form a precipitate with one of the dissolved cations but not the others. The appropriate reagent must form compounds with both metal cations with sufficiently different $K_{sp}$ values (a difference of a factor of at least $10^3$), so that one compound will remain dissolved while the other compound significantly precipitates.

16.25 Qualitative analysis is a systematic way to determine the metal ions present in an unknown solution by the selective precipitation of the ions. The word qualitative means involving quality or kind. So qualitative analysis involves finding the kind of ions present in the solution. Quantitative analysis is concerned with quantity, or the amounts of substances in a solution or mixture.

16.26 A general qualitative analysis scheme involves separating a mixture of the common ions into five groups by sequentially adding five different precipitating agents. After each precipitating agent is added, the mixture is put into a centrifuge to separate the solid from the liquid. The liquid is decanted for the next step, and the solid is set aside for subsequent analysis. Group I removes insoluble chlorides by treating the solution with dilute HCl. Since most chlorides are soluble, the chloride ions do not form a precipitate with the majority of the cations in mixture. However, Ag⁺, Pb₂⁺, and Hg₂⁺ do form insoluble chlorides and will precipitate out. The absence of a precipitate constitutes a negative test for Ag⁺, Pb₂⁺, and Hg₂⁺. After the solid is separated from the liquid, the solution is ready for the next step, where Group II, acid-insoluble sulfides are removed. This is accomplished by taking the aqueous mixture containing the remaining metal cations and treating it with H₂S, a weak diprotic acid that dissociates to form sulfide ions, $S^{2-}$. Since the solution is acidic from the first treatment, only the acid-insoluble sulfide metals will precipitate out. These include Hg²⁺, Cd²⁺, Bi³⁺, Cu²⁺, Sn⁴⁺, As³⁺, and Sb³⁺. If any of these metal cations are present, they precipitate out as sulfides. After the solid is separated from the liquid, the solution is ready for the next step. In the third step, Group III, the base-insoluble sulfides and hydroxides, are removed by taking the acidic aqueous mixture containing the remaining metal cations and treating it with a base and additional H₂S. The added base reacts with acid, shifting the H₂S ionization equilibria to the right and creating a higher $S^{2-}$ concentration. This causes the precipitation of those sulfides that were too soluble to precipitate out in the previous step, but not soluble enough to prevent precipitation with the higher sulfide ion concentration. The ions that precipitate as sulfides at this point (if they are present) are Co³⁺, Zn²⁺, Mn²⁺, Ni²⁺, and Fe²⁺. In addition, the basic solution causes Cr³⁺ and Al³⁺ to precipitate as hydroxides. After the solid is separated from the liquid, the solution is ready for the next step, removing the Group IV, insoluble carbonate, metal ions. At this stage, all of the cations have been precipitated except those belonging to the alkali metal family (group 1A in the periodic table) and the alkaline earth metal family (group 2A in the periodic table). The alkaline earth metal cations can be precipitated by adding sodium carbonate to the solution. The carbonate ion precipitates Mg²⁺, Ca²⁺, and Ba²⁺ as metal carbonates, which are separated from the liquid. The only dissolved ions belong to Group V, the alkali metals and NH₄⁺. The liquid decanted from the previous step can now contain are Na⁺, K⁺, and NH₄⁺. These cations do not form insoluble compounds with any anions and cannot be precipitated from the solution. Their presence can be tested by other means. Sodium and potassium ions, for example, are usually identified through flame tests. The sodium ion produces a yellow-orange flame and the potassium ion produces a violet flame. By applying the previous procedure, nearly two dozen metal cations can be separated from a solution initially containing all of them. Each of the groups can then be further analyzed to determine the specific ions present from that group.

The Common Ion Effect and Buffers

16.27 The only solution that HNO₂ will ionize less in is d) 0.10 M NaNO₂. It is the only solution that generates a common ion NO₂⁻ with nitrous acid.

16.28 Formic acid is HCHO₂ which dissociates to H⁺ and CHO₂⁻. The only solution that generates a common ion (CHO₂⁻) with formic acid is (c) NaCHO₂.

16.29 (a) Given: 0.20 M HCHO₂ and 0.15 M NaCHO₂ Find: pH Other: $K_a$ (HCHO₂) = 1.8 x 10⁻⁴

Conceptual Plan: M NaCHO₂ → M CHO₂⁻ + M HCHO₂, M CHO₂⁻ → [H₃O⁺] → pH

NaCHO₂ (aq) → Na⁺ (aq) + CHO₂⁻ (aq)  \[ \text{ICE Chart} \]  \[ \text{pH} = -\log[H₃O⁺] \]

Solution: Since 1 CHO₂⁻ ion is generated for each NaCHO₂, [CHO₂⁻] = 0.15 M CHO₂⁻.
16.30 (a) Given: 0.195 M HCHO₂ and 0.125 M KCl

Find: pH

Other: $K_b$ (NH₃) = 1.79 x 10⁻⁵

Conceptual Plan: M KCl $\rightarrow$ M NH⁺ then M NH₃, M NH₄⁺ $\rightarrow$ [OH⁻] $\rightarrow$ [H₂O] $\rightarrow$ pH

Solution: Since 1 NH₄⁺ ion is generated for each KCl, $\text{[NH}_4^+\text{]} = 0.125\text{ M KCl}$

Check: The units (none) are correct. The magnitude of the answer makes physical sense because pH should be greater than $\text{- log}(0.20) = 0.70$ because this is a weak acid and there is a common ion effect.

(b) Given: 0.16 M NH₃ and 0.22 M NH₄Cl

Find: pH

Other: $K_b$ (NH₃) = 1.79 x 10⁻⁵

Conceptual Plan: M NH₄Cl $\rightarrow$ M NH₄⁺ then M NH₃, M NH₄⁺ $\rightarrow$ [OH⁻] $\rightarrow$ [H₂O] $\rightarrow$ pH

Solution: Since 1 NH₄⁺ ion is generated for each NH₄Cl, $\text{[NH}_4^+\text{]} = 0.22\text{ M NH₄Cl}$

Check: The units (none) are correct. The magnitude of the answer makes physical sense because pH should be greater than $\text{- log}(0.20) = 0.70$ because this is a weak acid and there is a common ion effect.
Chapter 16 Aqueous Ionic Equilibrium

### Chapter 16 Aqueous Ionic Equilibrium

**Equation:**

\[
\text{HCHO}_2^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + \text{CH}_2\text{O}_2^- (aq)
\]

**Initial**

<table>
<thead>
<tr>
<th>[HCHO_2^-(aq)]</th>
<th>[H_3O^+(aq)]</th>
<th>[\text{CH}_2\text{O}_2^-(aq)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>0.00</td>
<td>0.10</td>
</tr>
</tbody>
</table>

**Change**

<table>
<thead>
<tr>
<th>[x]</th>
<th>[+x]</th>
<th>[+x]</th>
</tr>
</thead>
</table>

**Equil**

<table>
<thead>
<tr>
<th>[0.15 - x]</th>
<th>[+x]</th>
<th>[0.10 + x]</th>
</tr>
</thead>
</table>

**Equilibrium Constant:**

\[
K_a = \frac{[H_3O^+] [\text{CH}_2\text{O}_2^-]}{[HCHO_2^-]} = 6.5 \times 10^{-5} = \frac{x(0.10 + x)}{0.15 - x}
\]

Assume \(x\) is small \((x << 0.10 < 0.15)\) so \(x(0.10 + x) \approx x(0.10)\) and \(x = 9.75 \times 10^{-5} M = [H_3O^+]\), then:

\[
\frac{[H_3O^+]_{\text{eqil}}}{[HCHO_2^-]_0} \times 100\% = \frac{9.75 \times 10^{-5}}{0.15} \times 100\% = 0.065\% \text{, which also confirms that the assumption is valid (since it is less than 5%). The percent ionization in the sodium benzoate solution is less than in pure water because of the common ion effect. An increase in one of the products (benzoate ion) shifts the equilibrium to the left, so less acid dissociates.}

**Check:** The units \((\%)\) are correct. The magnitude of the answer makes physical sense because the acid is weak and so the percent ionization is low. With a common ion present, the percent ionization decreases.

