH(aq)</td>
<td>0</td>
<td>+x</td>
<td></td>
</tr>
<tr>
<td>OH⁻(aq)</td>
<td>0</td>
<td>+x</td>
<td></td>
</tr>
</tbody>
</table>

$K_b$ of C₆H₅O⁻ = $\frac{K_w}{K_a}$

$K_b = 1.0 \times 10^{-4}$

$K_b = 1.0 \times 10^{-4} = \frac{[C₆H₅OH][OH⁻]}{[C₆H₅O⁻]}$

Assume x is small compared to 0.100.

$K_b = 1.0 \times 10^{-4} = \frac{(x)(x)}{(0.100)}$

$x = 3.1622777 \times 10^{-3} \text{ M OH}^-$

Check assumption: (3.1622777x10⁻³/0.100)x100% = 3% error, so the assumption is valid.

$[H₂O]^+ = K_w/[OH⁻] = (1.0\times10^{-14})/(3.162277766\times10^{-3}) = 3.1622776\times10^{-12} \text{ M H}_3\text{O}^+$

$pH = –\log [H₃O^+] = –\log (3.16227762\times10^{-12}) = 11.50$

b) The salt methylammonium bromide in water dissociates into two ions: CH₃NH₃⁺ and Br⁻. Bromide ion is the conjugate base of a strong acid so it will not influence the pH of the solution. Methylammonium ion is the conjugate acid of a weak base, so the acid-dissociation reaction below determines the pH of the solution.

Concentration (M) | CH₃NH₃⁺(aq) + H₂O(l) ⇌ CH₃NH₂(aq) + H₃O⁺(aq)
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.15</td>
</tr>
<tr>
<td>Change</td>
<td>–x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.15 – x</td>
</tr>
</tbody>
</table>

$K_a$ of CH₃NH₃⁺ = $\frac{K_w}{K_b}$

$K_a = 2.272727x10^{-11}$

$K_a = 2.272727x10^{-11} = \frac{[H₂O⁺][CH₃NH₂]}{[CH₃NH₃⁺]}$

Assume x is small compared to 0.15.

$K_a = 2.272727x10^{-11} = \frac{(x)(x)}{(0.15 – x)}$

$[H₂O⁺] = x = 1.84637\times10^{-6}$

Check assumption: (1.84637x10⁻⁶/0.15)x100% = 0.001% error, so the assumption is valid.

$pH = –\log [H₃O⁺] = –\log (1.84637\times10^{-6}) = 5.73368 = 5.73$

18.113 Plan: In part a), potassium formate, when placed in water, dissociates into potassium ions, K⁺, and formate ions, HCOO⁻. Potassium ion is the conjugate acid of a strong base, KOH, so K⁺ does not react with water. Formate ion is the conjugate base of a weak acid, HCOOH, so it does react with a base-dissociation reaction. To find the pH first set up a reaction table and use $K_b$ for HCOO⁻ to calculate [OH⁻]. Find the $K_b$ for HCOO⁻ from the equation $K_w = K_a x K_b$. In part b), the salt ammonium bromide in water dissociates into two ions: NH₄⁺ and Br⁻. Bromide ion is the conjugate base of a strong acid so it will not influence the pH of the solution. Ammonium ion is the conjugate acid of the weak base NH₃, so an acid-dissociation reaction determines the pH of the solution. To find
the pH first set up a reaction table and use $K_a$ for NH$_4^+$ to calculate [H$_3$O$^+$]. Find the $K_a$ for NH$_4^+$ from the equation $K_w = K_a \times K_b$.

Solution:

a) HCOO$^-$($aq$) + H$_2$O($l$) $\rightleftharpoons$ HCOOH($aq$) + OH$^-$($aq$)

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>Initial</th>
<th>Change</th>
<th>Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCOO$^-$($aq$) + H$_2$O($l$) $\rightleftharpoons$ HCOOH($aq$) + OH$^-$($aq$)</td>
<td>0.65</td>
<td>-x</td>
<td>0.65 - x</td>
</tr>
<tr>
<td>HCOOH($aq$) + OH$^-$($aq$)</td>
<td>0</td>
<td>+x</td>
<td>x</td>
</tr>
</tbody>
</table>

$K_b$ of HCOO$^-$ = $\frac{K_w}{K_a}$ = $\frac{1.0 \times 10^{-14}}{1.8 \times 10^{-4}}$ = 5.5556x10$^{-11}$

$K_b = 5.5556x10^{-11} = \frac{[HCOOH][OH^-]}{[HCOO^-]}$

Assume x is small compared to 0.65.

$K_b = 5.5556x10^{-11} = \frac{x^2}{0.65}$

x = 6.0925x10$^{-6}$ M OH$^-$

Check assumption that x is small compared to 0.65:

$\frac{6.0925x10^{-6}(100)}{0.65} = 0.0009\%$ error, so the assumption is valid.

$[H_3O^+] = K_w = 1.0 \times 10^{-14}$

$pH = -log [H_3O^+] = -log (1.66410x10^{-9}) = 8.78$

b) NH$_4^+$($aq$) + H$_2$O($l$) $\rightleftharpoons$ H$_3$O$^+$($aq$) + NH$_3$($aq$)

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>Initial</th>
<th>Change</th>
<th>Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4^+$($aq$) + H$_2$O($l$) $\rightleftharpoons$ NH$_3$($aq$) + H$_3$O$^+$($aq$)</td>
<td>0.85</td>
<td>-x</td>
<td>0.85 - x</td>
</tr>
<tr>
<td>H$_3$O$^+$($aq$)</td>
<td>0</td>
<td>+x</td>
<td>x</td>
</tr>
</tbody>
</table>

$K_a$ of NH$_4^+$ = $\frac{K_w}{K_b}$ = $\frac{1.0 \times 10^{-14}}{1.76 \times 10^{-5}}$ = 5.681818x10$^{-10}$

$K_a = 5.681818x10^{-10} = \frac{[H_3O^+][NH_3]}{[NH_4^+]}$

Assume x is small compared to 0.85.

$K_a = 5.681818x10^{-10} = \frac{x^2}{0.85}$

$[H_3O^+] = x = 2.1976x10^{-5}$ M

Check assumption that x is small compared to 0.85:

$\frac{2.1976x10^{-5}(100)}{0.85} = 0.003\%$ error, so the assumption is valid.

$pH = -log [H_3O^+] = -log (2.1976x10^{-5}) = 4.66$

18.114 a) The fluoride ion, F$^-$, acts as the base as shown by the following equation:

F$^-$($aq$) + H$_2$O($l$) $\rightleftharpoons$ HF($aq$) + OH$^-$($aq$)
Because NaF is a soluble salt, \([F^-] = [NaF]\). The sodium ion is from a strong base; therefore, it will not affect the pH, and can be ignored.

\[
\text{Concentration (M)} \quad \begin{array}{cccc}
F^{(aq)} & \text{+} & H_2O(l) & \rightleftharpoons & HF(aq) & \text{+} & OH^{-}(aq) \\
\text{Initial} & 0.75 & \text{---} & 0 & 0 \\
\text{Change} & -x & \text{+}x & \text{+}x \\
\text{Equilibrium} & 0.75 - x & x & x
\end{array}
\]

\[
K_b \text{ of } F^{-} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}} = 1.470588 \times 10^{-11}
\]

\[
K_b = 1.470588 \times 10^{-11} = \frac{[HF][OH^-]}{[F^-]}
\]

Assume \(x\) is small compared to 0.75.

\[
x = 3.3210558 \times 10^{-6} \text{ M} \text{ OH}^{-}
\]

Check assumption: \((3.3210558 \times 10^{-6}/0.75) \times 100\% = 0.0040\%\) error, so the assumption is valid.

\[
[H_2O] = K_a/[OH^-] = (1.0 \times 10^{-14})/(3.3210558 \times 10^{-6}) = 3.01109 \times 10^{-9} \text{ M} \text{ H}_3\text{O}^+
\]

\[
\text{pH} = \log [H_3O^+] = \log (3.01109 \times 10^{-9}) = 8.521276 = 8.52
\]

b) The pyridinium ion, \(C_5H_5NH^+\), acts as an acid shown by the following equation:

\[
\text{C}_5\text{H}_5\text{NH}^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_5\text{H}_5\text{N} (aq)
\]

Because \(C_5\text{H}_5\text{NHCl}\) is a soluble salt, \([C_5\text{H}_5\text{NH}^+] = [C_5\text{H}_5\text{NHCl}].\) The chloride ion is from a strong acid; therefore, it will not affect the pH, and can be ignored.

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>(C_5\text{H}_5\text{NH}^+(aq)) + H_2O(l) \rightleftharpoons C_5\text{H}_5\text{NH}(aq) + H_3O^+(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.88 \text{ ---} \text{ 0} \text{ 0}</td>
</tr>
<tr>
<td>Change</td>
<td>-x \text{ +}x \text{ +}x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.88 - x \text{ x} \text{ x}</td>
</tr>
</tbody>
</table>

\[
K_a \text{ of } NH_4^+ = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-9}} = 5.88235 \times 10^{-6}
\]

\[
K_a = 5.88235 \times 10^{-6} = \frac{[H_3O^+] [C_5\text{H}_5\text{N}] }{[C_5\text{H}_5\text{NH}^+]} \quad \text{Assume } x \text{ is small compared to 0.88.}
\]

\[
K_a = 5.88235 \times 10^{-6} = \frac{(x)(x)}{0.88 - x}
\]

Check assumption: \((2.275185 \times 10^{-3}/0.88) \times 100\% = 0.3\%\) error, so the assumption is valid.

\[
\text{pH} = -\log [H_3O^+] = -\log (2.275185 \times 10^{-3}) = 2.64298 = 2.64
\]

18.115 Plan: First, calculate the initial molarity of \(\text{ClO}^-\) from the mass percent. Then, set up reaction table with base dissociation of \(\text{ClO}^-\). Find the \(K_a\) for \(\text{ClO}^-\) from the equation \(K_w = K_a \times K_b\), using the \(K_a\) for \(\text{HClO}\) from Appendix C.

Solution:

\[
\text{Molarity of } \text{ClO}^- = \frac{1 \text{ mL solution} \times 1.0 \text{ g solution} \times 6.5\% \ \text{NaClO} \times 1 \text{ mol NaClO}}{10^{-3} \text{ L solution} \times 100\% \ \text{Solution} \times 74.44 \text{ g NaClO} \times 1 \text{ mol NaClO}}
\]

\[
= 0.873186 \text{ M } \text{ClO}^-
\]

The sodium ion is from a strong base; therefore, it will not affect the pH, and can be ignored.
Concentration (M) \( \ce{ClO^-} + \ce{H2O} \leq \ce{HClO} + \ce{OH^-} \)

<table>
<thead>
<tr>
<th></th>
<th>Initial</th>
<th>Change</th>
<th>Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \ce{ClO^-} )</td>
<td>0.873186</td>
<td>-x</td>
<td>0.873186 - x</td>
</tr>
<tr>
<td>( \ce{H2O} )</td>
<td>0</td>
<td>+x</td>
<td>x</td>
</tr>
<tr>
<td>( \ce{HClO} )</td>
<td>0</td>
<td>+x</td>
<td>x</td>
</tr>
<tr>
<td>( \ce{OH^-} )</td>
<td>0</td>
<td></td>
<td>x</td>
</tr>
</tbody>
</table>

\[ K_b \text{ of } \ce{ClO^-} = K_w = 1.0 \times 10^{-14} \]
\[ K_b = 3.448275862 \times 10^{-7} = \frac{[\ce{HClO}][\ce{OH^-}]}{[\ce{ClO^-}]} \]
\[ K_b = 3.448275862 \times 10^{-7} = \frac{[\ce{HClO}][\ce{OH^-}]}{[\ce{ClO^-}]} \]

Assume \( x \) is small compared to 0.873186.

\[ x = 5.4872 \times 10^{-4} = 5.5 \times 10^{-4} M \ce{OH^-} \]

Check assumption that \( x \) is small compared to 0.873186:

\[ \frac{5.4872 \times 10^{-4}}{0.873186} \times 100 = 0.606\% \text{ error}, \text{ so the assumption is valid.} \]

\[ [\ce{H3O^+}] = 5.4872 \times 10^{-4} \times \frac{1.0 \times 10^{-14}}{5.4872 \times 10^{-4}} = 1.82242 \times 10^{-11} M \ce{H3O^+} \]
\[ \text{pH} = -\log [\ce{H3O^+}] = -\log (1.82242 \times 10^{-11}) = 10.73935 = 10.74 \]

18.116 The cation, \( \ce{HC18H21NO3^+} \), acts as an acid shown by the following equation:

\[ \ce{HC18H21NO3^+} + \ce{H2O} \leq \ce{C18H21NO3^-} + \ce{H3O^+} \]

Because \( \ce{HC18H21NO3Cl} \) is a soluble salt, \( [\ce{HC18H21NO3^-}] = [\ce{HC18H21NO3Cl}] \). The chloride ion is from a strong acid; therefore, it will not affect the pH, and can be ignored.

\[ K_a = 10^{pK_a} = 10^{-5.80} \times 6.309586 \times 10^{-9} \]

\[ [\ce{H3O^+}] = x = 1.7761737 \times 10^{-5} M \]

Check assumption: \( (1.7761737 \times 10^{-5} \times 0.050) \times 100 = 0.04\% \text{ error}, \text{ so the assumption is valid.} \)

\[ \text{pH} = -\log [\ce{H3O^+}] = -\log (1.7761737 \times 10^{-5}) = 4.75051 = 4.75 \]

18.117 Salts contain anions of weak acids and cations of strong bases are basic. Salts that contain cations of weak bases or small, highly charged metal cations, and anions of strong acids are acidic. Salts that contain cations of strong bases and anions of strong acids are neutral.

**Basic salt:** \( \ce{KCN} \) (\( K^+ \) is the cation from the strong base \( \ce{KOH} \); \( \ce{CN^-} \) is the anion from the weak acid, \( \ce{HCN} \)).