**Conceptual Plan:**

- **Pure water:** \([HCHO_2^-] \rightleftharpoons [H_3O^+] + [CH_2O_2^-]\) (ICE Chart)
  - \(\% \text{ ionization} = \frac{[H_3O^+]_{\text{eqil}}}{[HCHO_2^-]_0} \times 100\%\)

- **Solution:** Since 1 \(\text{CHO}_2^-\) ion is generated for each \(\text{KCHO}_2\) \([\text{CHO}_2^-] = 0.11 M \text{ CH}_2O_2^-\)

**Solution in pure water:**

<table>
<thead>
<tr>
<th>[HCHO_2^- (aq) + H_2O (l) \rightleftharpoons H_3O^+(aq) + CH_2O_2^-(aq)]</th>
<th>[HCHO_2^- (aq)]</th>
<th>[H_3O^+(aq)]</th>
<th>[CH_2O_2^-(aq)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.13</td>
<td>0.00</td>
<td>0.10</td>
</tr>
<tr>
<td>Change</td>
<td>(-x)</td>
<td>(+x)</td>
<td>(+x)</td>
</tr>
<tr>
<td>Equil</td>
<td>(0.13 - x)</td>
<td>(+x)</td>
<td>(0.10 + x)</td>
</tr>
</tbody>
</table>

**Initial Concentration:**

\[
\text{K}_a = \frac{[H_3O^+] [\text{CH}_2\text{O}_2^-]}{[HCHO_2^-]} = 1.8 \times 10^{-4} = \frac{x^2}{0.13 - x}
\]

Assume \(x\) is small \((x << 0.10)\) so \(x^2 \approx 1.8 \times 10^{-4} = x^2\) and \(x = 4.8374 \times 10^{-3} M = [H_3O^+]\). Then:

\[
\% \text{ ionization} = \frac{[H_3O^+]_{\text{eqil}}}{[HCHO_2^-]_0} \times 100\% = \frac{4.8374 \times 10^{-3}}{0.13} \times 100\% = 3.7\% \text{ which also confirms that the assumption is valid (since it is less than 5%).}
\]

**In KCHO_2 Solution:** Since 1 \(\text{CHO}_2^-\) ion is generated for each \(\text{KCHO}_2\) \([\text{CHO}_2^-] = 0.11 M \text{ CH}_2O_2^-\)

<table>
<thead>
<tr>
<th>[HCHO_2^- (aq) + H_2O (l) \rightleftharpoons H_3O^+(aq) + CH_2O_2^-(aq)]</th>
<th>[HCHO_2^- (aq)]</th>
<th>[H_3O^+(aq)]</th>
<th>[CH_2O_2^-(aq)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.13</td>
<td>0.00</td>
<td>0.11</td>
</tr>
<tr>
<td>Change</td>
<td>(-x)</td>
<td>(+x)</td>
<td>(+x)</td>
</tr>
<tr>
<td>Equil</td>
<td>(0.13 - x)</td>
<td>(+x)</td>
<td>(0.11 + x)</td>
</tr>
</tbody>
</table>

**Initial Concentration:**

\[
\text{K}_a = \frac{[H_3O^+] [\text{CH}_2\text{O}_2^-]}{[HCHO_2^-]} = 1.8 \times 10^{-4} = \frac{x(0.11 + x)}{0.13 - x}
\]

Assume \(x\) is small \((x << 0.11 < 0.13)\) so \(x(0.11 + x) \approx x(0.11)\) and \(x = 2.1273 \times 10^{-4} M = [H_3O^+]\). Then:

\[
\% \text{ ionization} = \frac{[H_3O^+]_{\text{eqil}}}{[HCHO_2^-]_0} \times 100\% = \frac{2.1273 \times 10^{-4}}{0.13} \times 100\% = 0.16\% \text{, which also confirms that the assumption is valid (since it is less than 5%). The percent ionization in the potassium formate solution is less than in pure water because of the common ion effect. An increase in one of the products (formate ion) shifts the equilibrium to the left, so less acid dissociates.}

**Given:** 0.13 M \text{HCHO}_2\ in pure water and in 0.11 M \text{KCHO}_2 Find: \% ionization in both solutions

**Conceptual Plan:**

- **Pure water:** \(\text{HCHO}_2^- \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_2\text{O}_2^- (\text{aq})\)

**Solution:**

\[
\frac{[H_3O^+]_{\text{eqil}}}{[HCHO_2^-]_0} \times 100\% = \frac{4.8374 \times 10^{-3}}{0.13} \times 100\% = 3.7\%
\]

\[
\frac{[H_3O^+]_{\text{eqil}}}{[HCHO_2^-]_0} \times 100\% = \frac{2.1273 \times 10^{-4}}{0.13} \times 100\% = 0.16\%
\]

**Check:** The units \((\%)\) are correct. The magnitude of the answer makes physical sense because the acid is weak and so the percent ionization is low. With a common ion present, the percent ionization decreases.
Check: The units (%) are correct. The magnitude of the answer makes physical sense because the acid is weak and so the percent ionization is low. With a common ion present, the percent ionization decreases.

16.33 (a) Given: 0.15 M HF  Find: pH  Other: $K_a(\text{HF}) = 3.5 \times 10^{-4}$

Conceptual Plan: $\text{M HF} \rightarrow [\text{H}_3\text{O}^+ (aq)] \rightarrow \text{pH}$

Solution:

\[
\begin{align*}
\text{(HF)} + \text{H}_2\text{O} (l) & \rightleftharpoons [\text{H}_3\text{O}^+ (aq)] + [\text{F}^- (aq)] \\
\text{Initial} & \quad 0.15 \quad 0.00 \quad 0.00 \\
\text{Change} & \quad -x \quad +x \quad +x \\
\text{Equil} & \quad 0.15 - x \quad +x \quad +x
\end{align*}
\]

\[
K_a = \frac{[\text{H}_3\text{O}^+] [\text{F}^-]}{[\text{HF}]} = 3.5 \times 10^{-4} = \frac{x^2}{0.15 - x} \quad \text{Assume } x < 0.15 \text{ so}
\]

\[
\frac{x^2}{0.15 - x} = 3.5 \times 10^{-4} = \frac{x^2}{0.15} \quad \text{and } x = 7.2457 \times 10^{-3} \text{ M} = [\text{H}_3\text{O}^+]. \text{Confirm that assumption is valid}
\]

\[
K_w = [\text{H}_3\text{O}^+] [\text{OH}^-] \quad \text{so } \frac{[\text{H}_3\text{O}^+]}{[\text{OH}^-]} = 4.8305 \times 10^{-9} \text{ M}. 
\]

Finally, $pH = -\log [\text{H}_3\text{O}^+] = -\log (7.2457 \times 10^{-3}) = 2.14$.

Check: The units (none) are correct. The magnitude of the answer makes physical sense because pH should be greater than $-\log (0.15) = 0.82$ because this is a weak acid.

(b) Given: 0.15 M NaF  Find: pH  Other: $K_a(\text{HF}) = 3.5 \times 10^{-4}$

Conceptual Plan: $\text{M NaF} \rightarrow \text{M F}^- \rightarrow [\text{F}^- (aq)] \rightarrow [\text{H}_3\text{O}^+] \rightarrow \text{pH}$

Solution: Since 1 F⁻ ion is generated for each NaF, $[\text{F}^-] = 0.15 \text{ M F}^-$. Since $K_w = K_a K_b$, rearrange to

\[
K_a K_b = \frac{1.0 \times 10^{-14}}{3.5 \times 10^{-4}} = \frac{2.8571 \times 10^{-11}}{F^- (aq)} [\text{HF} (aq)] + [\text{OH}^- (aq)]
\]

\[
\begin{align*}
\text{Initial} & \quad 0.15 \quad 0.00 \quad 0.00 \\
\text{Change} & \quad -x \quad +x \quad +x \\
\text{Equil} & \quad 0.15 - x \quad +x \quad +x
\end{align*}
\]

\[
K_b = \frac{[\text{HF}] [\text{OH}^-]}{[\text{F}^-]} = \frac{2.8571 \times 10^{-11}}{0.15 - x} \\
\text{Assume } x \text{ is small (x < 0.15) so}
\]

\[
\frac{x^2}{0.15 - x} = 2.8571 \times 10^{-11} = \frac{x^2}{0.15} \quad \text{and } x = 2.0702 \times 10^{-6} \text{ M} = [\text{OH}^-].
\]

Confirm that assumption is valid

\[
K_w = [\text{H}_3\text{O}^+] [\text{OH}^-] \quad \text{so } [\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{2.0702 \times 10^{-6}} = 4.8305 \times 10^{-9} \text{ M}. 
\]

Finally, $pH = -\log [\text{H}_3\text{O}^+] = -\log (4.8305 \times 10^{-9}) = 8.32$.