**Acid salt:** \( \ce{FeCl3} \) or \( \ce{NH4NO3} \) (\( \ce{Fe^{3+}} \) is a small, highly charged metal cation and \( \ce{Cl^-} \) is the anion of the strong acid \( \ce{HCl} \); \( \ce{NH_4^+} \) is the cation of the weak base \( \ce{NH_3} \), while \( \ce{NO_3^-} \) is the anion of the strong acid \( \ce{HNO_3} \)).

**Neutral salt:** \( \ce{KNO3} \) (\( K^+ \) is the cation of the strong base \( \ce{KOH} \), while \( \ce{NO_3^-} \) is the anion of the strong acid \( \ce{HNO_3} \)).
18.118 Sodium fluoride, NaF, contains the cation of a strong base, NaOH, and anion of a weak acid, HF. This combination yields a salt that is basic in aqueous solution as the F– ion acts as a base:

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

Sodium chloride, NaCl, is the salt of a strong base, NaOH, and strong acid, HCl. This combination yields a salt that is neutral in aqueous solution as neither Na+ or Cl– react in water to change the [H3O+].

18.119 If \( K_a \) for the conjugate acid of the anion is approximately equal to \( K_b \) for the conjugate base of the cation, the solution will be close to neutral. Otherwise, the solution will be acidic or basic. In this case, the \( K_a \) for the conjugate acid (CH3COOH) is \( 1.8 \times 10^{-5} \), and the \( K_b \) for the conjugate base (NH3) is \( 1.76 \times 10^{-5} \).

18.120 **Plan:** For each salt, first break into the ions present in solution and then determine if either ion acts as a weak acid or weak base to change the pH of the solution. Cations are neutral if they are from a strong base; other cations will be weakly acidic. Anions are neutral if they are from a strong acid; other anions are weakly basic.

**Solution:**

a) KBr(s) \[ \rightleftharpoons \] K+(aq) + Br–(aq)

K+ is the conjugate acid of a strong base, so it does not influence pH.

Br– is the conjugate base of a strong acid, so it does not influence pH.

Since neither ion influences the pH of the solution, it will remain at the **neutral** pH of pure water.

b) NH4I(s) \[ \rightleftharpoons \] NH4+(aq) + I–(aq)

NH4+ is the conjugate acid of a weak base, so it will act as a weak acid in solution and produce H3O+ as represented by the acid-dissociation reaction:

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

I– is the conjugate base of a strong acid, so it will not influence the pH.

The production of H3O+ from the ammonium ion makes the solution of NH4I **acidic**.

c) KCN(s) \[ \rightleftharpoons \] K+(aq) + CN–(aq)

K+ is the conjugate acid of a strong base, so it does not influence pH.

CN– is the conjugate base of a weak acid, so it will act as a weak base in solution and impact pH by the base-dissociation reaction:

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

Hydroxide ions are produced in this equilibrium so solution will be **basic**.

18.121 a) SnCl2(s) + nH2O(l) \[ \rightarrow \] Sn(H2O)n2+(aq) + 2Cl–(aq)

\[ \text{Sn(H}_2\text{O)}_{n}^{2+}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{Sn(H}_2\text{O)}_{n-1}^+\text{OH}^-(aq) + \text{H}_3\text{O}^+(aq) \] **acidic**

b) NaHS(s) + H2O(l) \[ \rightarrow \] Na+(aq) + HS–(aq)

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

c) Zn(CH3COO)2(s) + nH2O(l) \[ \rightarrow \] Zn(H2O)n2+(aq) + 2CH3COO–(aq)

\[ \text{Zn(H}_2\text{O)}_{n}^{2+}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{Zn(H}_2\text{O)}_{n-1}^+\text{OH}^-(aq) + \text{H}_3\text{O}^+(aq) \]

\[ K_a (\text{Zn(H}_2\text{O)}_{n}^{2+}) = 1 \times 10^{-9} \]

\[ K_b (\text{CH}_3\text{COO}^-) = K_w/K_a = (1.0 \times 10^{-14})/(1.8 \times 10^{-5}) = 5.556 \times 10^{-10} \]

The two \( K \) values are similar, so the solution is close to **neutral or slightly acidic**.

18.122 **Plan:** For each salt, first break into the ions present in solution and then determine if either ion acts as a weak acid or weak base to change the pH of the solution. Cations are neutral if they are from a strong base; other cations will be weakly acidic. Anions are neutral if they are from a strong acid; other anions are weakly basic.

**Solution:**

a) The two ions that comprise sodium carbonate, Na2CO3, are sodium ion, Na+, and carbonate ion, CO32–.

\[ \text{Na}_2\text{CO}_3(s) \rightleftharpoons 2\text{Na}^+(aq) + \text{CO}_3^{2-}(aq) \]

Sodium ion is derived from the strong base NaOH. Carbonate ion is derived from the weak acid HCO3–. A salt derived from a strong base and a weak acid produces a **basic** solution.

Na+ does not react with water.

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

b) The two ions that comprise calcium chloride, CaCl2, are calcium ion, Ca2+, and chloride ion, Cl–.
CaCl$_2(s) \xrightarrow{H_2O} Ca^{2+}(aq) + 2Cl^-(aq)$

Calcium ion is derived from the strong base Ca(OH)$_2$. Chloride ion is derived from the strong acid HCl. A salt derived from a strong base and strong acid produces a neutral solution. Neither Ca$^{2+}$ nor Cl$^-$ reacts with water.

c) The two ions that comprise cupric nitrate, Cu(NO$_3$)$_2$, are the cupric ion, Cu$^{2+}$, and the nitrate ion, NO$_3^-$.

Cu(NO$_3$)$_2(s) \xrightarrow{H_2O} Cu^{2+}(aq) + 2NO$_3^-(aq)$

Small metal ions are acidic in water (assume the hydration of Cu$^{2+}$ is 6):

Cu(H$_2$O)$_6^{2+}(aq) + H_2O(l) \rightleftharpoons Cu(H_2O)$_5$OH$^+(aq) + H_3O^+(aq)$

Nitrate ion is derived from the strong acid HNO$_3$. Therefore, NO$_3^-$ does not react with water. A solution of cupric nitrate is acidic.

18.123 a) CH$_3$NH$_3$Cl(s) + H$_2$O(l) → CH$_3$NH$_3^+(aq) + Cl^-(aq)$

CH$_3$NH$_3^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH$_3$NH$_2$(aq) neutral

b) LiClO$_4(s) + H_2O(l) → Li^+(aq) + ClO$_4^-(aq)$ neutral

c) CoF$_2(s) + nH_2O(l) → Co(H_2O)$_n^{2+}(aq) + 2F^-(aq)$

Co(H$_2$O)$_n^{2+}(aq) + H_2O(l) \rightleftharpoons Co(H_2O)$_{n-1}$OH$^+(aq) + H_3O^+(aq)$

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

$K_a$ (Co(H$_2$O)$_n^{2+}$) = 2x10$^{-10}$

$K_a$ (F) = $K_a$/$K_b = (1.0x10^{-14})/(6.8x10^{-4}) = 1.47x10^{-11}$

The two $K_a$ values are similar so the solution is close to neutral or slightly acidic.

18.124 Plan: For each salt, first break into the ions present in solution and then determine if either ion acts as a weak acid or weak base to change the pH of the solution. Cations are neutral if they are from a strong base; other cations will be weakly acidic. Anions are neutral if they are from a strong acid; other anions will be weakly basic.

Solution:

a) A solution of strontium bromide is neutral because Sr$^{2+}$ is the conjugate acid of a strong base, Sr(OH)$_2$, and Br$^-$ is the conjugate base of a strong acid, HBr, so neither change the pH of the solution.

b) A solution of barium acetate is basic because CH$_3$COO$^-$ is the conjugate base of a weak acid and therefore forms OH$^-$ in solution whereas Ba$^{2+}$ is the conjugate acid of a strong base, Ba(OH)$_2$, and does not influence solution pH. The base-dissociation reaction of acetate ion is:

CH$_3$COO$^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$.

c) A solution of dimethylammonium bromide is acidic because (CH$_3$)$_2$NH$^+$ is the conjugate acid of a weak base and therefore forms H$_3$O$^+$ in solution whereas Br$^-$ is the conjugate base of a strong acid and does not influence the pH of the solution. The acid-dissociation reaction for methylammonium ion is:

(CH$_3$)$_2$NH$^+(aq) + H_2O(l) \rightleftharpoons (CH$_3$)$_2$NH(aq) + H$_3$O$^+(aq)$.

18.125 a) Fe(HCOO)$_3(s) + nH_2O(l) → Fe(H_2O)$_n^{3+}(aq) + 3HCOO^-(aq)$

Fe(H$_2$O)$_n^{3+}(aq) + H_2O(l) \rightleftharpoons Fe(H_2O)$_{n-1}$OH$^{2+}(aq) + H_3O^+(aq)$

HCOO$^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HCOOH(aq)$

$K_a$ (Fe$^{3+}$) = 6x10$^{-1}$

$K_a$ (HCOO$^-$) = $K_w$/($K_b$ (HCOO$^-$)) = (1.0x10$^{-14}$)/(1.8x10$^{-4}$) = 5.5556x10$^{-11}$

$K_a$ (Fe$^{3+}$) > $K_b$ (HCOO$^-$) acidic

b) KHC$_3$O$_3(s) + H_2O(l) → K^+(aq) + HCO$_3^-(aq)$

HCO$_3^-(aq) + H_2O(l) \rightleftharpoons H_2O^+(aq) + CO$_3^{2-}(aq)$

HCO$_3^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HCO$_3^-(aq)$

$K_b$ (HCO$_3^-$) > $K_a$ (HCO$_3^-$) basic

c) K$_2$S(s) + H$_2$O(l) $\rightleftharpoons 2K^+(aq) + S^{2-}(aq)$

S$^{2-}(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HS^- (aq)$ basic
a) The two ions that comprise ammonium phosphate, \((NH_4)_2PO_4\), are the ammonium ion, \(NH_4^+\), and the phosphate ion, \(PO_4^{3-}\).

\[
\begin{align*}
\text{NH}_4^+(aq) + H_2O(l) &\rightleftharpoons NH_3(aq) + H_3O^+(aq) \quad K_a = K_{w}/K_b (NH_4^+) = 5.7 \times 10^{-10} \\
\text{PO}_4^{3-}(aq) + H_2O(l) &\rightleftharpoons \text{HPO}_4^{2-}(aq) + OH^-(aq) \quad K_b = K_{w}/K_a (\text{HPO}_4^{2-}) = 2.4 \times 10^{-2}
\end{align*}
\]

A comparison of \(K_a\) and \(K_b\) is necessary since both ions are derived from a weak base and weak acid.

The \(K_a\) of \(NH_4^+\) is determined by using the \(K_a\) of its conjugate base, \(NH_3\) (Appendix). The \(K_b\) of \(PO_4^{3-}\) is determined by using the \(K_b\) of its conjugate acid, \(HPO_4^{2-}\). The \(K_a\) of \(HPO_4^{2-}\) comes from \(K_a\) of \(H_3PO_4\) (Appendix). Since \(K_b > K_a\), a solution of \((NH_4)_2PO_4\) is basic.

b) The two ions that comprise sodium sulfate, \(Na_2SO_4\), are sodium ion, \(Na^+\), and sulfate ion, \(SO_4^{2-}\). The sodium ion is derived from the strong base \(NaOH\). The sulfate ion is derived from the weak acid, \(HSO_4^-\).

\[
\text{SO}_4^{2-}(aq) + H_2O(l) \rightleftharpoons \text{H}_2\text{SO}_4(aq) + OH^-(aq)
\]

A solution of sodium sulfate is basic.

c) The two ions that comprise lithium hypochlorite, \(LiClO\), are lithium ion, \(Li^+\), and hypochlorite ion, \(ClO^-\).

\[
\text{Li}^+(aq) + \text{OH}^-(aq) \rightleftharpoons \text{LiOH}(aq)
\]

A solution of lithium hypochlorite is basic.

18.127  
a) \(\text{Pb(CH}_3\text{COO)}_2\text{)}(s) + n\text{H}_2\text{O}(l) \rightarrow \text{Pb(H}_2\text{O)}_{n-1}\text{CH}_3\text{COO}\text{)}^+(aq) + 2\text{CH}_3\text{COO}^-(aq)

\[
K_a (\text{CH}_3\text{COO}^-) = 3 \times 10^{-8}
\]

\[
\text{Pb(H}_2\text{O)}_{n-1}\text{CH}_3\text{COO}\text{)}^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{Pb(H}_2\text{O)}_{n-1}\text{OH}^+(aq) + \text{H}_3\text{O}^+(aq)
\]

\[
K_a = (1.0 \times 10^{-14})/1.8 \times 10^{-5} = 5.556 \times 10^{-10}
\]

\[
K_b (\text{Pb}^{2+}) = K_a (\text{CH}_3\text{COO}^-)
\]

b) \(\text{Cr(NO}_2\text{)}_3\text{)}(s) + n\text{H}_2\text{O}(l) \rightarrow \text{Cr(H}_2\text{O)}_{n-1}\text{NO}_2^-\text{)}(aq) + 3\text{NO}_2^-\text{)}(aq)

\[
K_a (\text{NO}_2^-) = 1 \times 10^{-4}
\]

\[
\text{Cr(H}_2\text{O)}_{n-1}\text{NO}_2^-\text{)}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{Cr(H}_2\text{O)}_{n-1}\text{OH}^-(aq) + \text{H}_3\text{O}^+(aq)
\]

\[
K_a = (1.0 \times 10^{-14})/7.1 \times 10^{-4} = 1.40845 \times 10^{-11}
\]

\[
K_b (\text{Cr}^{3+}) = K_a (\text{NO}_2^-)
\]

c) \(\text{CsH}(s) + \text{H}_2\text{O}(l) \rightarrow \text{Cs}^+(aq) + \text{H}^+(aq)
\]

18.128  
**Plan:** For each salt, first break into the ions present in solution and then determine if either ion acts as a weak acid or weak base to change the pH of the solution. Cations are neutral if they are from a strong base; other cations will be weakly acidic. Anions are neutral if they are from a strong acid; other anions are weakly basic. Use \(K_a\) and \(K_b\) values to rank the pH; the larger the \(K_a\) value, the lower the pH and the larger the \(K_b\) value, the higher the pH.

**Solution:**

a) Order of increasing pH: \(\text{Fe(NO}_3\text{)}_2 < \text{KNO}_3 < \text{K}_2\text{SO}_3 < \text{K}_2\text{S}\) (assuming concentrations equivalent)

Iron(II) nitrate, \(\text{Fe(NO}_3\text{)}_2\), is an acidic solution because the iron ion is a small, highly charged metal ion that acts as a weak acid and nitrate ion is the conjugate base of a strong acid, so it does not influence pH.

Potassium nitrate, \(\text{KNO}_3\), is a neutral solution because potassium ion is the conjugate acid of a strong base and nitrate ion is the conjugate base of a strong acid, so neither influences solution pH.

Potassium sulfite, \(\text{K}_2\text{SO}_3\), and potassium sulfide, \(\text{K}_2\text{S}\), are similar in that the potassium ion does not influence solution pH, but the anions do because they are conjugate bases of weak acids. \(K_a\) for \(\text{SO}_3^-\) is \(6.5 \times 10^{-8}\), so \(K_b\) for \(\text{SO}_3^-\) is \(1.5 \times 10^{-7}\), which indicates that sulfite ion is a weak base. \(K_a\) for \(\text{HS}^-\) is \(1 \times 10^{-17}\) (see the table of \(K_a\) values for polyprotic acids), so sulfide ion has a \(K_b\) equal to \(1 \times 10^7\). Sulfide ion is thus a strong base. The solution of a strong base will have a greater concentration of hydroxide ions (and higher pH) than a solution of a weak base of equivalent concentrations.

b) In order of increasing pH: \(\text{NaHSO}_4 < \text{NH}_4\text{NO}_3 < \text{NaHCO}_3 < \text{Na}_2\text{CO}_3\)

In solutions of ammonium nitrate, only the ammonium will influence pH by dissociating as a weak acid:

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

With \(K_a = 1.0 \times 10^{-14}/1.8 \times 10^{-5} = 5.6 \times 10^{-10}\)

Therefore, the solution of ammonium nitrate is acidic.

In solutions of sodium hydrogen sulfate, only \(\text{HSO}_4^-\) will influence pH. The hydrogen sulfate ion is amphoteric so both the acid and base dissociations must be evaluated for influence on pH. As a base, \(\text{HSO}_4^-\) is the conjugate
base of a strong acid, so it will not influence pH. As an acid, HSO$_4^-$ is the conjugate acid of a weak base, so the acid dissociation applies:

$$\text{HSO}_4^- (aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{SO}_4^{2-} (aq) + \text{H}_3\text{O}^+ (aq) \quad K_{a2} = 1.2 \times 10^{-2}$$

In solutions of sodium hydrogen carbonate, only the HCO$_3^-$ will influence pH and it, like HSO$_4^-$, is amphoteric:

As an acid: $$\text{HCO}_3^- (aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CO}_3^{2-} (aq) + \text{H}_3\text{O}^+ (aq) \quad K_a = 4.7 \times 10^{-11}, \text{the second } K_a \text{ for carbonic acid}$$

As a base: $$\text{HCO}_3^- (aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{CO}_3(aq) + \text{OH}^- (aq) \quad K_b = 1.0 \times 10^{-14}/4.7 \times 10^{-11} = 2.1 \times 10^{-4}$$

Since $K_b > K_a$, a solution of sodium hydrogen carbonate is basic.

Therefore, the solution of sodium carbonate is basic.

Two of the solutions are acidic. Since the $K_a$ of HSO$_4^-$ is greater than that of NH$_4^+$, the solution of sodium hydrogen sulfate has a lower pH than the solution of ammonium nitrate, assuming the concentrations are relatively close.

Two of the solutions are basic. Since the $K_b$ of CO$_3^{2-}$ is greater than that of HCO$_3^-$, the solution of sodium carbonate has a higher pH than the solution of sodium hydrogen carbonate, assuming concentrations are not extremely different.

18.129 a) $\text{KClO}_2 > \text{MgCl}_2 > \text{FeCl}_2 > \text{FeCl}_3$

b) $\text{NaBrO}_2 > \text{NaClO}_2 > \text{NaBr} > \text{NH}_4\text{Br}$

18.130 Both methoxide ion and amide ion produce OH$^-$ in aqueous solution. In water, the strongest base possible is OH$^-$. Since both bases produce OH$^-$ in water, both bases appear equally strong.

$$\text{CH}_3\text{O}^- (aq) + \text{H}_2\text{O}(l) \rightarrow \text{OH}^- (aq) + \text{CH}_3\text{OH}(aq)$$

$$\text{NH}_2^- (aq) + \text{H}_2\text{O}(l) \rightarrow \text{OH}^- (aq) + \text{NH}_3(aq)$$

18.131 H$_2$SO$_4$ is a strong acid and would be 100% dissociated in H$_2$O and any solvent more basic than H$_2$O (such as NH$_3$). It would be less than 100% dissociated in solvents more acidic than H$_2$O (such as CH$_3$COOH).

18.132 Ammonia, NH$_3$, is a more basic solvent than H$_2$O. In a more basic solvent, weak acids like HF act like strong acids and are 100% dissociated.

18.133 A Lewis base must have an electron pair to donate. A Lewis acid must have a vacant orbital or the ability to rearrange its bonding to make one available. The Lewis acid-base reaction involves the donation and acceptance of an electron pair to form a new covalent bond in an adduct.

18.134 A Lewis acid is defined as an electron-pair acceptor, while a Brønsted-Lowry acid is a proton donor. If only the proton in a Brønsted-Lowry acid is considered, then every Brønsted-Lowry acid fits the definition of a Lewis acid since the proton is accepting an electron pair when it bonds with a base. There are Lewis acids that do not include a proton, so all Lewis acids are not Brønsted-Lowry acids.

A Lewis base is defined as an electron-pair donor and a Brønsted-Lowry base is a proton acceptor. In this case, the two definitions are essentially the same.

18.135 a) No, a weak Brønsted-Lowry base is not necessarily a weak Lewis base. For example, the following equation shows that the weak Brønsted-Lowry base NH$_3$ is a good Lewis base.

$$\text{Ni(H}_2\text{O)}_6^{2+} (aq) + 6 \text{NH}_3(aq) \rightleftharpoons \text{Ni(NH}_3)_6^{2+} (aq) + 6\text{H}_2\text{O}(l)$$

b) The cyanide ion has a lone pair to donate from either the C or the N, and donates an electron pair to the Cu(H$_2$O)$_6^{2+}$ complex. It is the Lewis base for the forward direction of this reaction. In the reverse direction, water donates one of the electron pairs on the oxygen to the Cu(CN)$_2^-$ and is the Lewis base.

c) Because $K_c > 1$, the reaction proceeds in the direction written (left to right) and is driven by the stronger Lewis base, the cyanide ion.

18.136 All three concepts can have water as the product in an acid-base neutralization reaction. It is the only product in an Arrhenius neutralization reaction.
18.137 a) NH₃ can only act as a Brønsted-Lowry or Lewis base.  
b) AlCl₃ can only act as a Lewis acid.

18.138 Plan: A Lewis acid is an electron-pair acceptor and therefore must be able to accept an electron pair. A Lewis base is an electron-pair donor and therefore must have an electron pair to donate.
Solution:
  a) Cu²⁺ is a Lewis acid because it accepts electron pairs from molecules such as water.
  b) Cl⁻ is a Lewis base because it has lone pairs of electrons it can donate to a Lewis acid.
  c) Tin(II) chloride, SnCl₂, is a compound with a structure similar to carbon dioxide, so it will act as a Lewis acid to form an additional bond to the tin.
  d) Oxygen difluoride, OF₂, is a Lewis base with a structure similar to water, where the oxygen has lone pairs of electrons that it can donate to a Lewis acid.

18.139 a) Lewis acid  b) Lewis base  c) Lewis base  d) Lewis acid

18.140 Plan: A Lewis acid is an electron-pair acceptor and therefore must be able to accept an electron pair. A Lewis base is an electron-pair donor and therefore must have an electron pair to donate.
Solution:
  a) The boron atom in boron trifluoride, BF₃, is electron deficient (has six electrons instead of eight) and can accept an electron pair; it is a Lewis acid.
  b) The sulfide ion, S²⁻, can donate any of four electron pairs and is a Lewis base.
  c) The Lewis dot structure for the sulfite ion, SO₃²⁻, shows lone pairs on the sulfur and on the oxygen atoms. The sulfur atom has a lone electron pair that it can donate more easily than the electronegative oxygen in the formation of an adduct. The sulfite ion is a Lewis base.
  d) Sulfur trioxide, SO₃, acts as a Lewis acid.

18.141 a) Lewis acid  b) Lewis base  c) Lewis acid  d) Lewis acid

18.142 Plan: A Lewis acid is an electron-pair acceptor while a Lewis base is an electron-pair donor.
Solution:
  a) Sodium ion is the Lewis acid because it is accepting electron pairs from water, the Lewis base.
      \[ \text{Na}^+ + 6\text{H}_2\text{O} \rightleftharpoons \text{Na(H}_2\text{O)}_6^+ \]
      Lewis acid  Lewis base  adduct
  b) The oxygen from water donates a lone pair to the carbon in carbon dioxide. Water is the Lewis base and carbon dioxide the Lewis acid.
      \[ \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \]
      Lewis acid  Lewis base  adduct
  c) Fluoride ion donates an electron pair to form a bond with boron in BF₄⁻. The fluoride ion is the Lewis base and the boron trifluoride is the Lewis acid.
      \[ \text{F}^- + \text{BF}_3 \rightleftharpoons \text{BF}_4^- \]
      Lewis base  Lewis acid  adduct

18.143 a) Fe³⁺ + 2H₂O \rightleftharpoons \text{FeOH}^{2+} + \text{H}_3\text{O}^+
  \text{Lewis acid} \quad \text{Lewis base}

  b) H₂O + H⁻ \rightleftharpoons \text{OH}^- + \text{H}_2
  \text{Lewis acid} \quad \text{Lewis base}

  c) 4\text{CO} + \text{Ni} \rightleftharpoons \text{Ni(CO)}_4
  \text{Lewis base} \quad \text{Lewis acid}

18.144 Plan: In an Arrhenius acid-base reaction, H⁺ ions react with OH⁻ ions to produce H₂O. In a Brønsted-Lowry acid-base reaction, an acid donates H⁺ to a base. In a Lewis acid-base reaction, an electron pair is donated by the base and accepted by the acid.
Solution:
a) Since neither H+ nor OH– is involved, this is not an Arrhenius acid-base reaction. Since there is no exchange of protons, this is not a Brønsted-Lowry reaction. This reaction is only classified as **Lewis acid-base reaction**, where Ag+ is the acid and NH3 is the base.
b) Again, no OH– is involved, so this is not an Arrhenius acid-base reaction. This is an exchange of a proton, from H2SO4 to NH3, so it is a **Brønsted-Lowry acid-base reaction**. Since the Lewis definition is most inclusive, anything that is classified as a Brønsted-Lowry (or Arrhenius) reaction is automatically classified as a **Lewis acid-base reaction**.  
c) This is not an acid-base reaction.
d) For the same reasons listed in a), this reaction is only classified as **Lewis acid-base reaction**, where AlCl3 is the acid and Cl– is the base.

18.145  
a) **Lewis acid-base reaction**  
b) Brønsted-Lowry, Arrhenius, and Lewis acid-base reaction  
c) This is *not* an acid-base reaction.  
d) Brønsted-Lowry and Lewis acid-base reaction

18.146  
a) The hydrogen-bonded form would be:

\[
\text{Cl}_3C\text{---O} \cdots H \text{---O---H}
\]

The product of a Lewis acid-base reaction is:

\[
\text{Cl}_3C\text{---C---H} \quad \text{and} \quad \text{OH}
\]

The O atom of water (Lewis base) donates a lone pair to the C of the carbonyl group, which functions as a Lewis acid. The π bond is broken and a C–O bond is formed. The O atom of the carbonyl (Lewis base) accepts a proton from water (Lewis acid) to complete the reaction.
b) Infrared spectroscopy could be used. Infrared spectroscopy is very good at identifying functional groups. C=O bonds have a characteristic range of absorption wavelengths. The hydrogen-bonded structure would have a carbonyl group and the second structure would not.

18.147  
**Plan:** Calculate the [H3O+] using the pH values given. Determine the value of \( K_w \) from the p\( K_w \) given. The \([H_3O^+]\) is combined with the \( K_w \) value at 37°C to find [OH–] using \( K_w = [H_3O^+][OH^-] \).