Check: The units (none) are correct. The magnitude of the answer makes physical sense because pH should be slightly basic, since the fluoride ion is a very weak base.

(c) Given: 0.15 M HF and 0.15 M NaF  Find: pH  Other: $K_a(\text{HF}) = 3.5 \times 10^{-4}$

Conceptual Plan: $\text{M NaF} \rightarrow \text{M F}^- \rightarrow [\text{F}^- (aq)] \rightarrow [\text{H}_3\text{O}^+] \rightarrow \text{pH}$

Solution: Since 1 F⁻ ion is generated for each NaF, $[\text{F}^-] = 0.15 \text{ M F}^-$. 

\[
\begin{align*}
\text{NaF (aq)} + \text{H}_2\text{O} (l) & \rightarrow [\text{HF (aq)}] + [\text{F}^- (aq)] \\
\text{Initial} & \quad 0.15 \quad 0.00 \quad 0.00 \\
\text{Change} & \quad -x \quad +x \quad +x \\
\text{Equil} & \quad 0.15 - x \quad +x \quad +x
\end{align*}
\]
Confirm that assumption is valid $\frac{2.0226 \times 10^{-6}}{0.18} \times 100\% = 0.0012\% < 5\%$ so assumption is valid.

Finally, $pH = - \log [H_3O^+] = - \log (2.0226 \times 10^{-6}) = 5.69$.

Check: The units (none) are correct. The magnitude of the answer makes physical sense because pH should be slightly acidic, since the methylammonium cation is a very weak acid.

(c) Given: 0.18 M CH$_3$NH$_2$ and 0.18 M CH$_3$NH$_3$Cl. Find: pH Other: 

Conceptual Plan: M CH$_3$NH$_3$Cl $\rightarrow$ M CH$_3$NH$_2^+$ then 

ICE Chart

<table>
<thead>
<tr>
<th></th>
<th>CH$_3$NH$_3^+$</th>
<th>CH$_3$NH$_2^+$</th>
<th>OH$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.18</td>
<td>0.18</td>
<td>0.00</td>
</tr>
<tr>
<td>Change</td>
<td>$-x$</td>
<td>$+x$</td>
<td>$+x$</td>
</tr>
<tr>
<td>Equil</td>
<td>0.18 $- x$</td>
<td>0.18 $+ x$</td>
<td>$+x$</td>
</tr>
</tbody>
</table>

$K_b = \frac{[CH_3NH_2^+][OH^-]}{[CH_3NH_3^+]} = 4.4 \times 10^{-4}$ 

Assume $x$ is small $(x << 0.18)$ so $4.4 \times 10^{-4} \approx \frac{(0.18 + x)x}{0.18 - x}$ and $x = \frac{4.4 \times 10^{-4}M}{[OH^-]}$. 

Confirms that assumption is valid $4.4 \times 10^{-4} \times 100\% = 0.24\% < 5\%$ so assumption is valid.

Check: The units (none) are correct. The magnitude of the answer makes physical sense because pH should be less than 14 + log (0.18) = 13.3 because this is a weak base and there is a common ion effect.

16.35 When an acid (such as HCl) is added it will react with the conjugate base of the buffer system as follows: 

HCl + NaCl$\rightarrow$ H$_2$O + Na$^+$ + Cl$^-$.

16.36 When an acid (such as HCl) is added it will react with the conjugate base of the buffer system as follows: 

HCl + NH$_3$ $\rightarrow$ NH$_4^+$ + Cl$^-$. 

(a) Given: 0.20 M HCHO$_2$ and 0.15 M NaCHO$_2$. Find: pH Other: $K_a$ (HCHO$_2$) = 1.8 $\times 10^{-4}$

Conceptual Plan: Identify acid and base components then M NaCHO$_2$ $\rightarrow$ M CHO$_2^-$ then 

$K_a$ CHO$_2^-$ base = CHO$_2^-$. 

NaCHO$_2$ (aq) $\rightarrow$ Na$^+$ (aq) + CHO$_2^-$ (aq)

Note that in order to use the Henderson–Hasselbalch Equation, the assumption that $x$ is small must be valid. This was confirmed in Problem 29.

Check: The units (none) are correct. The magnitude of the answer makes physical sense because pH should be less than the $pK_a$ of the acid because there is more acid than base. The answer agrees with Problem 29.
16.39 (a) Given: 0.135 M HClO and 0.155 M KC1O
Find: pH
Other: pK_a = 2.9 \times 10^{-8}
Conceptual Plan: Identify acid and base components then M HClO \rightarrow M HClO^- and K_b \rightarrow pK_b → pK_a
then pK_w, M NH_3, M NH_3^- \rightarrow pH.

Solution: Base = NH_3, [base] = [NH_3] = 0.16 M Acid = NH_3^+. Since 1 NH_3^+ ion is generated for each
NH_3Cl, [NH_3^+] = 0.18 M NH_3^- = [acid].

Since K_b(NH_3) = 1.79 \times 10^{-5}; pK_b = - \log (1.79 \times 10^{-5}) = 4.75. Since 14 = pK_a + pK_b
pK_a = 14 - pK_b = 14 - 4.75 = 9.25 then pH = pK_a + log [acid] = 9.25 + \log \frac{0.16}{0.22} = 9.11.

Note that in order to use the Henderson-Hasselbalch Equation, the assumption that x is small must
be valid. This was confirmed in Problem 29.

Check: The units (none) are correct. The magnitude of the answer makes physical sense because pH
should be less than the pH of the acid because there is more acid than base. The answer agrees with
problem 29, within the error of the value.

16.38 (a) Given: 0.195 M HC_2H_3O_2 and 0.125 M KC_2H_3O_2
Find: pH
Other: pK_a(HC_2H_3O_2) = 1.8 \times 10^{-5}
Conceptual Plan: Identify acid and base components then M HC_2H_3O_2 \rightarrow M HC_2H_3O_2^- then
acid = HC_2H_3O_2 base = C_2H_3O_2^-; Kc_2H_3O_2 (aq) \rightarrow K^+(aq) + C_2H_3O_2^-(aq)
M HC_2H_3O_2, M C_2H_3O_2^- \rightarrow pH.

Solution: Acid = HC_2H_3O_2, so [acid] = [HC_2H_3O_2] = 0.195 M. Base = C_2H_3O_2^-; Since 1 C_2H_3O_2^- ion is
generated for each KC_2H_3O_2, [C_2H_3O_2^-] = 0.125 M C_2H_3O_2^- = [base]. Then

\[ pK_a = - \log K_a = - \log (1.8 \times 10^{-5}) = 4.55. \]

Note that in order to use the Henderson-Hasselbalch Equation, the assumption that x is small must
be valid. This was confirmed in Problem 30.

Check: The units (none) are correct. The magnitude of the answer makes physical sense because pH
should be less than the pH of the acid because there is more acid than base. The answer agrees with
Problem 30.