**Solution:**

\[
K_w = 10^{-13.63} = 2.34423 \times 10^{-14} \\
K_w = [H_3O^+][OH^-] = 2.34423 \times 10^{-14} \text{ at } 37°C
\]

**[H3O+] range**

- High value (low pH) = \( 10^{-pH} = 10^{-7.35} = 4.46684 \times 10^{-8} = 4.5 \times 10^{-8} \text{ M} \text{H}_3\text{O}^+ \)
- Low value (high pH) = \( 10^{-pH} = 10^{-7.45} = 3.54813 \times 10^{-8} = 3.5 \times 10^{-8} \text{ M} \text{H}_3\text{O}^+ \)
- Range: \( 3.5 \times 10^{-8} \text{ to } 4.5 \times 10^{-8} \text{ M} \text{H}_3\text{O}^+ \)

**[OH–] range**

\[
K_w = [H_3O^+][OH^-] = 2.34423 \times 10^{-14} \text{ at } 37°C
\]

\[
[\text{OH}^-] = \frac{K_w}{[H_3O^+]} \\
\text{High value (high pH)} = \frac{2.34423 \times 10^{-14}}{3.54813 \times 10^{-8}} = 6.60695 \times 10^{-7} = 6.6 \times 10^{-7} \text{ M OH}^- \\
\text{Low value (low pH)} = \frac{2.34423 \times 10^{-14}}{4.46684 \times 10^{-8}} = 5.24807 \times 10^{-7} = 5.2 \times 10^{-7} \text{ M OH}^-
\]
Range: $5.2 \times 10^{-7}$ to $6.6 \times 10^{-7}$ \text{ M OH}^-$

18.148 a) Acids will vary in the amount they dissociate (acid strength) depending on the acid-base character of the solvent. Water and methanol have different acid-base characters.

b) The $K_a$ is the measure of an acid’s strength. A stronger acid has a smaller $pK_a$. Therefore, phenol is a stronger acid in water than it is in methanol. In other words, water more readily accepts a proton from phenol than does methanol, i.e., methanol is a weaker base than water.

c) $C_6H_5OH(solvated) + CH_3OH(l) \rightleftharpoons CH_3OH_2^-(solvated) + C_6H_5O^-(solvated)$

The term “solvated” is analogous to “aqueous.” “Aqueous” would be incorrect in this case because the reaction does not take place in water.

d) In the autoionization process, one methanol molecule is the proton donor while another methanol molecule is the proton acceptor.

$CH_3OH(l) + CH_3OH(l) \rightleftharpoons CH_3O^-(solvated) + CH_3OH_2^+(solvated)$

The equilibrium constant for this reaction is the autoionization constant of methanol:

\[ K = [CH_3O^-][CH_3OH_2^+] \]

18.149 a) Step 1 $CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

Step 2 $H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$

b) Molarity of $CO_2 = kH \cdot P_{carbon\ dioxide} = (0.033 \text{ mol/L} \cdot \text{atm})(4 \times 10^{-4} \text{ atm}) = 1.320 \times 10^{-5} \text{ M CO}_2$

$K_{overall} = 4.5 \times 10^{-7}$

Check assumption that $x$ is small compared to $1.320 \times 10^{-5}$:

x = $2.4372 \times 10^{-6}$

Since the error is greater than 5%, it is not acceptable to assume $x$ is small compared to $1.320 \times 10^{-5}$, and it is necessary to use the quadratic equation.

\[ x^2 = (4.5 \times 10^{-7})(1.320 \times 10^{-5} - x) = 5.940 \times 10^{-12} - 4.5 \times 10^{-7}x \]

\[ x^2 + 4.5 \times 10^{-7}x - 5.940 \times 10^{-12} = 0 \]

\[ a = 1 \quad b = 4.5 \times 10^{-7} \quad c = -5.940 \times 10^{-12} \]

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

\[ x = \frac{-4.5 \times 10^{-7} \pm \sqrt{(4.5 \times 10^{-7})^2 - 4(1)(-5.940 \times 10^{-12})}}{2(1)} \]

x = $2.222575 \times 10^{-6}$ \text{ M H}_3\text{O}^+ \text{ pH} = -\log [H_3O^+] = -\log (2.222575 \times 10^{-6}) = 5.6531 = 5.6$

c) $HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$

$K_a = 4.7 \times 10^{-11} = \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]}$

Use the unrounded $x$ from part b).
\[ K_{\text{overall}} = 4.5 \times 10^{-11} = \frac{2.222575 \times 10^{-6} + x}{2.222575 \times 10^{-6} - x} \]

Assume \( x \) is small compared to \( 2 \times 10^{-6} \).

\[ K_{\text{overall}} = 4.5 \times 10^{-11} = \frac{2.222575 \times 10^{-6} x}{[2.222575 \times 10^{-6}]} \]

\([\text{CO}_3^{2-}] = x = 4.5 \times 10^{-11} = 5 \times 10^{-11} M \text{ CO}_3^{2-}\]

Check assumption that \( x \) is small compared to \( 2 \times 10^{-6} \):

\[ \frac{4.5 \times 10^{-11}}{2 \times 10^{-6}} \times 100 = 0.0023\% \text{ error, so the assumption is valid.} \]

d) New molarity of \( \text{CO}_2 = 2k_{\text{H}} \text{carbon dioxide} = 2(0.033 \text{ mol/L}\cdot\text{atm})(4 \times 10^{-4} \text{ atm}) = 2.640 \times 10^{-5} M \text{ CO}_2 \]

\[ K_{\text{overall}} = 4.5 \times 10^{-7} = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{CO}_2]} \]

\[ K_{\text{overall}} = 4.5 \times 10^{-7} = \frac{x}{[2.640 \times 10^{-5} - x]} \]

Assume \( x \) is small compared to \( 2.640 \times 10^{-5} \).

\[ x = 3.44674 \times 10^{-6} \]

Check assumption that \( x \) is small compared to \( 2.640 \times 10^{-5} \):

\[ \frac{3.44674 \times 10^{-6}}{2.640 \times 10^{-5}} \times 100 = 13\% \text{ error, so the assumption is not valid.} \]

Since the error is greater than 5%, it is not acceptable to assume \( x \) is small compared to \( 2.640 \times 10^{-5} \), and it is necessary to use the quadratic equation.

\[ x^2 = (4.5 \times 10^{-7})(2.640 \times 10^{-5} - x) = 1.1880 \times 10^{-11} - 4.5 \times 10^{-7} x \]

\[ x^2 + 4.5 \times 10^{-7} x - 1.1880 \times 10^{-11} = 0 \]

\[ a = 1 \quad b = 4.5 \times 10^{-7} \quad c = -1.1880 \times 10^{-11} \]

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

\[ x = \frac{-4.5 \times 10^{-7} \pm \sqrt{(4.5 \times 10^{-7})^2 - 4(1)(-1.1880 \times 10^{-11})}}{2(1)} \]

\[ x = 3.229 \times 10^{-6} M \text{ H}_3\text{O}^+ \]

\[ \text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (3.229 \times 10^{-6}) = 5.4909 = 5.5 \]

18.150 At great depths, the higher pressure increases the concentration of \( \text{H}_3\text{O}^+ \) and the effect is to shift the dissolving reaction to the right, so seashells dissolve more rapidly.

18.151 Plan: A Lewis acid is an electron-pair acceptor and a Lewis base is an electron-pair donor. Recall that \( n \) is the main energy level and \( l \) is the orbital type.

Solution:

a) \( \text{SnCl}_4 \) is the Lewis acid accepting an electron pair from \((\text{CH}_3)_3\text{N}, \) the Lewis base.

b) Tin is the element in the Lewis acid accepting the electron pair. The electron configuration of tin is \([\text{Kr}]5s^24d^{10}5p^2\). The four bonds to tin are formed by \( sp^3 \) hybrid orbitals, which completely fill the 5s and 5p orbitals. The \( 5d \) orbitals are empty and available for the bond with trimethylamine.

18.152 Plan: A 10-fold dilution means that the chemist takes 1 mL of the \( 1.0 \times 10^{-5} M \) solution and dilutes it to 10 mL (or dilute 10 mL to 100 mL). The chemist then dilutes the diluted solution in a 1:10 ratio, and repeats this process for the next two successive dilutions. \( M_1V_1 = M_2V_2 \) can be used to find the molarity after each dilution. After each dilution, find \([\text{H}_3\text{O}^+] \) and calculate the pH.
Solution:

Hydrochloric acid is a strong acid that completely dissociates in water. Therefore, the concentration of $\text{H}_3\text{O}^+$ is the same as the starting acid concentration: $[\text{H}_3\text{O}^+] = [\text{HCl}]$. The original solution pH:

$$\text{pH} = -\log (1.0 \times 10^{-5}) = 5.00 = \text{pH}$$

Dilution 1: $M_1 V_1 = M_2 V_2$

$(1.0 \times 10^{-5} \text{M})(1.0 \text{mL}) = (x)(10. \text{mL})$

$[\text{H}_3\text{O}^+]_{\text{HC}l} = 1.0 \times 10^{-6} \text{M} \text{H}_3\text{O}^+$

$\text{pH} = -\log (1.0 \times 10^{-6}) = 6.00$

Dilution 2:

$(1.0 \times 10^{-6} \text{M})(1.0 \text{mL}) = (x)(10. \text{mL})$

$[\text{H}_3\text{O}^+]_{\text{HC}l} = 1.0 \times 10^{-7} \text{M} \text{H}_3\text{O}^+$

Once the concentration of strong acid is close to the concentration of $\text{H}_3\text{O}^+$ from water autoionization, the $[\text{H}_3\text{O}^+]$ in the solution does not equal the initial concentration of the strong acid. The calculation of $[\text{H}_3\text{O}^+]$ must be based on the water ionization equilibrium:

$\text{H}_2\text{O}(l) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)$ with $K_w = 1.0 \times 10^{-14}$ at 25°C.

The dilution gives an initial $[\text{H}_3\text{O}^+]$ of $1.0 \times 10^{-7} \text{M}$. Assuming that the initial concentration of hydroxide ions is zero, a reaction table is set up.

<table>
<thead>
<tr>
<th>Concentration ($M$)</th>
<th>$2\text{H}_2\text{O}(l)$</th>
<th>$\text{H}_3\text{O}^+(aq)$</th>
<th>$\text{OH}^-(aq)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>—</td>
<td>$1 \times 10^{-7}$</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>+x</td>
<td>+x</td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>—</td>
<td>$1 \times 10^{-7} + x$</td>
<td>$x$</td>
</tr>
</tbody>
</table>

$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (1 \times 10^{-7} + x) x = 1.0 \times 10^{-14}$

Set up as a quadratic equation:

$$x^2 + 1.0 \times 10^{-7} x - 1.0 \times 10^{-14} = 0$$

$$a = 1, \quad b = 1.0 \times 10^{-7}, \quad c = -1.0 \times 10^{-14}$$

$$x = \frac{-1.0 \times 10^{-7} \pm \sqrt{(1.0 \times 10^{-7})^2 - 4(1)(-1.0 \times 10^{-14})}}{2(1)}$$

$$x = 6.18034 \times 10^{-8}$$

$[\text{H}_3\text{O}^+] = (1.0 \times 10^{-7} + x) M = (1.0 \times 10^{-7} + 6.18034 \times 10^{-8}) M = 1.618034 \times 10^{-7} \text{M} \text{H}_3\text{O}^+$

$pH = -\log [\text{H}_3\text{O}^+] = -\log (1.618034 \times 10^{-7}) = 6.79$

Dilution 3:

$(1.0 \times 10^{-7} \text{M})(1.0 \text{mL}) = (x)(10. \text{mL})$

$[\text{H}_3\text{O}^+]_{\text{HC}l} = 1.0 \times 10^{-8} \text{M} \text{H}_3\text{O}^+$

The dilution gives an initial $[\text{H}_3\text{O}^+]$ of $1.0 \times 10^{-8} \text{M}$. Assuming that the initial concentration of hydroxide ions is zero, a reaction table is set up.

<table>
<thead>
<tr>
<th>Concentration ($M$)</th>
<th>$2\text{H}_2\text{O}(l)$</th>
<th>$\text{H}_3\text{O}^+(aq)$</th>
<th>$\text{OH}^-(aq)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>—</td>
<td>$1 \times 10^{-8}$</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>+x</td>
<td>+x</td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>—</td>
<td>$1 \times 10^{-8} + x$</td>
<td>$x$</td>
</tr>
</tbody>
</table>

$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (1 \times 10^{-8} + x) x = 1.0 \times 10^{-14}$

Set up as a quadratic equation:

$$x^2 + 1.0 \times 10^{-8} x - 1.0 \times 10^{-14} = 0$$

$$a = 1, \quad b = 1.0 \times 10^{-8}, \quad c = -1.0 \times 10^{-14}$$

$$x = \frac{-1.0 \times 10^{-8} \pm \sqrt{(1.0 \times 10^{-8})^2 - 4(1)(-1.0 \times 10^{-14})}}{2(1)}$$

$$x = 9.51249 \times 10^{-9}$$

$[\text{H}_3\text{O}^+] = (1.0 \times 10^{-8} + x) M = (1.0 \times 10^{-8} + 9.51249 \times 10^{-9}) M = 1.051249 \times 10^{-7} \text{M} \text{H}_3\text{O}^+$

$pH = -\log [\text{H}_3\text{O}^+] = -\log (1.051249 \times 10^{-7}) = 6.98$

Dilution 4:

$(1.0 \times 10^{-8} \text{M})(1.0 \text{mL}) = (x)(10. \text{mL})$

$[\text{H}_3\text{O}^+]_{\text{HC}l} = 1.0 \times 10^{-9} \text{M} \text{H}_3\text{O}^+$

The dilution gives an initial $[\text{H}_3\text{O}^+]$ of $1.0 \times 10^{-9} \text{M}$. Assuming that the initial concentration of hydroxide ions is zero, a reaction table is set up.