(b) Given: 0.255 M CH_3NH_2 and 0.135 M CH_3NH_3Br
Find: pH Other: K_b(CH_3NH_2) = 4.4 \times 10^{-4}
Conceptual Plan: Identify acid and base components then M CH_3NH_3Br \rightarrow M CH_3NH_3^+ and
acid = CH_3NH_3^+ base = CH_3NH_2 CH_3NH_3Br (aq) \rightarrow CH_3NH_3^+(aq) + Br^-(aq)
K_b \rightarrow pK_b \rightarrow pK_a then pK_w, M NH_3, M NH_3^- \rightarrow pH.

\[ pK_a = - \log K_a = 14 = pK_a + pK_b \rightarrow \text{pH} = pK_a + \log [\text{acid}] \]

Solution: Base = CH_3NH_2, [base] = [CH_3NH_2] = 0.255 M Acid = NH_3^+. Since 1 CH_3NH_2 ion is generated
for each CH_3NH_3Br, [CH_3NH_3^+] = 0.135 M CH_3NH_3^+ = [acid].

Since K_b(CH_3NH_2) = 4.4 \times 10^{-4}, pK_b = - \log K_b = - \log (4.4 \times 10^{-4}) = 3.36.

Since 14 = pK_a + pK_b, pK_a = 14 - pK_b = 14 - 3.36 = 10.64 then
\[ \text{pH} = pK_a + \log [\text{acid}] = 10.64 + \log \frac{0.255}{0.135} = 10.92. \]

Note that in order to use the Henderson-Hasselbalch Equation, the assumption that x is small must
be valid. This was confirmed in Problem 30.

Check: The units (none) are correct. The magnitude of the answer makes physical sense because pH
should be less than the pH of the acid because there is more base than acid. The answer agrees with
Problem 30.
(a) Given: 250.0 mL buffer 0.250 M HCl and 0.250 M NaCl. Find: initial pH

Conceptual Plan: Identify acid and base components then M NaCl → M C$_2$H$_5$O$_2$ then

\[ \text{pH} = pK_a + \log \left[ \frac{[\text{acid}]}{[\text{base}]} \right] \]

Solution: Acid = HCl, base = C$_2$H$_5$O$_2$. Since 1 C$_2$H$_5$O$_2$ ion is generated for each NaCl, then

\[ [\text{acid}] = [\text{HC}l] = 0.250 \text{ M}, [\text{base}] = 0.250 \text{ M} \]

\[ \text{pH} = pK_a + \log \left[ \frac{[\text{acid}]}{[\text{base}]} \right] = 4.74. \]

Check: The units (none) are correct. The magnitude of the answer makes physical sense because pH is equal to the pK$_a$ of the acid because there are equal amounts of acid and base.

(c) Given: 250.0 mL buffer 0.250 M HCl and 0.250 M NaCl. Find: pH

Conceptual Plan: Part I: Stoichiometry:

\[ \text{mL buffer} \times \frac{1 \text{ L}}{1000 \text{ mL}} = \text{mol NaCl} = \text{mol HCl} \]

Set up stoichiometry table

Part II: Equilibrium:

\[ \text{mol NaCl} \times \text{mol HCl} \times \text{K}_a = \text{pH} \]

\[ \text{pH} = pK_a + \log \left[ \frac{[\text{acid}]}{[\text{base}]} \right] \]

Solution: NaCl and HCl. Since the amount of HCl is small, there are still significant amounts of both buffer components, so the Henderson-Hasselbalch equation can be used to calculate the new pH.

\[ \text{pH} = pK_a + \log \left[ \frac{[\text{acid}]}{[\text{base}]} \right] = 4.68. \]

Check: The units (none) are correct. The magnitude of the answer makes physical sense because the pH dropped slightly when acid was added.
Chapter 16 Aqueous Ionic Equilibrium

Conceptual Plan: Part I: Stoichiometry:

\[ \text{mL} \to \text{L then } \text{mol NaC}_2\text{H}_3\text{O}_2 \text{ and } \text{mol HC}_2\text{H}_3\text{O}_2 \]  

write balanced equation then

\[ \text{NaOH} + \text{HC}_2\text{H}_3\text{O}_2 \to \text{H}_2\text{O} + \text{NaC}_2\text{H}_3\text{O}_2 \]

\[ \text{mol NaC}_2\text{H}_3\text{O}_2, \text{ mol HC}_2\text{H}_3\text{O}_2, \text{ mol NaOH} \to \text{ mol NaC}_2\text{H}_3\text{O}_2, \text{ mol HC}_2\text{H}_3\text{O}_2 \text{ then} \]

Part II: Equilibrium:

\[ \text{mol NaC}_2\text{H}_3\text{O}_2, \text{ mol HC}_2\text{H}_3\text{O}_2, \text{ L, } K_a \to \text{pH} \]

Solution: 250.0 mL \( \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.2500 \text{ L} \) then

\[ 0.250 \text{ mol HC}_2\text{H}_3\text{O}_2 \times 0.2500 \text{ L} = 0.0625 \text{ mol HC}_2\text{H}_3\text{O}_2 \]

\[ 0.250 \text{ mol NaC}_2\text{H}_3\text{O}_2 \times 0.2500 \text{ L} = 0.0625 \text{ mol NaC}_2\text{H}_3\text{O}_2 \]

set up stoichiometry table

<table>
<thead>
<tr>
<th>Reaction</th>
<th>HC(_2)H(_3)O(_2)</th>
<th>Na(_2)C(_2)H(_3)O(_2)</th>
<th>H(_2)O (l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before addition</td>
<td>0.00 mol</td>
<td>0.0625 mol</td>
<td>0.0625 mol</td>
</tr>
<tr>
<td>Addition</td>
<td>0.0050 mol</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>After addition</td>
<td>0.0050 mol</td>
<td>0.0575 mol</td>
<td>0.0675 mol</td>
</tr>
</tbody>
</table>

Since the amount of NaOH is small, there are still significant amounts of both buffer components, so the Henderson-Hasselbalch equation can be used to calculate the new pH.

\[ \text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]} \]

Check: The units (none) are correct. The magnitude of the answer makes physical sense because the pH rose slightly when base was added.

16.48 (a) Given: 100.0 mL buffer 0.175 M HClO and 0.150 M NaClO Find: initial pH

Other: \( K_a \) (HClO) = 2.9 \( \times \) 10\(^{-8} \)

Conceptual Plan: Identify acid and base components then M NaClO \( \to \) M ClO\(^-\) then

\[ \text{M HC}_2\text{H}_3\text{O}_2, \text{ M ClO}^- \to \text{pH} \]

\[ \text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]} \]

Solution: Acid = HClO, so [acid] = [HClO] = 0.175 M. Base = ClO\(^-\). Since 1 ClO\(^-\) ion is generated for each NaClO, [ClO\(^-\)] = 0.150 M ClO\(^-\) = [base].

Then \[ \text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]} = - \log (2.9 \times 10^{-8}) + \log \frac{0.150 M}{0.175 M} = 7.47 \]

Check: The units (none) are correct. The magnitude of the answer makes physical sense because pH is less than the pK\(_a\) of the acid because there is more acid than base.

(b) Given: 100.0 mL buffer 0.175 M HClO and 0.150 M NaClO, add 150.0 mg HBr

Find: pH

Other: \( K_a \) (HClO) = 2.9 \( \times \) 10\(^{-8} \)

Conceptual Plan: Part I: Stoichiometry:

\[ \text{mol NaClO, mol HClO, mol HBr} \to \text{mol NaClO, mol HClO then} \]

set up stoichiometry table
For HI: \(1.5 \text{ g HI} \times \frac{1 \text{ mol HI}}{127.91 \text{ g HI}} = 0.011727 \text{ mol HI}\). Since HI is a strong acid, \([\text{HI}] = [\text{H}^+]\), and set up a table to track changes:

<table>
<thead>
<tr>
<th></th>
<th>Before Addition</th>
<th>Addition</th>
<th>After Addition</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}^+ (aq))</td>
<td>0.00 mol</td>
<td>0.011727 mol</td>
<td>0.00 mol</td>
</tr>
<tr>
<td>(\text{NO}_2^- (aq))</td>
<td>0.145 mol</td>
<td>0.125 mol</td>
<td>0.133 mol</td>
</tr>
</tbody>
</table>

Because the concentrations of the acid and base components have not changed much, the buffer is still able to do its job. Finally, since there is 1.0 L of solution, \([\text{HNO}_2] = 0.14 \text{ M}\) and \([\text{NaNO}_2] = 0.13 \text{ M}\). Check: The units (M) are correct. Since the number of moles added is small compared to the buffer components, the buffer still remains active. Adding acid increases the amount of the conjugate base. Adding base increases the amount of the weak acid.

### Titrations, pH Curves, and Indicators

16.61

(i) The equivalence point of a titration is where the pH rises sharply as base is added. The pH at the equivalence point is the midpoint of the sharp rise at \(-50\) mL added base. For (a) the pH = \(-8\) and for (b) the pH = \(-7\).

(ii) Graph (a) represents a weak acid and graph (b) represents a strong acid. A strong acid titration starts at a lower pH, has a flatter initial region and a sharper rise at the equivalence point than a weak acid. The pH at the equivalence point of a strong acid is neutral, while the pH at the equivalence point of a weak acid is basic.

16.62

**Given:** 25.0 mL 0.100 M HCl and 0.100 M HF titrated with 0.200 M KOH

**Find:** volume of base to reach equivalence point

**Conceptual Plan:** The answer for both titrations will be the same since the initial concentration and volumes of the acids are the same and both acids are monoprotic. Write balanced equation

\[
\begin{align*}
\text{HCl} + \text{KOH} &\rightarrow \text{KCl} + \text{H}_2\text{O} \\
\text{HF} + \text{KOH} &\rightarrow \text{KF} + \text{H}_2\text{O}
\end{align*}
\]

then \(\text{mol acid} \rightarrow \text{mol base} \rightarrow \text{mol KOH}

**Solution:**

\[
\begin{align*}
\frac{25.0 \text{ mL acid}}{1000 \text{ mL}} \times \frac{1 \text{ L}}{1 \text{ mL}} = 0.0250 \text{ L acid then}
\end{align*}
\]

\[
\begin{align*}
0.0250 \times 0.200 = 0.00250 \text{ mol KOH}
\end{align*}
\]

**Check:** The units (mL) are correct. The volume of base is half the volume of acids because the concentration of the base is twice that of the acids. The answer for both titrations is the same because the stoichiometry is the same for both titration reactions.

(b) The pH at the equivalence point will be neutral for HCl (since it is a strong acid) and it will be basic for HF (since it is a weak acid).

(c) The initial pH will be lower for HCl (since it is a strong acid) and so it dissociates completely. The HF (since it is a weak acid) will only partially dissociate and not drop the pH as low as HCl at the same acid concentration.
Chapter 16 Aqueous Ionic Equilibrium

(d) The titration curves will look like the following:

![Graphs showing titration curves for HCl and HF]

Important features to include are a low initial pH (if strong acid pH is 1 and higher for a weak acid), flat initial region (very flat for strong acid, not as flat for weak acid where pH halfway to equivalence point is the $pK_a$ of the acid), sharp rise at equivalence point, pH at equivalence point (neutral for strong acid and higher for weak acid), and then flatten out at high pH.

16.63 Given: 20.0 mL of 0.200 M KOH and 0.200 M CH$_3$NH$_2$ titrated with 0.100 M HI

(a) Find: volume of base to reach equivalence point

Conceptual Plan: The answer for both titrations will be the same since the initial concentration and volumes of the bases are the same. Write balanced equation then mL $\rightarrow$ L then $\text{HI} + \text{KOH} \rightarrow \text{KCl} + \text{H}_2\text{O}$ and $\text{HI} + \text{CH}_3\text{NH}_2 \rightarrow \text{KCl} + \text{H}_2\text{O}$ $\rightarrow$ $\text{L} \rightarrow \text{mol base then set mol base} = \text{mol acid and} \ [\text{HI}]$, \ $\text{mol HI} \rightarrow \text{L} \rightarrow \text{mL HI}$

Solution: $20.0 \text{ mL base} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.0200 \text{ L base then}$

$0.200 \text{ mol base} \times \frac{0.0200 \text{ L base}}{0.00400 \text{ mol}} = 0.00400 \text{ mol base. So mol base} = 0.00400 \text{ mol = mol HI then}$

$0.00400 \text{ mol HI} \times \frac{1 \text{ L HI}}{0.100 \text{ mol HI}} = 0.0400 \text{ L HI} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 40.0 \text{ mL HI for both titrations.}$

Check: The units (mL) are correct. The volume of acid is twice the volume of bases because the concentration of the base is twice that of the acid in each case. The answer for both titrations is the same because the stoichiometry is the same for both titration reactions.

(b) The pH at the equivalence point will be neutral for KOH (since it is a strong base) and it will be acidic for CH$_3$NH$_2$ (since it is a weak base).

(c) The initial pH will be lower for CH$_3$NH$_2$ (since it is a weak base and will only partially dissociate and not raise the pH as high as KOH (since it is a strong base and so it dissociates completely) at the same base concentration.

(d) The titration curves will look like the following:

![Graphs showing titration curves for KOH and CH$_3$NH$_2$]

Important features to include are a high initial pH (if strong base pH is over 13 and lower for a weak base), flat initial region (very flat for strong base, not as flat for weak base where pH halfway to
equivalence point is the $pK_b$ of the base), sharp drop at equivalence point, pH at equivalence point (neutral for strong base and lower for weak base), and then flatten out at low pH.

16.64 (i) The equivalence point of a titration is where the pH drops sharply as acid is added. The pH at the equivalence point is the midpoint of the sharp drop at ~ 25 mL added acid. For (a) the pH = ~ 7 and for (b) the pH = ~ 5.

(ii) Graph (a) represents a strong base and graph (b) represents a weak base. A strong base titration starts at a higher pH, has a flatter initial region and a sharper drop at the equivalence point than a weak base. The pH at the equivalence point of a strong base is neutral, while the pH at the equivalence point of a weak base is acidic.

16.65 (a) The equivalence point of a titration is where the pH rises sharply as base is added. The volume at the equivalence point is ~ 30 mL. The pH at the equivalence point is the midpoint of the sharp rise at ~ 30 mL added base, which is a pH = ~ 9.

(b) At 0 mL the pH is calculated by doing an equilibrium calculation of a weak acid in water (as done in Chapter 15).

(c) The pH one-half way to the equivalence point is equal to the $pK_a$ of the acid, or ~ 15 mL.

(d) The pH at the equivalence point, or ~ 30 mL, is calculated by doing an equilibrium problem with the $K_a$ of the acid. At the equivalence point, all of the acid has been converted to its conjugate base.

(e) Beyond the equivalence point (30 mL) there is excess base. All of the acid has been converted to its conjugate base and so the pH is calculated by focusing on this excess base concentration.

16.66 (a) The equivalence point of a titration is where the pH drops sharply as acid is added. The volume at the equivalence point is ~ 25 mL. The pH at the equivalence point is the midpoint of the sharp drop at ~ 25 mL added acid, which is a pH = ~ 5.

(b) At 0 mL the pH is calculated by doing an equilibrium calculation of a weak base in water (as done in Chapter 15).

(c) The pH one-half way to the equivalence point is equal to the $14 - pK_b = pK_a$ of the base, or ~ 12 mL.

(d) The pH at the equivalence point, or ~ 25 mL, is calculated by doing an equilibrium problem with the $K_a$ of the base. At the equivalence point, all of the base has been converted to its conjugate acid.

(e) Beyond the equivalence point (25 mL) there is excess acid. All of the base has been converted to its conjugate acid and so the pH is calculated by focusing on this excess acid concentration.

Given: 35.0 mL of 0.175 M HBr titrated with 0.200 M KOH

(a) Find: initial pH

Conceptual Plan: Since HBr is a strong acid, it will dissociate completely, so initial pH = $-\log [H_3O^+] = -\log [HBr]$.

Solution: pH = $-\log [HBr] = -\log 0.175 = 0.757$

Check: The units (none) are correct. The pH is reasonable since the concentration is greater than 0.1 M and the acid dissociates completely, the pH is less than 1.