<table>
<thead>
<tr>
<th>Concentration ($M$)</th>
<th>$2\text{H}_2\text{O}(l)$</th>
<th>$\text{H}_3\text{O}^+(aq)$</th>
<th>$\text{OH}^-(aq)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>—</td>
<td>$1 \times 10^{-9}$</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>+x</td>
<td>+x</td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>—</td>
<td>$1 \times 10^{-9} + x$</td>
<td>$x$</td>
</tr>
</tbody>
</table>

$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (1 \times 10^{-9} + x) x = 1.0 \times 10^{-14}$

Set up as a quadratic equation:

$$x^2 + 1.0 \times 10^{-9} x - 1.0 \times 10^{-14} = 0$$

$$a = 1, \quad b = 1.0 \times 10^{-9}, \quad c = -1.0 \times 10^{-14}$$

$$x = \frac{-1.0 \times 10^{-9} \pm \sqrt{(1.0 \times 10^{-9})^2 - 4(1)(-1.0 \times 10^{-14})}}{2(1)}$$

$$x = 9.99999 \times 10^{-10}$$

$[\text{H}_3\text{O}^+] = (1.0 \times 10^{-9} + x) M = (1.0 \times 10^{-9} + 9.99999 \times 10^{-10}) M = 1.00000 \times 10^{-9} \text{M} \text{H}_3\text{O}^+$

$pH = -\log [\text{H}_3\text{O}^+] = -\log (1.00000 \times 10^{-9}) = 8.00$
Initial $\quad 1 \times 10^{-9} \quad 0$

Change $\quad +x \quad +x$

Equilibrium $\quad 1 \times 10^{-9} + x \quad x$

$K_w = [H_3O^+][OH^-] = (1 \times 10^{-9} + x)(x) = 1.0 \times 10^{-14}$

Set up as a quadratic equation: $x^2 + 1.0 \times 10^{-9} x - 1.0 \times 10^{-14} = 0$

$a = 1 \quad b = 1.0 \times 10^{-9} \quad c = -1.0 \times 10^{-14}$

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

$x = 9.95012 \times 10^{-8}$

$[H_3O^+] = (1.0 \times 10^{-9} + x) M = (1.0 \times 10^{-9} + 9.95012 \times 10^{-8}) M = 1.005012 \times 10^{-7} M H_3O^+$

$pH = -\log [H_3O^+] = -\log (1.005012 \times 10^{-7}) = 6.9978 = 7.00$

As the HCl solution is diluted, the pH of the solution becomes closer to 7.0. Continued dilutions will not significantly change the pH from 7.0. Thus, a solution with a basic pH cannot be made by adding acid to water.

18.153  a) **Steps 1, 2, and 4** are Lewis acid-base reactions.

b) **Step 1** $Cl_2 + FeCl_3 \rightleftharpoons FeCl_5 \text{ (or } Cl^+FeCl_4^- \text{)}$

**Lewis acid** = $FeCl_3 \quad$ **Lewis base** = $Cl_2$

**Step 2** $C_6H_6 + Cl^+FeCl_4^- \rightleftharpoons C_6H_6Cl^+ + FeCl_4^-$

**Lewis acid** = $C_6H_6 \quad$ **Lewis base** = $Cl^+FeCl_4^-$

**Step 4** $H^+ + FeCl_4^- \rightleftharpoons HCl + FeCl_3$

**Lewis acid** = $H^+ \quad$ **Lewis base** = $FeCl_4^-$

18.154  a) $HY(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Y^-(aq)$

$K_a = \frac{[H_3O^+][Y^-]}{[HY]}$

Concentrations in Beaker A:

$[HY] = (8 \text{ particles}) \left(\frac{0.010 \text{ mol}}{1 \text{ particle}}\right) \left(\frac{1}{0.300 \text{ L}}\right) = 0.266667 M$

$[H_3O^+] = [Y^-] = (4 \text{ particles}) \left(\frac{0.010 \text{ mol}}{1 \text{ particle}}\right) \left(\frac{1}{0.300 \text{ L}}\right) = 0.133333 M$

$K_a = \frac{[H_3O^+][Y^-]}{[HY]} = \frac{0.133333 \times 0.133333}{0.266667} = 0.066667 = 0.067$

Calculate the concentrations in Beakers B-D, then calculate $Q$ to determine which are at equilibrium.

Concentrations in Beaker B:

$[HY] = (6 \text{ particles}) \left(\frac{0.010 \text{ mol}}{1 \text{ particle}}\right) \left(\frac{1}{0.300 \text{ L}}\right) = 0.20 M$

$[H_3O^+] = [Y^-] = (2 \text{ particles}) \left(\frac{0.010 \text{ mol}}{1 \text{ particle}}\right) \left(\frac{1}{0.300 \text{ L}}\right) = 0.066667 M$

$Q = \frac{[H_3O^+][Y^-]}{[HY]} = \frac{0.066667 \times 0.066667}{0.20} = 0.022222 = 0.022$

**Beaker B is not at equilibrium.**

Concentrations in Beaker C:

$[HY] = (4 \text{ particles}) \left(\frac{0.010 \text{ mol}}{1 \text{ particle}}\right) \left(\frac{1}{0.300 \text{ L}}\right) = 0.133333 M$
\[ [\text{H}_3\text{O}^+] = [\text{Y}^-] = (2 \text{ particles}) \left( \frac{0.010 \text{ mol}}{1 \text{ particle}} \right) \left( \frac{1}{0.300 \text{ L}} \right) = 0.066667 \text{ M} \]

\[ Q = \frac{[\text{H}_3\text{O}^+] [\text{Y}^-]}{[\text{HY}]} = \frac{0.066667 \cdot 0.066667}{0.13333} = 0.0333345 = 0.033 \]

**Beaker C is not at equilibrium.**

Concentrations in Beaker D:

\[ [\text{HY}] = (2 \text{ particles}) \left( \frac{0.010 \text{ mol}}{1 \text{ particle}} \right) \left( \frac{1}{0.300 \text{ L}} \right) = 0.066667 \text{ M} \]

\[ [\text{H}_3\text{O}^+] = [\text{Y}^-] = (2 \text{ particles}) \left( \frac{0.010 \text{ mol}}{1 \text{ particle}} \right) \left( \frac{1}{0.300 \text{ L}} \right) = 0.066667 \text{ M} \]

\[ Q = \frac{[\text{H}_3\text{O}^+] [\text{Y}^-]}{[\text{HY}]} = \frac{0.066667 \cdot 0.066667}{0.066667} = 0.066667 = 0.067 \]

**Beaker D is at equilibrium.**

b) For both beakers B and C, \( Q < K_a \). Therefore, the reaction is proceeding to the right to produce more products.

c) Yes, dilution affects the extent of dissociation of a weak acid. Dilution increases the degree of dissociation.

For example, in Beaker A, 4 of 12 HY molecules have dissociated for a \((4/12)100 = 33\%\) dissociation. In Beaker D, 2 of 4 HY molecules have dissociated for a \((2/4)100 = 50\%\) dissociation.

18.155 a) Electrical conductivity of 0.1 \( M \) HCl is **higher** than that of 0.1 \( M \) CH\(_3\)COOH. Conductivity is proportional to the concentration of charge in the solution. Since HCl dissociates to a greater extent than CH\(_3\)COOH, the concentration of ions, and thus the charge, is greater in 0.1 \( M \) HCl than in 0.1 \( M \) CH\(_3\)COOH.

b) The electrical conductivity of the two solutions will be **approximately the same** because at low concentrations the autoionization of water is significant causing the concentration of ions, and thus the charge, to be about the same in the two solutions. In addition, the percent dissociation of a weak electrolyte such as acetic acid increases with decreasing concentration.

18.156 In step (1), the RCOOH is the Lewis base and the H\(^+\) is the Lewis acid. In step (2), the RC(OH)\(_2\)^+ is the Lewis acid and the R'OH is the Lewis base.

18.157 a) \( \text{pH} = -\log [\text{H}_3\text{O}^+] \)

HCl is a strong acid so \([\text{H}_3\text{O}^+] = M \text{HCl} \)

\( \text{pH} = -\log (0.10) = 1.00 \)

HClO\(_2\) and HClO are weak acids requiring a \( K_a \) from the Appendix.

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

\[ 0.10 - x \quad x \quad x \]

\[ K_a = 2.9 \times 10^{-8} = \frac{[\text{H}_3\text{O}^+] [\text{ClO}^-]}{[\text{HClO}]} \]

\[ K_a = 2.9 \times 10^{-8} = \frac{(x)(x)}{0.10 - x} \quad \text{Assume } x \text{ is small compared to } 0.10. \]

\[ K_a = 2.9 \times 10^{-8} = \frac{(x)(x)}{0.10} \]

\([\text{H}_3\text{O}^+] = x = 5.38516 \times 10^{-5} \text{ M} \)

Check assumption: \((5.38516 \times 10^{-5}/0.10) \times 100\% = 0.05\%. \) The assumption is good.

\( \text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (5.38516 \times 10^{-5}) = 4.2688 = 4.27 \)

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

\[ 0.10 - x \quad x \quad x \]

\[ K_a = 1.1 \times 10^{-2} = \frac{[\text{H}_3\text{O}^+] [\text{ClO}_2^-]}{[\text{HClO}_2]} \]

18-55
\[ K_a = 1.1 \times 10^{-2} = \frac{[x][x]}{0.10 - x} \]

Assume \( x \) is small compared to 0.10.

\[ K_a = 1.1 \times 10^{-2} = \frac{[x][x]}{0.10} \]

\[ x = 0.033166 \]

Check assumption: \( (0.033166/0.10) \times 100\% = 33\% \). The assumption is not valid. The problem will need to be solved as a quadratic.

\[ x^2 = (1.1 \times 10^{-2})(0.10 - x) = 1.1 \times 10^{-3} - 1.1 \times 10^{-2} x \]

\[ x^2 + 1.1 \times 10^{-2} x - 1.1 \times 10^{-3} = 0 \]

\[ a = 1 \quad b = 1.1 \times 10^{-2} \quad c = -1.1 \times 10^{-3} \]

\[ x = \frac{-1.1 \times 10^{-2} \pm \sqrt{(1.1 \times 10^{-2})^2 - 4(1)(-1.1 \times 10^{-3})}}{2(1)} \]

\[ x = 2.8119 \times 10^{-2} \quad M \text{H}_3\text{O}^+ \]

\[ \text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (2.8119 \times 10^{-2}) = 1.550997 = 1.55 \]

b) The lowest \( \text{H}_3\text{O}^+ \) concentration is from the \( \text{HClO} \). Leave the \( \text{HClO} \) beaker alone, and dilute the other acids until they yield the same \( \text{H}_3\text{O}^+ \) concentration. A dilution calculation is needed to calculate the amount of water added.

\[ \text{HCl} \quad M_i = 0.10 \quad M \quad V_i = 100. \text{ mL} \quad M_f = 5.38516 \times 10^{-5} \quad M \quad V_f = ? \]

\[ V_f = M_f V_f / M_i = (0.10 \times 100. \text{ mL})/5.38516 \times 10^{-5} \quad M = 1.85695 \times 10^5 \text{ mL} \]

Volume water added = \( (1.85695 \times 10^5 \text{ mL}) - 100. \text{ mL} = 1.85595 \times 10^5 \text{ mL} \text{ H}_2\text{O} \) added

\[ \text{HClO}_2 \text{ requires the } K_a \text{ for the acid with the ClO}_2^- \text{ concentration equal to the H}_3\text{O}^+ \text{ concentration}. \text{ The final molarity of the acid will be } M_f, \text{ which may be used in the dilution equation.} \]

\[ \text{HClO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \Leftrightarrow \text{H}_3\text{O}^+ (\text{aq}) + \text{ClO}_2^- (\text{aq}) \]

\[ x - 5.38516 \times 10^{-5} \quad \text{5.38516} \times 10^{-5} \quad 5.38516 \times 10^{-5} \]

\[ K_a = 1.1 \times 10^{-2} = \frac{[\text{H}_3\text{O}^+][\text{ClO}_2^-]}{[\text{HClO}_2]} \]

\[ K_a = 1.1 \times 10^{-2} = \frac{[\text{H}_3\text{O}^+][\text{ClO}_2^-]}{[\text{HClO}_2]} \]

\[ x = M_f = 5.41152 \times 10^{-5} \quad M \]

\[ M_i = 0.10 \quad M \quad V_i = 100. \text{ mL} \quad M_f = 5.41152 \times 10^{-5} \quad M \quad V_f = ? \]

\[ V_f = M_f V_f / M_i = (0.10 \times 100. \text{ mL})/5.41152 \times 10^{-5} \quad M = 1.8479 \times 10^5 \text{ mL} \text{ H}_2\text{O} \] added

18.158 Plan: Determine the hydrogen ion concentration from the \( \text{pH} \). The molarity and the volume will give the number of moles, and with the aid of Avogadro’s number, the number of ions may be found.

Solution:

\[ \text{M H}_3\text{O}^+ = 10^{-\text{pH}} = 10^{-6.2} = 6.30957 \times 10^{-7} \quad M \]

\[ \left( \frac{6.30957 \times 10^{-7} \text{ mol H}_3\text{O}^+}{\text{L}} \right) \left( 10^{-3} \text{ L} \right) \left( \frac{1250 \text{ mL}}{\text{d}} \right) \left( \frac{7 \text{ d}}{1 \text{ wk}} \right) \left( \frac{6.022 \times 10^{23} \text{ mol H}_3\text{O}^+}{1 \text{ mol H}_3\text{O}^+} \right) = 3.32467 \times 10^{18} = 3 \times 10^{18} \text{ H}_3\text{O}^+ \]

The \( \text{pH} \) has only one significant figure, and limits the significant figures in the final answer.