(b) Find: volume of base to reach equivalence point

Conceptual Plan: Write balanced equation then mL $\rightarrow$ L then [HBr], L $\rightarrow$ mol HBr then

\[
\text{balanced equation has 1:1 stoichiometry}
\]

Solution: 35.0 mL HBr $x \frac{1 \text{ L}}{1000 \text{ mL}} = 0.0350 \text{ L HBr then}$

\[
0.175 \text{ mol HBr}  \times 0.0350 \text{ L} = 0.006125 \text{ mol HBr}.
\]
So \( \text{mol acid} = \text{mol HBr} = 0.006125 \text{ mol} = \text{mol KOH} \) then
\[
0.006125 \frac{\text{mol KOH}}{1 \text{ L}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.0030625 \frac{\text{L KOH}}{1 \text{ L}} = 30.6 \text{ mL KOH}.
\]
Check: The units (mL) are correct. The volume of base is a little less than the volume of acid because
the concentration of the base is a little greater than that of the acid.

(c) Find: pH after adding 10.0 mL of base

Conceptual Plan: Use calculations from part b. Then mL \( \rightarrow \) L then [KOH], L \( \rightarrow \) mol KOH then
\[
\frac{1 \text{ L}}{1000 \text{ mL}} = \text{mol KOH}
\]
Set up stoichiometry table

<table>
<thead>
<tr>
<th>L HBr + L KOH = total L</th>
</tr>
</thead>
</table>
\[
\begin{align*}
\text{mol excess HBr} & \rightarrow [\text{HBr}] & \rightarrow \text{pH} \\
M = \text{mol KOH} & \rightarrow \text{L KOH} & = \text{mol KOH}
\end{align*}
\]
Solution: 10.0 mL KOH \( \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.0100 \text{ L KOH} \) then
\[
0.200 \text{ mol KOH} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.200 \text{ mol KOH}.
\]
Since KOH is a strong base, [KOH] = [OH\(^-\)], and set up a table to track changes:

| KOH (aq) + HBr (aq) \( \rightarrow \) KBr (aq) + \( \text{H}_2\text{O} \) (l) |
|-----------------|-----------------|
| Before addition | 0.00 mol        | 0.006125 mol    | 0.00 mol |
| Addition        | 0.00200 mol     | —                | —        |
| After addition  | 0.00 mol        | 0.004125 mol     | 0.00200 mol |
Then 0.0350 L HBr + 0.0100 L KOH = 0.0450 L total volume.
So mol excess acid = mol HBr = 0.004125 mol in 0.0450 L so
\[
0.004125 \text{ mol HBr} \times \frac{1 \text{ L}}{0.0450 \text{ L}} = 0.0916667 \text{ M} \text{ HBr}
\]
\[
\text{pH} = \log [\text{HBr}] = -\log 0.0916667 = 1.038.
\]
Check: The units (none) are correct. The pH is a little higher than the initial pH, which is expected
since this is a strong acid.

(d) Find: pH at equivalence point

Solution: Since this is a strong acid–strong base titration, the pH at the equivalence point is neutral or 7.

(e) Find: pH after adding 5.0 mL of base beyond the equivalence point

Conceptual Plan: Use calculations from parts b & c. Then the pH is only dependent on the amount
of excess base and the total solution volumes.

\[
\frac{1 \text{ L}}{1000 \text{ mL}} = \text{mol KOH}
\]
then L HBr, L KOH to equivalence point, L KOH excess \( \rightarrow \) total L then
\[
\text{mol KOH excess} \rightarrow [\text{KOH}] = [\text{OH}^-] \rightarrow \text{pH}
\]
Solution: 5.0 mL KOH \( \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.0050 \text{ L KOH excess} \) then
\[
0.200 \text{ mol KOH} \times \frac{1 \text{ L}}{0.0050 \text{ L}} = 0.0010 \text{ mol KOH excess} \rightarrow 0.0350 \text{ L HBr} + 0.0306 \text{ L KOH} + 0.0050 \text{ L KOH excess} = 0.0706 \text{ L KOH excess total volume}.
\]
\[
\frac{1 \text{ L}}{0.0706 \text{ L}} = 0.014164 \text{ M KOH excess}
\]
Since KOH is a strong base, [KOH] excess = [OH\(^-\)], \( K_w = [\text{H}_3\text{O}^+] [\text{OH}^-] \) so
\[
[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{7.06 \times 10^{-13}} = 0.014164 \text{ M}. \text{ Finally,}
\]
\[
\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (7.06 \times 10^{-13}) = 12.15.
\]
Chapter 16 Aqueous Ionic Equilibrium

Check: The units (none) are correct. The pH is rising sharply at the equivalence point, so the pH after 5 mL past the equivalence point should be quite basic.

16.68 Given: 20.0 mL of 0.125 M HNO₃ titrated with 0.150 M NaOH
Find: pH at five different points and plot titration curve

Conceptual Plan: Choose points to calculate: (i) initial pH, (ii) pH after 5.0 mL, (iii) pH after 10.0 mL, (iv) pH at equivalence point, and (v) pH after 25.0 mL. Points should be on both sides of the equivalence point.

(i) Since HNO₃ is a strong acid, it will dissociate completely, so initial pH = - log [H₃O⁺] = - log [HNO₃].

Solution: pH = - log [HNO₃] = - log 0.125 = 0.903

Check: The units (none) are correct. The pH is reasonable since the concentration is greater than 0.1 M and the acid dissociates completely; the pH is less than 1.

(ii) Find: pH after adding 5.0 mL of base

Conceptual Plan: Write balanced equation then mL —> L then [HNO₃], L —> mol HNO₃ then

\[ \text{HNO}_3 + \text{NaOH} \rightarrow \text{NaNO}_3 + \text{H}_2\text{O} \]

and L HNO₃, L NaOH —> total L then mol excess HNO₃, L —> [HNO₃] —> pH.

Solution: 20.0 mL HNO₃ \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.0200 \text{ L HNO₃}

0.125 mol HNO₃ \times 0.0200 \text{ L} = 0.00250 \text{ mol HNO₃} and 5.0 mL NaOH \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.0050 \text{ L NaOH}

0.150 mol NaOH \times 0.0050 \text{ L} = 0.00075 \text{ mol NaOH}.

This is a strong acid-strong base titration, so set up a table to track changes:

<table>
<thead>
<tr>
<th>NaOH (aq) + HNO₃ (aq) → NaNO₃ (aq) + H₂O (l)</th>
</tr>
</thead>
</table>

Before addition 0.00 mol 0.00250 mol 0.00 mol

Addition 0.00075 mol

After addition = 0.00 mol 0.00175 mol 0.00075 mol

Then 0.0200 L HNO₃ + 0.0050 L NaOH = 0.0250 L total volume. So mol excess acid = mol HNO₃ = 0.00175 mol in 0.0250 L, so [HNO₃] = \frac{0.00175 \text{ mol}}{0.0250 \text{ L}} = 0.0700 \text{ M and}

pH = - log [HNO₃] = - log 0.0700 = 1.155.

Check: The units (none) are correct. The pH remains very low in a strong acid-strong base titration before the equivalence point.

(iii) Find: pH after adding 10.0 mL of base

Conceptual Plan: Use calculations for point (ii) then mL —> L then [NaOH], L —> mol NaOH then

mol HNO₃, mol NaOH —> mol excess HNO₃ and L HNO₃, L NaOH —> total L then

set up stoichiometry table

<table>
<thead>
<tr>
<th>L HNO₃ + L NaOH —&gt; total L</th>
</tr>
</thead>
</table>

Solution: 10.0 mL NaOH \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.0100 \text{ L NaOH}

0.150 mol NaOH \times 0.0100 \text{ L} = 0.00150 \text{ mol NaOH}. Set up a table to track changes:

<table>
<thead>
<tr>
<th>NaOH (aq) + HNO₃ (aq) → NaNO₃ (aq) + H₂O (l)</th>
</tr>
</thead>
</table>

Before addition 0.00 mol 0.00250 mol 0.00 mol

Addition 0.00075 mol

After addition = 0.00 mol 0.00325 mol 0.00075 mol

Then 0.0200 L HNO₃ + 0.0100 L NaOH = 0.0300 L total volume. So mol excess acid = mol HNO₃ = 0.000175 mol in 0.0300 L, so [HNO₃] = \frac{0.000175 \text{ mol}}{0.0300 \text{ L}} = 0.000583 M and
Chapter 16 Aqueous Ionic Equilibrium

(a) For HF, the $K_a = 3.5 \times 10^{-4}$ and so the above equation approximates the pH at the equivalence point of $\approx 8.0$. Looking at Table 16.1, phenol red or m-nitrophenol will change at the appropriate pH range.