18.159 a) \( \text{NH}_3(\text{l}) \Leftrightarrow \text{NH}_4^+(\text{am}) + \text{NH}_2(\text{am}) \)

In this equilibrium “(am)” indicated ammoniated, solvated by ammonia, instead of “(aq)” to indicate aqueous, solvated by water.
Initially, based on the equilibrium: \[ K_c = \frac{[\text{NH}_4^+][\text{NH}_2^-]}{[\text{NH}_3]} \]

Since NH$_3$ is a liquid and a solvent:

\[ K_c \ [\text{NH}_3]^2 = K_{am} = [\text{NH}_4^+][\text{NH}_2^-] \]

b) Strongest acid = NH$_4^+$  Strongest base = NH$_2^-$

c) NH$_2^-$ > NH$_4^+$: basic  \( \text{NH}_4^+ > \text{NH}_2^- \): acidic

\[ \text{HNO}_3 \text{(am)} + \text{NH}_3 \text{(l)} \rightarrow \text{NH}_4^+ \text{(am)} + \text{NO}_3^- \text{(am)} \]

HCOOH is a strong acid in water while HCOOH is a weak acid in water. However, both acids are equally strong (i.e., their strengths are leveled) in NH$_3$ because they dissociate completely to form NH$_4^+$.  

d) \[ K_{am} = [\text{NH}_4^+][\text{NH}_2^-] = 5.1 \times 10^{-27} \]

\[ [\text{NH}_4^+] = [\text{NH}_2^-] = x \]

\[ K_{am} = [x][x] = 5.1 \times 10^{-27} \]

\[ x = 7.1414 \times 10^{-14} = 7.1 \times 10^{-14} \text{M} \]

e) \[ 2\text{H}_2\text{SO}_4(l) \rightarrow \text{H}_3\text{SO}_4^+(sa) + \text{HSO}_4^-(sa) \]  
\( (sa) = \text{solvated by sulfuric acid (sulf)} \)

\[ K_{sulf} = [\text{H}_3\text{SO}_4^+][\text{HSO}_4^-] = 2.7 \times 10^{-4} \]

\[ [\text{H}_3\text{SO}_4^+] = [\text{HSO}_4^-] = x \]

\[ K_{sulf} = [x][x] = 2.7 \times 10^{-4} \]

\[ x = 1.643 \times 10^{-2} = 1.6 \times 10^{-2} \text{M} \]

18.160 \( M \) is the unknown molarity of the thiamine.

\[ \text{C}_{12}\text{H}_{18}\text{ON}_4\text{SCl}_2(aq) + \text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{O}^+(aq) + \text{C}_{12}\text{H}_{17}\text{ON}_4\text{SCl}_2^-(aq) \]

\[ M - x \quad x \quad x \]

pH = 3.50

\[ [\text{H}_3\text{O}^+] = 10^{-3.50} = 3.1623 \times 10^{-4} \text{M} = x \]

\[ K_a = 3.37 \times 10^{-7} = \frac{[\text{H}_3\text{O}^+][\text{C}_{12}\text{H}_{18}\text{ON}_4\text{SCl}_2^-]}{[\text{C}_{12}\text{H}_{17}\text{ON}_4\text{SCl}_2]} \]

\[ K_a = 3.37 \times 10^{-7} = \frac{(x)(x)}{M - x} \]

\[ K_a = 3.37 \times 10^{-7} = \frac{(3.1623 \times 10^{-4})(3.1623 \times 10^{-4})}{M - 3.1623 \times 10^{-4}} \]

\[ M = 0.29705633 \text{ M} \]

Mass (g) = \( \left( \frac{0.29705633 \text{ mol thiamine HCl}}{\text{L}} \right) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left( 10.00 \text{ mL} \right) \left( \frac{337.27 \text{ g thiamine HCl}}{1 \text{ mol thiamine HCl}} \right) \]

\[ = 1.00188 = 1.0 \text{ g thiamine hydrochloride} \]

18.161 **Plan:** Determine \( K_b \) using the relationship \( K_b = 10^{-pK_b} \). Write the base-dissociation equation and set up a reaction table in which \( x = \) the amount of OH$^-$ produced. Use the \( K_b \) expression to find \( x \). From \([\text{OH}^-], [\text{H}_2\text{O}^-] \) and then pH can be calculated.

**Solution:**

\[ K_b = 10^{5.91} = 1.23027 \times 10^{-6} \]

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

Initial: 0.075  —  0  0

Change:  \(-x\)  \(+x\)  \(+x\)

Equilibrium: 0.075 \(-x\)  \(x\)  \(x\)

\[ K_b = 1.23027 \times 10^{-6} = \frac{[\text{HTRIS}^+]\text{[OH}^-]}{[\text{TRIS}]} \]
\[ K_b = 1.23027 \times 10^{-6} = \frac{[x][x]}{[0.075 - x]} \]

Assume \( x \) is small compared to 0.075.

\[ K_b = 1.23027 \times 10^{-6} = \frac{[x][x]}{[0.075]} \]

\( x = [OH^-] = 3.03760 \times 10^{-4} \text{ M} \)

Check assumption that \( x \) is small compared to 0.075:

\[
\frac{3.03760 \times 10^{-4}}{0.075} (100) = 0.40\% \text{ error, so the assumption is valid.}
\]

\[
[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{3.03760 \times 10^{-4}} = 3.292073 \times 10^{-11} \text{ M}
\]

\[ \text{pH} = -\log [H_3O^+] = -\log (3.292073 \times 10^{-11}) = 10.4825 = 10.48 \]

18.162 \( \text{Fe}^{3+}(aq) + 6\text{H}_2\text{O}(l) \rightleftharpoons \text{Fe(H}_2\text{O)}_6^{3+}(aq) \) Lewis acid-base reaction

\( \text{Fe(H}_2\text{O)}_6^{3+}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{Fe(H}_2\text{O)}_5\text{OH}_2^+(aq) + \text{H}_3\text{O}^+(aq) \) Bronsted-Lowry acid-base reaction

18.163 The pH is dependent on the molar concentration of \( H_3O^+ \). Convert % w/v to molarity, and use the \( K_a \) of acetic acid to determine \([H_3O^+]\) from the equilibrium expression.

Convert % w/v to molarity using the molecular weight of acetic acid (CH\(_3\)COOH):

\[
\text{Molarity} = \frac{5.0 \text{ g CH}_3\text{COOH}}{100 \text{ mL solution}} \times \frac{1 \text{ mol CH}_3\text{COOH}}{60.05 \text{ g CH}_3\text{COOH}} \times \frac{1 \text{ mL}}{10^{-3} \text{ L}} = 0.832639 \text{ M CH}_3\text{COOH}
\]

Acetic acid dissociates in water according to the following equation and equilibrium expression:

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

Initial

|      | 0.832639 | 0 | 0 |

| Change | \(-x\) | \(+x\) | \(+x\) |

| Equilibrium | 0.832639 | \(x\) | \(x\) |

\[
K_a = 1.8 \times 10^{-5} = \frac{[H_3O^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \]

\[
K_a = 1.8 \times 10^{-5} = \frac{[x][x]}{[0.832639 - x]} \]

Assume \( x \) is small compared to 0.832639.

\[
K_a = 1.8 \times 10^{-5} = \frac{[x][x]}{[0.832639]}
\]

\[
x = 3.8714 \times 10^{-3} \text{ M} = [H_3O^+]
\]

Check assumption: \([3.871 \times 10^{-3}/0.832639] \times 100\% = 0.46\%, \text{ therefore the assumption is good.}

\[ \text{pH} = -\log [H_3O^+] = -\log (3.8714 \times 10^{-3}) = 2.412132 = 2.41 \]

18.164 Plan: When an initial acid concentration is diluted, the percent dissociation of the acid increases.

Solution: When the solution is diluted, the percent dissociation of the acid HB increases. There is no single correct scene. Any scene in which the total number of HB + B\(^-\) is less than in the original solution yet the relative number of HB dissociated is greater would be correct. In the original scene, 2 of 12 HB molecules, or 16.7%, have dissociated. One possible scene after dilution could show 8 HB molecules, 2 B\(^-\) and 2 H\(_3\)O\(^+\) ions. Then the dissociation is 2 B\(^-\)/10 HB = 20% dissociation.

18.165 a) The strong acid solution would have a larger electrical conductivity.

b) The strong acid solution would have a lower pH.

c) The strong acid solution would bubble more vigorously.

18.166 Plan: Assuming that the pH in the specific cellular environment is equal to the optimum pH for the enzyme, the hydronium ion concentrations are \([H_3O^+] = 10^{-\text{pH}}\).
Solution:
Salivary amylase, mouth: \([\text{H}_3\text{O}^+] = 10^{-6.8} = 1.58489 \times 10^{-7} = 2 \times 10^{-7} \text{ M}\)

Pepsin, stomach: \([\text{H}_3\text{O}^+] = 10^{-2.0} = 1 \times 10^{-2} \text{ M}\)

Trypsin, pancreas: \([\text{H}_3\text{O}^+] = 10^{-9.5} = 3.1623 \times 10^{-10} = 3 \times 10^{-10} \text{ M}\)

18.167

a) \(\text{CH}_3\text{COOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CH}_3\text{COO}^-(aq)\)

\[K_a = 1.8 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}\]

\[K_a = 1.8 \times 10^{-5} = \frac{x(x)}{(0.240 - x)} \quad \text{Assume } x \text{ is small compared to 0.240.}\]

\[x = 2.07846 \times 10^{-3}\]

Check assumption: \([2.07846 \times 10^{-3}/0.240] \times 100\% = 0.9\%, \text{ therefore the assumption is good.}\)

\[x = [\text{H}_3\text{O}^+] = 2.07846 \times 10^{-3} = 2.1 \times 10^{-3} \text{ M}\]

\[\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (2.07846 \times 10^{-3}) = 2.68\]

\[\text{pOH} = -\log [\text{OH}^-] = -\log (4.81125 \times 10^{-12}) = 11.32\]

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

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

\[K_b = 1.8 \times 10^{-5} = \frac{x(x)}{(0.240 - x)} \quad \text{Assume } x \text{ is small compared to 0.240.}\]

\[x = 2.07846 \times 10^{-3}\]

Check assumption: \([2.07846 \times 10^{-3}/0.240] \times 100\% = 0.9\%, \text{ therefore the assumption is good.}\)

\[x = [\text{OH}^-] = 2.07846 \times 10^{-3} = 2.1 \times 10^{-3} \text{ M}\]

\[\text{pOH} = -\log [\text{OH}^-] = -\log (4.81125 \times 10^{-12}) = 11.32\]

\[\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (2.07846 \times 10^{-3}) = 2.68\]

18.168

Concentration = \(M = \left(\frac{33 \text{ g Na}_3\text{PO}_4}{1 \text{ L}}\right) \left(\frac{1 \text{ mol Na}_3\text{PO}_4}{163.94 \text{ g Na}_3\text{PO}_4}\right) \left(\frac{1 \text{ mol PO}_4^{3-}}{1 \text{ mol Na}_3\text{PO}_4}\right) = 0.20129 \text{ M PO}_4^{3-}\)

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

\[K_b = K_w/K_s = (1.0 \times 10^{-14} \times 2.07846 \times 10^{-3}) = 0.0238095 \quad \text{(Use } K_{s3} \text{ for } \text{H}_3\text{PO}_4)\]

\[K_b = 0.0238095 = \frac{[\text{HPO}_4^{2-}][\text{OH}^-]}{[\text{PO}_4^{3-}]}\]

\[K_b = 0.0238095 = \frac{x(x)}{(0.020129 - x)} \quad \text{A quadratic is required.}\]

\[x^2 + 0.0238095x - 0.00479261 = 0\]

\[a = 1 \quad b = 0.0238095 \quad c = -0.00479261\]
\[ x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \]
\[ x = \frac{-0.0238095 \pm \sqrt{(0.0238095)^2 - 4\left(1\right)(-0.00479261)}}{2\left(1\right)} \]
\[ x = 0.058340 = 0.058 \text{ MOH} \]
\[ \left[\text{H}_3\text{O}^+\right] = K_w/[\text{OH}^-] = (1.0 \times 10^{-14})/(0.058340) = 1.7140898 \times 10^{-13} \text{ M} \]
\[ \text{pH} = -\log \left[\text{H}_3\text{O}^+\right] = -\log (1.7140898 \times 10^{-13}) = 12.765966 = 12.77 \]

18.169  

a) \( \text{PH}_3\text{BCl}_3(s) \rightleftharpoons \text{PH}_3(g) + \text{BCl}_3(g) \)

\[ x = [\text{PH}_3] = [\text{BCl}_3] \]

\[ K_c = [\text{PH}_3][\text{BCl}_3] = (x)^2 = \left[8.4 \times 10^{-3}/3.0 \text{ L}\right]^2 = 7.84 \times 10^{-6} = 7.8 \times 10^{-6} \]

b) 

\[ \begin{array}{c}
\text{H} \\
\text{P} \\
\text{H} \\
\text{B} \\
\text{H} \\
\end{array} \quad \begin{array}{c}
\vdots \\
\vdots \\
\vdots \\
\vdots \\
\vdots \\
\end{array} \quad \begin{array}{c}
\text{Cl} \\
\vdots \\
\vdots \\
\vdots \\
\vdots \\
\end{array} \]

18.170  The freezing point depression equation is required to determine the molality of the solution.

\[ \Delta T = [0.00 - (-1.93°C)] = 1.93°C = iK_f m \]

Temporarily assume \( i = 1 \).

\[ m = \frac{\Delta T}{iK_f} = \frac{1.93°C}{(1)(1.86°C/m)} = 1.037634 \text{ m} = 1.037634 \text{ M} \]

This molality is the total molality of all species in the solution, and is equal to their molarity.

From the equilibrium:

\[ \text{ClCICH}_2\text{COOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{ClCICH}_2\text{COO}^-(aq) \]

<table>
<thead>
<tr>
<th>Initial</th>
<th>1.000 M</th>
<th>x</th>
<th>x</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>1.000 - x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

The total concentration of all species is:

\[ [\text{ClCICH}_2\text{COOH}] + [\text{H}_3\text{O}^+] + [\text{ClCICH}_2\text{COO}^-] = 1.037634 \text{ M} \]

\[ [1.000 - x] + [x] + [x] = 1.000 + x = 1.037634 \text{ M} \]

x = 0.037634 M

\[ K_a = \frac{[\text{H}_3\text{O}^+][\text{ClCICH}_2\text{COO}^-]}{[\text{ClCICH}_2\text{COOH}]} \]

\[ K_a = \frac{(0.037634)(0.037634)}{(1.000 - 0.037634)} = 0.0014717 = 0.00147 \]

18.171  Molarity = \( \frac{0.42 \text{ g C}_{17}\text{H}_{35}\text{COONa}}{10.0 \text{ mL}} \left( \frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left( \frac{1 \text{ mol C}_{17}\text{H}_{35}\text{COONa}}{306.45 \text{ g C}_{17}\text{H}_{35}\text{COONa}} \right) \left( \frac{1 \text{ mol C}_{17}\text{H}_{35}\text{COO}^-}{1 \text{ mol C}_{17}\text{H}_{35}\text{COONa}} \right) \]

\[ = 0.137053 \text{ M C}_{17}\text{H}_{35}\text{COO}^- \]

\[ K_b = K_w/K_a = (1.0 \times 10^{-14})/(1.3 \times 10^{-5}) = 7.69231 \times 10^{-10} \]

\[ \text{C}_{17}\text{H}_{35}\text{COO}^- (aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_{17}\text{H}_{35}\text{COO}(aq) + \text{OH}^- (aq) \]

x = 0.137053 \text{ M} \quad x = x

\[ K_b = 7.69231 \times 10^{-10} = \frac{[\text{C}_{17}\text{H}_{35}\text{COOH}][\text{OH}^-]}{[\text{C}_{17}\text{H}_{35}\text{COO}^-]} \]
$K_b = 7.69231 \times 10^{-10} = \frac{(x)(x)}{(0.137053 - x)}$  
Assume $x$ is small compared to 0.137053.

$x = 1.026769 \times 10^{-5}$ = [OH$^-$]

Check assumption: $[1.026769 \times 10^{-5}/0.137053] \times 100\% = 0.007\%$, therefore the assumption is good.

$[H_3O^+] = K_w/[OH^-] = (1.0 \times 10^{-14})/(1.026769 \times 10^{-5}) = 9.739298 \times 10^{-10}$ $M$ $H_3O^+$

$pH = -\log [H_3O^+] = -\log (9.739298 \times 10^{-10}) = 9.01147 = 9.01$

18.172 a) The two ions that comprise this salt are Ca$^{2+}$ (derived from the strong base Ca(OH)$_2$) and CH$_3$CH$_2$COO$^-$ (derived from the weak acid, propionic acid, CH$_3$CH$_2$COOH). A salt derived from a strong base and weak acid produces a basic solution.

Ca$^{2+}$ does not react with water.

CH$_3$CH$_2$COO$^-$ (aq) + $H_2$O(l) ⇄ CH$_3$CH$_2$COOH(aq) + OH$^-$ (aq)

b) Calcium propionate is a soluble salt and dissolves in water to yield two propionate ions:

Ca(CH$_3$CH$_2$COO)$_2$ + $H_2$O(l) → Ca$^{2+}$(aq) + 2CH$_3$CH$_2$COO$^-$ (aq)

The molarity of the solution is:

\[
\text{Molarity} = \left(\frac{8.75 \text{ g Ca(CH}_3\text{CH}_2\text{COO)}_2}{0.500 \text{ L}}\right) \left(\frac{1 \text{ mol Ca(CH}_3\text{CH}_2\text{COO)}_2}{186.22 \text{ g Ca(CH}_3\text{CH}_2\text{COO)}_2}\right) \left(\frac{2 \text{ mol CH}_3\text{CH}_2\text{COO}^-}{1 \text{ mol Ca(CH}_3\text{CH}_2\text{COO)}_2}\right)
\]

\[
= 0.1879497 \text{ M CH}_3\text{CH}_2\text{COO}^-
\]

\[
\text{CH}_3\text{CH}_2\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CH}_2\text{COOH} + \text{OH}^-
\]

Initial: 0.1879497 M

Change: $-x$ $+$ x $+$ x

Equilibrium: $0.1879497 - x$ $x$ $x$

\[
K_b = K_w/K_a = (1.0 \times 10^{-14})/(1.3 \times 10^{-5}) = 7.69231 \times 10^{-10}
\]

\[
K_b = 7.69231 \times 10^{-10} = \frac{(x)(x)}{(0.1879497 - x)}
\]

Assume $x$ is small compared to 0.1879497.

\[
x = 1.202401 \times 10^{-5}
\]

Check assumption: $[1.202401 \times 10^{-5}/0.1879497] \times 100\% = 0.006\%$, therefore the assumption is good.

$[H_3O^+] = K_w/[OH^-] = (1.0 \times 10^{-14})/(1.202401 \times 10^{-5}) = 8.31669 \times 10^{-10}$ $M$ $H_3O^+$

$pH = -\log [H_3O^+] = -\log (8.31669 \times 10^{-10}) = 9.0800 = 9.08$

18.173 a) Annual depositions:

(NH$_4$)$_2$SO$_4$: \[
\left(\frac{3.0 \text{ (NH}_4\text{)}_2\text{SO}_4}{9.5 \text{ total}}\right)(2.688 \text{ g/m}^2) = 0.8488421 = 0.85 \text{ g/m}^2
\]

NH$_4$HSO$_4$: \[
\left(\frac{5.5 \text{ NH}_4\text{HSO}_4}{9.5 \text{ total}}\right)(2.688 \text{ g/m}^2) = 1.55621 = 1.56 \text{ g/m}^2
\]

H$_2$SO$_4$: \[
\left(\frac{1.0 \text{ H}_2\text{SO}_4}{9.5 \text{ total}}\right)(2.688 \text{ g/m}^2) = 0.282947 = 0.28 \text{ g/m}^2
\]

(NH$_4$)$_2$SO$_4$ is a weak acid; NH$_4$HSO$_4$ has half the acidity per mole as H$_2$SO$_4$ so the equivalent amount of sulfuric acid deposition would be:

\[
\left(\frac{1.56 \text{ g NH}_4\text{HSO}_4}{\text{m}^2}\right)\left(\frac{0.50 \text{ M NH}_4\text{HSO}_4}{1 \text{ M H}_2\text{SO}_4}\right)\left(\frac{98.08 \text{ g H}_2\text{SO}_4}{115.11 \text{ g NH}_4\text{HSO}_4}\right) = 0.664602 \text{ g/m}^2
\]
Total as sulfuric acid = 0.66 g/m² + 0.28 g/m² = 0.94 g/m²

\[ \left( \frac{0.94 \text{ g H}_2\text{SO}_4}{\text{m}^2} \right) \left( \frac{1000 \text{ m}}{1 \text{ km}} \right)^2 \left( \frac{1 \text{ kg}}{1000 \text{ g}} \right) = 9.4 \times 10^3 \text{ kg} \]

b) \( \text{H}_2\text{SO}_4(aq) + \text{CaCO}_3(s) \rightarrow \text{H}_2\text{O}(l) + \text{CO}_2(g) + \text{CaSO}_4(s) \)
There is a 1:1 mole ratio between \( \text{H}_2\text{SO}_4 \) and \( \text{CaCO}_3 \).
Mass (lb) of \( \text{CaCO}_3 \) =

\[ \left( \frac{9.4 \times 10^3 \text{ kg H}_2\text{SO}_4}{1 \text{ kg}} \right) \left( \frac{1000 \text{ g H}_2\text{SO}_4}{1 \text{ mol H}_2\text{SO}_4} \right) \left( \frac{1 \text{ mol CaCO}_3}{1 \text{ mol H}_2\text{SO}_4} \right) \left( \frac{2.205 \text{ lb}}{98.08 \text{ g H}_2\text{SO}_4} \right) \left( \frac{1000 \text{ g}}{1 \text{ mol CaCO}_3} \right) = 2.1154 \times 10^4 \text{ lb CaCO}_3 \]

c) Moles of \( \text{H}^+ \) =

\[ \left( \frac{9.4 \times 10^3 \text{ kg H}_2\text{SO}_4}{1 \text{ kg}} \right) \left( \frac{1 \text{ mol H}_2\text{SO}_4}{98.08 \text{ g H}_2\text{SO}_4} \right) \left( \frac{2 \text{ mol H}^+}{1 \text{ mol H}_2\text{SO}_4} \right) = 1.91680 \times 10^5 \text{ mol H}^+ \]

Volume of lake =

\[ \left( \frac{10 \text{ km}^2}{1 \text{ km}^2} \right) \left( \frac{1000 \text{ m}}{1 \text{ km}} \right)^2 \left( \frac{1 \text{ L}}{1 \text{ m}^3} \right) = 3.0 \times 10^{10} \text{ L} \]

Molarity of \( \text{H}^+ \) =

\[ \frac{1.91680 \times 10^5 \text{ mol H}^+}{3.0 \times 10^{10} \text{ L}} = 6.3893 \times 10^{-6} \text{ M} \]

\( \text{pH} = –\log [\text{H}^+] = –\log (6.3893 \times 10^{-6}) = 5.19 \)

18.174 a) \( 0^\circ \text{C} \) \( K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (x)(x) = 1.139 \times 10^{-15} \)
\( x = [\text{H}_3\text{O}^+] = 3.374907 \times 10^{-8} = 3.37 \times 10^{-8} \text{ M H}_3\text{O}^+ \)
\( \text{pH} = –\log [\text{H}_3\text{O}^+] = –\log (3.374907 \times 10^{-8}) = 7.47 \)

50°C \( K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (x)(x) = 5.474 \times 10^{-14} \)
\( x = [\text{H}_3\text{O}^+] = 2.33956 \times 10^{-7} = 2.34 \times 10^{-7} \text{ M H}_3\text{O}^+ \)
\( \text{pH} = –\log [\text{H}_3\text{O}^+] = –\log (2.33956 \times 10^{-7}) = 6.63 \)

b) \( 0^\circ \text{C} \) \( K_w = [\text{D}_3\text{O}^+][\text{OD}^-] = (x)(x) = 3.64 \times 10^{-16} \)
\( x = [\text{D}_3\text{O}^+] = 1.907878 \times 10^{-8} = 1.91 \times 10^{-8} \text{ M D}_3\text{O}^+ \)
\( \text{pH} = –\log [\text{D}_3\text{O}^+] = –\log (1.907878 \times 10^{-8}) = 7.71 \)

50°C \( K_w = [\text{D}_3\text{O}^+][\text{OD}^-] = (x)(x) = 8.88 \times 10^{-15} \)
\( x = [\text{D}_3\text{O}^+] = 8.882567 \times 10^{-8} = 8.88 \times 10^{-8} \text{ M D}_3\text{O}^+ \)
\( \text{pH} = –\log [\text{D}_3\text{O}^+] = –\log (8.882567 \times 10^{-8}) = 7.05 \)

c) The deuterium atom has twice the mass of a normal hydrogen atom. The deuterium atom is held more strongly to the oxygen atom, so the degree of ionization is decreased.

18.175 Molarity of \( \text{HX} \) =

\[ \left( \frac{12.0 \text{ g HX}}{150. \text{ g HX}} \right) \left( \frac{1 \text{ mol HX}}{1 \text{ mol HX}} \right) = 0.0800 \text{ M HX} \]

Molarity of \( \text{HY} \) =

\[ \left( \frac{6.00 \text{ g HY}}{50.0 \text{ g HY}} \right) \left( \frac{1 \text{ mol HY}}{1 \text{ mol HY}} \right) = 0.120 \text{ M HY} \]

\( \text{HX} \) must be the stronger acid because a lower concentration of \( \text{HX} \) has the same \( \text{pH} \) (it produces the same number of \( \text{H}^+ \) ions) as a higher concentration of \( \text{HY} \).

18.176 Acid HA: \( \text{HA}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq) \)

\[ K_a = \frac{(0.010 \text{ mol/L})(0.010 \text{ mol/L})}{(0.050 \text{ mol/L})(0.050 \text{ mol/L})} = 4.0 \times 10^{-3} \]

Acid HB: \( \text{HB}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{B}^-(aq) \)

\[ K_a = \frac{(0.010 \text{ mol/L})(0.010 \text{ mol/L})}{(0.040 \text{ mol/L})(0.025 \text{ L})} = 1.0 \times 10^{-2} \]
Acid HB, with the larger $K_a$ value, is the stronger acid.

18.177 Treat H$_3$O$^+(aq)$ as H$^+(aq)$ because this corresponds to the listing in the Appendix.

a) $K^+(aq) + OH^−(aq) + H^+(aq) + NO_3^−(aq) \rightarrow K^+(aq) + NO_3^−(aq) + H_2O(l)$

Net ionic equation: $OH^−(aq) + H^+(aq) \rightarrow H_2O(l)$

b) The neutralization reaction of a strong acid and a strong base is essentially the reaction between H$^+(aq)$ and OH$^−(aq)$ to form H$_2$O(l). Therefore, $\Delta H^\circ_{rxn}$ for KOH and HCl would be expected to be $-55.90$ kJ.

18.178 $NH_2(CH_2)_4NH_2(aq) + H_2O(l) \rightleftharpoons NH_2(CH_2)_4NH_3^+(aq) + OH^−(aq)$

$K_b = \frac{[NH_2(CH_2)_4NH_3^+] [OH^−]}{[NH_2(CH_2)_4NH_2]} = \frac{2.1 \times 10^{-3} \times 2.1 \times 10^{-3}}{0.10 - 2.1 \times 10^{-3}} = 4.5 \times 10^{-5}$

18.179 a) There are 20 OH$^−$ ions for every 2 H$_3$O$^+$ ions; in other words, [OH$^−$] = 10 x [H$_3$O$^+$]

$K_w = 1.0 \times 10^{-14} = [H_2O^+][OH^-]

1.0 \times 10^{-14} = [H_2O^+][10][H_3O^+]

[H$_2O^+ ] = 3.162278 \times 10^{-8} M

pH = -log [H$_2O^+$] = -log (3.162278x10$^{-8}$) = 7.4999999 = 7.5

b) For a pH of 4, [H$_3O^+$] = 10$^{-pH} = 10^{-4} M

[OH$^−$] = $K_w/[H_3O^+] = (1.0 \times 10^{-14})/(1.0 \times 10^{-4}) = 1.0 \times 10^{-10} M \ OH^−$

[H$_3O^+$]/[OH$^−$] = 1.0 x 10$^{-7}$/1.0 x 10$^{-10}$ = 1.0 x 10$^3$

The H$_3O^+$ concentration is one million times greater than that of OH$^−$. You would have to draw one million H$_3O^+$ ions for every one OH$^−$.

18.180 a) As the pH of a water solution containing casein increases, the H$^+$ ions from the carboxyl groups on casein will be removed. This will increase the number of charged groups, and the solubility of the casein will increase.

b) As the pH of a water solution containing histones decreases, –NH$_2$ and =NH groups will accept H$^+$ ions from solution. This will increase the number of charged groups, and the solubility of the histones will increase.