(b) For HCl, the pH at the equivalence point is 7, since HCl is a strong acid. Looking at Table 16.1, alizarin, bromthymol blue, or phenol red will change at the appropriate pH range.

(c) For HCN, the $K_a = 4.9 \times 10^{-10}$ and so the above equation approximates the pH at the equivalence point of $\approx 11.0$. Looking at Table 16.1, alizarin yellow R will change at the appropriate pH range.

16.84 Since the exact conditions of the titration are not given, a rough calculation will suffice. Looking at the pattern of earlier problems, the pH at the equivalence point of a titration of a weak base and a strong acid is the hydrolysis of the conjugate acid of the weak base that has been diluted by a factor of roughly 2 with acid. If it is assumed that the initial concentration of the weak base is $\approx 0.1$ M, then the conjugate acid concentration will be $\approx 0.05$ M. From earlier calculations it can be seen that the $K_a = \frac{[H_3O^+]}{K_b}$ thus $[H_3O^+] = \frac{0.05 K_w}{K_b} = \sqrt{5 \times 10^{-16}}$ and the pH = $-\log \sqrt{5 \times 10^{-16}}$.

(a) For CH$_3$NH$_2$, the $K_b = 4.4 \times 10^{-10}$ and so the above equation approximates the pH at the equivalence point of $\approx 6.0$. Looking at Table 16.1, methyl red, Eriochrome Black T, bromocresol purple, alizarin or bromthymol blue will change at the appropriate pH range.

For NaOH, the pH at the equivalence point is 7, since NaOH is a strong base. Looking at Table 16.1, alizarin, bromthymol blue, or phenol red will change at the appropriate pH range.

(c) For C$_6$H$_5$NH$_2$, the $K_b = 3.9 \times 10^{-10}$ and so the above equation approximates the pH at the equivalence point of $\approx 2.9$. Looking at Table 16.1, erythrosin B or 2,4-dinitrophenol will change at the appropriate pH range.

Solubility Equilibria

For the dissolution reaction, start with the ionic compound as a solid and put it in equilibrium with the appropriate cation and anion, making sure to include the appropriate stoichiometric coefficients. The $K_{sp}$ expression is the product of the concentrations of the cation and anion concentrations raised to the stoichiometric coefficients.

(a) $\text{BaSO}_4(s) \rightleftharpoons \text{Ba}^{2+} + \text{SO}_4^{2-}$ and $K_{sp} = [\text{Ba}^{2+}] [\text{SO}_4^{2-}]$.

(b) $\text{PbBr}_2(s) \rightleftharpoons \text{Pb}^{2+} + 2\text{Br}^-$ and $K_{sp} = [\text{Pb}^{2+}] [\text{Br}^-]^2$.

(c) $\text{Ag}_2\text{CrO}_4(s) \rightleftharpoons 2\text{Ag}^+ + \text{CrO}_4^{2-}$ and $K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$.

16.86 For the dissolution reaction, start with the ionic compound as a solid and put it in equilibrium with the appropriate cation and anion, making sure to include the appropriate stoichiometric coefficients. The $K_{sp}$ expression is the product of the concentrations of the cation and anion concentrations raised to their stoichiometric coefficients.

(a) $\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$ and $K_{sp} = [\text{Ca}^{2+}] [\text{CO}_3^{2-}]$.

(b) $\text{PbCl}_2(s) \rightleftharpoons \text{Pb}^{2+} + 2\text{Cl}^-$ and $K_{sp} = [\text{Pb}^{2+}] [\text{Cl}^-]^2$.

(c) $\text{AgI(s)} \rightleftharpoons \text{Ag}^+ + \text{I}^-$ and $K_{sp} = [\text{Ag}^+] [\text{I}^-]$.

16.87 Given: ionic compound formula and Table 16.2 of $K_{sp}$ values. Find: molar solubility ($S$)

Conceptual Plan: The expression of the solubility product constant of $A_mX_n$ is $K_{sp} = [A^{m+}]^m [X^{n-}]^n$. The molar solubility of a compound, $A_mX_n$, can be computed directly from $K_{sp}$ by solving for $S$ in the expression $K_{sp} = (mS)^m (nS)^n = m^n n^m S^{m+n}$.

Solution:

(a) For AgBr, $K_{sp} = 5.35 \times 10^{-13}$, $A = \text{Ag}^+$, $m = 1$, $X = \text{Br}^-$, and $n = 1$ so $K_{sp} = 5.35 \times 10^{-13} = S^2$. Rearrange to solve for $S$. $S = \sqrt{5.35 \times 10^{-13}} = 7.31 \times 10^{-7}$ M.
The molar solubility of a compound, $A$, can be computed directly from $K_{sp}$ by solving for $S$ in the equation:

$$K_{sp} = S^{m+n}$$

Rearrange to solve for $S$. $S = \sqrt[m+n]{\frac{K_{sp}}{m+n}}$

Example: For $\text{BaCrO}_4$, $K_{sp} = 1.46 \times 10^{-10}$, $A = \text{CrO}_4^{2-}$, $m = 1$, $X = \text{CrO}_4^{2-}$, and $n = 2$ so $K_{sp} = 1.46 \times 10^{-10} = 2^2S^3$. Rearrange to solve for $S$. $S = \sqrt[2+3]{\frac{1.46 \times 10^{-10}}{2+3}} = 3.32 \times 10^{-4} \text{ M}$.

Check: The units (M) are correct. The molar solubilities are much less than one and dependent not only on the value of the $K_{sp}$, but also the stoichiometry of the ionic compound. The more ions that are generated, the greater the molar solubility for the same value of the $K_{sp}$.

**Example:**

- **For $\text{BaCrO}_4$, $K_{sp} = 1.46 \times 10^{-10}$, $A = \text{CrO}_4^{2-}$, $m = 1$, $X = \text{CrO}_4^{2-}$, and $n = 2$ so $K_{sp} = 1.46 \times 10^{-10} = 2^2S^3$. Rearrange to solve for $S$. $S = \sqrt[2+3]{\frac{1.46 \times 10^{-10}}{2+3}} = 3.32 \times 10^{-4} \text{ M}$.**
- **For $\text{CaF}_2$, $K_{sp} = 1.12 \times 10^{-12}$, $A = \text{Ag}^+$, $m = 2$, $X = \text{CrO}_4^{2-}$, and $n = 1$ so $K_{sp} = 1.12 \times 10^{-12} = 2^2S^3$. Rearrange to solve for $S$. $S = \sqrt[2+3]{\frac{1.12 \times 10^{-12}}{2+3}} = 6.54 \times 10^{-5} \text{ M}$.**
- **For $\text{Ca(OH)}_2$, $K_{sp} = 4.68 \times 10^{-6}$, $A = \text{Ca}^{2+}$, $m = 1$, $X = \text{OH}^-$, and $n = 2$ so $K_{sp} = 4.68 \times 10^{-6} = 2^2S^3$. Rearrange to solve for $S$. $S = \sqrt[2+3]{\frac{4.68 \times 10^{-6}}{2+3}} = 1.05 \times 10^{-2} \text{ M}$.**

**Given:** ionic compound formula and Table 16.2 of $K_{sp}$ values. Find: molar solubility ($S$)

**Conceptual Plan:** The expression of the solubility product constant of $A_nX_m$ is $K_{sp} = [A^{\text{ions}}]^m[X^{\text{ions}}]^{-n}$.

**Check:** The units (M) are correct. The molar solubilities are much less than one and dependent not only on the value of the $K_{sp}$, but also the stoichiometry of the ionic compound. The more ions that are generated, the greater the molar solubility for the same value of the $K_{sp}$.