18.181 Plan: Use Le Chatelier’s principle.

Solution:

a) The concentration of oxygen is higher in the lungs so the equilibrium shifts to the right.

b) In an oxygen deficient environment, the equilibrium would shift to the left to release oxygen.

c) A decrease in the [H$_3O^+$] concentration would shift the equilibrium to the right. More oxygen is absorbed, but it will be more difficult to remove the O$_2$.

d) An increase in the [H$_3O^+$] concentration would shift the equilibrium to the left. Less oxygen is absorbed, but it will be easier to remove the O$_2$.

18.182 $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^−(aq)$

Convert to a $K_s$ relationship:

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

$K_s = K_w/K_b = (1.0 \times 10^{-14})/(1.76 \times 10^{-5}) = 5.68 \times 10^{-10}$
\[
K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]} \\
\frac{[NH_3]}{[NH_4^+][H_3O^+]} = \frac{K_a}{[H_3O^+]} = \frac{K_a}{[H_3O^+]} = \frac{K_a}{[H_3O^+]} \\
\]

a) \[\text{pH} = 10^{-7.00} = 1.0 \times 10^{-7} \text{ M} \]

\[
\frac{[NH_3]}{[NH_4^+][H_3O^+]} = \frac{1.0 \times 10^{-7}}{5.6818 \times 10^{-10}} = 0.56818 = 5.68 \times 10^{-3} \\
\frac{[NH_3]}{[NH_4^+][H_3O^+]} = \frac{1.0 \times 10^{-7}}{5.6818 \times 10^{-10}} = 0.56818 = 5.68 \times 10^{-3} \\
\]

b) \[\text{pH} = 10^{-10.00} = 1.0 \times 10^{-10} \text{ M} \]

\[
\frac{[NH_3]}{[NH_4^+][H_3O^+]} = \frac{1.0 \times 10^{-10}}{5.6818 \times 10^{-10}} = 0.8503397 = 0.85 \\
\frac{[NH_3]}{[NH_4^+][H_3O^+]} = \frac{1.0 \times 10^{-10}}{5.6818 \times 10^{-10}} = 0.8503397 = 0.85 \\
\]

c) Increasing the pH shifts the equilibria towards \(NH_3\). Ammonia is able to escape the solution as a gas.

18.183 Plan: The molarity of the acid is calculated by dividing moles of acid by the volume of solution. Set up a reaction table for the dissociation of the acid, in which \(x\) = the amount of propanoate ion at equilibrium. The freezing point depression is used to calculate the apparent molality and thus the apparent molarity of the solution. The total concentration of all species at equilibrium equals the apparent molarity and is used to find \(x\). Percent dissociation is the concentration of dissociated acid divided by the initial concentration of the acid and multiplied by 100.

Solution:

a) Calculate the molarity of the solution (before acid dissociation).

\[
M = \left( \frac{7.500 \text{ g CH}_3\text{CH}_2\text{COOH}}{100.0 \text{ mL solution}} \right) \left( \frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left( \frac{1 \text{ mol CH}_3\text{CH}_2\text{COOH}}{74.08 \text{ g CH}_3\text{CH}_2\text{COOH}} \right) = 1.012419 = 1.012 \text{ M CH}_3\text{CH}_2\text{COOH} \\
\]

b) The freezing point depression equation is required to determine the molality of the solution.

\[
\Delta T = iK_f m = [0.000 - (-1.890°C)] = 1.890°C \\
\]

Temporarily assume \(i = 1\).

\[
m = \frac{\Delta T}{iK_f} = \frac{1.890°C}{(1)(1.86°C/\text{m})} = 1.016129032 \text{ m} = 1.016129032 M \\
\]

This molality is the total molality of all species in the solution, and is equal to their molarity.

From the equilibrium:

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

Initial 1.012419 \( M \) 0 0
Change \(-x\) \(+x\) \(+x\)
Equilibrium 1.012419 \(-x\) \(x\) \(x\)

The total concentration of all species is:

\[
[\text{CH}_3\text{CH}_2\text{COOH}] + [\text{H}_3\text{O}^+] + [\text{CH}_3\text{CH}_2\text{COO}^-] = 1.016129032 M \\
[1.012419 - x] + [x] + [x] = 1.012419 + x = 1.016129032 M \\
x = 0.00371003 = 0.004 \text{ M CH}_3\text{CH}_2\text{COO}^- \\
\]

c) The percent dissociation is the amount dissociated (\(x\) from part b)) divided by the original concentration from part a).

\[
\text{Percent dissociation} = \frac{0.00371003 \text{ M}}{1.012419 \text{ M}} \times 100 = 0.366452 = 0.4% \\
\]

18.184 Plan: For parts a) and b), write the base-dissociation reaction and the \(K_b\) expression. Set up a reaction table in which \(x\) = the amount of reacted base and the concentration of \(OH^-\). Solve for \(x\), calculate \([H_3O^+]\), and find the pH. For parts c) and d), write the acid-dissociation reaction for the conjugate acid of quinine. Find the \(K_a\) value.
from \( K_w = K_a \times K_b \). Set up a reaction table in which \( x = \) dissociated acid and the concentration of \([H_3O]^+\), and find the pH.

**Solution:**

Note that both \( pK_b \) values only have one significant figure. This will limit the final answers.

\[ K_{b(\text{tertiary amine N})} = 10^{-pK_b} = 10^{-5.1} = 7.94328 \times 10^{-6} \]

\[ K_{b(\text{aromatic ring N})} = 10^{-pK_b} = 10^{-9.7} = 1.995262 \times 10^{-10} \]

**a)** Ignoring the smaller \( K_b \):

\[
C_{20}H_{24}N_2O_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + \text{HC}_{20}H_{24}N_2O_2^+(aq)
\]

<table>
<thead>
<tr>
<th>Initial</th>
<th>1.6x10^{-3} M</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change</td>
<td>(-x)</td>
<td>(+x)</td>
<td>(+x)</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>1.6x10^{-3} - x</td>
<td>(x)</td>
<td>(x)</td>
</tr>
</tbody>
</table>

\[
K_b = 7.94328 \times 10^{-6} = \frac{[\text{HC}_{20}H_{24}N_2O_2^+][\text{OH}^-]}{[\text{C}_{20}H_{24}N_2O_2]}
\]

\[
K_b = 7.94328 \times 10^{-6} = \frac{[\text{x}][\text{x}]}{1.6 \times 10^{-3} - \text{x}}
\]

Assume \( x \) is small compared to \( 1.6 \times 10^{-3} \):

\[
x = 1.127353 \times 10^{-4}
\]

Check assumption that \( x \) is small compared to \( 1.6 \times 10^{-3} \):

\[
\frac{1.127353 \times 10^{-4}}{1.6 \times 10^{-3}} (100) = 7\% \text{ error, so the assumption is not valid.}
\]

Since the error is greater than 5%, it is not acceptable to assume \( x \) is small compared to \( 1.6 \times 10^{-3} \), and it is necessary to use the quadratic equation.

\[
x^2 = (7.94328 \times 10^{-6})(1.6 \times 10^{-3} - x) = 1.27092 \times 10^{-8} - 7.94328 \times 10^{-6}x
\]

\[
x^2 + 7.94328 \times 10^{-6}x - 1.27092 \times 10^{-8} = 0
\]

\[
a = 1 \hspace{1cm} b = 7.94328 \times 10^{-6} \hspace{1cm} c = -1.27092 \times 10^{-8}
\]

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

\[
x = \frac{-7.94328 \times 10^{-6} \pm \sqrt{(7.94328 \times 10^{-6})^2 - 4(1)(-1.27092 \times 10^{-8})}}{2(1)} = 1.08834 \times 10^{-4} \text{ M OH}^-
\]

\[
[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.08834 \times 10^{-4}} = 9.18830513 \times 10^{-11} \text{ M H}_2\text{O}^+
\]

\[
pH = -\log [H_3O^+] = -\log (9.18830513 \times 10^{-11}) = 10.03676 = 10.0
\]

**b)** (Assume the aromatic N is unaffected by the tertiary amine N.) Use the \( K_b \) value for the aromatic nitrogen.

\[
C_{20}H_{24}N_2O_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + \text{HC}_{20}H_{24}N_2O_2^+(aq)
\]

<table>
<thead>
<tr>
<th>Initial</th>
<th>1.6x10^{-3} M</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change</td>
<td>(-x)</td>
<td>(+x)</td>
<td>(+x)</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>1.6x10^{-3} - x</td>
<td>(x)</td>
<td>(x)</td>
</tr>
</tbody>
</table>

\[
K_b = 1.995262 \times 10^{-10} = \frac{[\text{HC}_{20}H_{24}N_2O_2^+][\text{OH}^-]}{[\text{C}_{20}H_{24}N_2O_2]}
\]

\[
K_b = 1.995262 \times 10^{-10} = \frac{[\text{x}][\text{x}]}{1.6 \times 10^{-3} - \text{x}}
\]

Assume \( x \) is small compared to \( 1.6 \times 10^{-3} \).
\[ K_b = 1.995262 \times 10^{-10} = \left[ \frac{x}{[x]} \right] \frac{1.6 \times 10^{-3}}{1} \]

\[ x = 5.65015 \times 10^{-7} \text{ M OH}^- \]

The hydroxide ion from the smaller \( K_b \) is much smaller than the hydroxide ion from the larger \( K_b \) (compare the powers of ten in the concentration).

c) \( \text{HC}_2\text{H}_2\text{N}_2\text{O}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{C}_2\text{H}_2\text{N}_2\text{O}_2(aq) \)

<table>
<thead>
<tr>
<th>Initial</th>
<th>0.33 M</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change</td>
<td>(-x)</td>
<td>(+x)</td>
<td>(+x)</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.33 - x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[ K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{7.94328 \times 10^{-6}} = 1.25893 \times 10^{-9} \]

\[ K_a = 1.25893 \times 10^{-9} = \left[ \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_2\text{N}_2\text{O}_2^-]}{[\text{HC}_2\text{H}_2\text{N}_2\text{O}_2]} \right] \]

\[ K_a = 1.25893 \times 10^{-9} = \frac{(x)(x)}{(0.33 - x)} \quad \text{Assume x is small compared to 0.33.} \]

\[ K_a = 1.25893 \times 10^{-9} = \frac{(x)(x)}{(0.33)} \]

\[ [\text{H}_3\text{O}^+] = x = 2.038252 \times 10^{-5} \text{ M} \]

Check assumption that x is small compared to 0.33:

\[ \frac{2.038252 \times 10^{-5} (100)}{0.33} = 0.006\% \quad \text{The assumption is good.} \]

pH = \(-\log [\text{H}_3\text{O}^+] = \log (2.038252 \times 10^{-5}) = 4.69074 = 4.7 \]

d) Quinine hydrochloride will be indicated as QHCl.

\[ M = \frac{1.5\%}{100\%} \frac{1.0 \text{ g}}{1 \text{ mL}} \frac{1 \text{ mL}}{10^{-3} \text{ L}} \frac{1 \text{ mol QHCl}}{360.87 \text{ g QHCl}} = 0.041566 \text{ M} \]

\( \text{HC}_2\text{H}_2\text{N}_2\text{O}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{C}_2\text{H}_2\text{N}_2\text{O}_2(aq) \)

<table>
<thead>
<tr>
<th>Initial</th>
<th>0.041566 M</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change</td>
<td>(-x)</td>
<td>(+x)</td>
<td>(+x)</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.041566 - x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[ K_a = 1.25893 \times 10^{-9} = \left[ \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_2\text{N}_2\text{O}_2^-]}{[\text{HC}_2\text{H}_2\text{N}_2\text{O}_2]} \right] \]

\[ K_a = 1.25893 \times 10^{-9} = \frac{(x)(x)}{(0.041566 - x)} \quad \text{Assume x is small compared to 0.041566.} \]

\[ [\text{H}_3\text{O}^+] = x = 7.233857 \times 10^{-6} \text{ M} \]

Check assumption that x is small compared to 0.33:

\[ \frac{7.233857 \times 10^{-6} (100)}{0.041566} = 0.02\% \quad \text{The assumption is good.} \]

pH = \(-\log [\text{H}_3\text{O}^+] = \log (7.233857 \times 10^{-6}) = 5.1406 = 5.1 \]

18.185 a) At pH = 7.00, \([\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-7.00} = 1.0 \times 10^{-7} \text{ M} \)

\[ \frac{[\text{HClO}]}{[\text{HClO}]+[\text{ClO}^-]} = \frac{[\text{H}_3\text{O}^+]}{K_a} \]
\[
\frac{[\text{HClO}]}{[\text{HClO}^+][\text{ClO}^-]} = \frac{1.0 \times 10^{-7}}{1.0 \times 10^{-7} + 2.9 \times 10^{-8}} = 0.775194 = 0.78
\]

b) At pH = 10.00, \([\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-10.00} = 1.0 \times 10^{-10} \text{M}
\]
\[
\frac{[\text{HClO}]}{[\text{HClO}^+][\text{ClO}^-]} \frac{[\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-10}}{1.0 \times 10^{-10} + 2.9 \times 10^{-8}} = 0.003436 = 0.0034
\]

18.186 a) All scenes indicate equal initial amounts of each acid. The more \(\text{H}_3\text{O}^+\) present, the stronger the acid is (greater \(K_a\)).

Increasing \(K_a\): \(\text{HX} < \text{HZ} < \text{HY}\)

b) The p\(K_a\) values increase in order of decreasing \(K_a\) values.

Increasing p\(K_a\): \(\text{HY} < \text{HZ} < \text{HX}\)

c) The order of p\(K_b\) is always the reverse of p\(K_a\) values:

Increasing p\(K_b\): \(\text{HX} < \text{HZ} < \text{HY}\)

d) Percent dissociation = \((2/8) \times 100\% = 25\%\)

e) \(\text{NaY}\), the weakest base, will give the highest pOH and the lowest pH.