**Chapter 16 Aqueous Ionic Equilibrium**

**Example:**

- **For $\text{Mg(OH)}_2$, $K_{sp} = 2.06 \times 10^{-13}$, $A = \text{Mg}^{2+}$, $m = 1$, $X = \text{OH}^-$, and $n = 2$ so $K_{sp} = 2.06 \times 10^{-13} = 2^2S^3$. Rearrange to solve for $S$. $S = \sqrt[2+3]{\frac{2.06 \times 10^{-13}}{2+3}} = 3.72 \times 10^{-5} \text{ M}$.**
- **For $\text{CaF}_2$, $K_{sp} = 1.17 \times 10^{-3}$, $A = \text{Ca}^{2+}$, $m = 1$, $X = \text{F}^-$, and $n = 2$ so $K_{sp} = 1.17 \times 10^{-3} = 2^2S^3$. Rearrange to solve for $S$. $S = \sqrt[2+3]{\frac{1.17 \times 10^{-3}}{2+3}} = 3.92 \times 10^{-2} \text{ M}$.**
- **For $\text{PbF}_2$, $S = 2.06 \times 10^{-13}$, $A = \text{Pb}^{2+}$, $m = 1$, $X = \text{F}^-$, and $n = 2$ so $K_{sp} = 2.06 \times 10^{-13} = 2^2S^3$. Rearrange to solve for $S$. $S = \sqrt[2+3]{\frac{2.06 \times 10^{-13}}{2+3}} = 3.12 \times 10^{-5} \text{ M}$.**

**Check:** The units (M) are correct. The molar solubilities are much less than one and dependent not only on the value of the $K_{sp}$, but also the stoichiometry of the ionic compound. The more ions that are generated, the greater the molar solubility for the same value of the $K_{sp}$.
The molar solubility of a compound, \( A_m X_n \), can be computed directly from \( K_{sp} \) by solving for \( S \) in the expression:

\[
K_{sp} = (mS)^m \cdot (nS)^n.
\]

Solution: \( MX \), \( K_{sp} = 1.27 \times 10^{-36} \), \( A = M^{2+} \), \( m = 1 \), \( X = X^2^- \), and \( n = 1 \). There is a 1:1 ratio of the cation:anion, so \( K_{sp} = 1.27 \times 10^{-36} = S^2 \). Rearrange to solve for \( S \). \( S = 1.13 \times 10^{-18} M \).

(b) Given: \( MX \) Find: molar solubility \( S \) in 0.25 M \( MC_1 \)

Other: \( K_{sp} (MX) = 1.27 \times 10^{-36} \)

Conceptual Plan: \( M C_1 \rightarrow M^{2+} \) then \( M^{2+}, K_{sp} \rightarrow S \)

Solution: Since 1 \( M^{2+} \) ion is generated for each \( MC_1 \), \( [M^{2+}] = 0.25 M \).

\[
\begin{align*}
\text{Initial} & \quad 0.25 & 0.00 \\
\text{Change} & \quad S & S \\
\text{Equil} & \quad 0.25 + S & S \\
\end{align*}
\]

Assume \( S \ll 0.25 \), \( 1.27 \times 10^{-36} = (0.25 + S)S \), and \( S = 5.08 \times 10^{-36} M \). Confirm that the assumption is valid.

\[
S = 5.08 \times 10^{-36} M, \\
5.08 \times 10^{-36} \left(\frac{100\%}{100}\right) = 5.08 \times 10^{-35} \%
\]

so the assumption is valid.

(c) Given: \( MX \) Find: molar solubility \( S \) in 0.20 M \( NaX \)

Other: \( K_{sp} (MX) = 1.27 \times 10^{-36} \)

Conceptual Plan: \( M NaX \rightarrow M X^2^- \) then \( M X^2^- \), \( K_{sp} \rightarrow S \)

Solution: Since 1 \( X^2^- \) ion is generated for each \( NaX \), \( [X^2^-] = 0.20 M \).

\[
\begin{align*}
\text{Initial} & \quad 0.00 & 0.20 \\
\text{Change} & \quad S & S \\
\text{Equil} & \quad 0.20 + S & S \\
\end{align*}
\]

Assume \( S \ll 0.20 \), \( 1.27 \times 10^{-36} = (0.20 + S)S \), and \( S = 6.35 \times 10^{-36} M \). Confirm that the assumption is valid.

\[
S = 6.35 \times 10^{-36} M, \\
6.35 \times 10^{-36} \left(\frac{100\%}{100}\right) = 6.35 \times 10^{-35} \%
\]

so the assumption is valid.

Check: The units (M) are correct. The solubility of the MX decreases in the presence of a common ion.

Given: \( Ca(OH)_2 \) Find: molar solubility \( S \) in buffers at a) pH = 4, b) pH = 7, and c) pH = 9

Other: \( K_{sp} (Ca(OH)_2) = 4.68 \times 10^{-6} \)

Conceptual Plan: pH \( \rightarrow \) \( [H_3O^+] \rightarrow [OH^-] \) then \( M OH, K_{sp} \rightarrow S \)

Solution:

(a) pH = 4, so \( [H_3O^+] = 10^{-pH} = 10^{-4} = 1 \times 10^{-4} M \) then \( K_w = [H_3O^+] [OH^-] \) so\n
\[
\begin{align*}
[OH^-] & = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{10^{-4}} = 1 \times 10^{-10} M \\
\text{Initial} & \quad 0.00 & 1 \times 10^{-10} \\
\text{Change} & \quad S & \quad \text{S} \\
\text{Equil} & \quad 1 \times 10^{-10} & \quad 1 \times 10^{-10}
\end{align*}
\]

\( K_{sp} (Ca(OH)_2) = [Ca^{2+}] [OH^-] = 4.68 \times 10^{-6} = S (1 \times 10^{-10})^2 \) and \( S = 5 \times 10^{14} M \).

(b) pH = 7, so \( [H_3O^+] = 10^{-pH} = 10^{-7} = 1 \times 10^{-7} M \) then \( K_w = [H_3O^+] [OH^-] \) so\n
\[
\begin{align*}
[OH^-] & = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{10^{-7}} = 1 \times 10^{-7} M \\
\text{Initial} & \quad 0.00 & 1 \times 10^{-7} \\
\text{Change} & \quad S & \quad \text{S} \\
\text{Equil} & \quad 1 \times 10^{-7} & \quad 1 \times 10^{-7}
\end{align*}
\]

\( K_{sp} (Ca(OH)_2) = [Ca^{2+}] [OH^-] = 4.68 \times 10^{-6} = S (1 \times 10^{-7})^2 \) and \( S = 5 \times 10^6 M \).
(c) pH = 9, so \([H_3O^+] = 10^{-pH} = 10^{-9} = 1 \times 10^{-9} \text{ M}\) then \(K_w = [H_3O^+] \cdot [OH^-]\) so

\[
\begin{array}{c|c|c}
\text{Ca(OH)}_2 (s) & \rightarrow & \text{Ca}^{2+} (aq) + 2 \text{OH}^- (aq) \\
\hline
\text{Initial} & 0.00 & 1 \times 10^{-5} \\
\text{Change} & S & - \\
\text{Equil} & S & 1 \times 10^{-5} \\
\end{array}
\]

\[K_w (\text{Ca(OH)}_2) = [\text{Ca}^{2+}] [OH^-]^2 = 4.68 \times 10^{-6} = S (1 \times 10^{-5})^2, \text{ and } S = 5 \times 10^4 \text{ M}.
\]

Check: The units (M) are correct. The solubility of the Ca(OH)_2 decreases as the pH increases (and the hydroxide ion concentration increases). Realize that these molar solubilities are not achievable because the saturation point of pure Ca(OH)_2 is ~ 30 M. The bottom line is that as long as the hydroxide ion concentration can be controlled with a buffer, the Ca(OH)_2 will be very soluble.

16.98 Given: \(\text{Mg(OH)}_2\) in 1.00 \times 10^{-2} \text{ mL solution}

Find: grams of \(\text{Mg(OH)}_2\) in pure water and buffer at pH = 10

Other: \(K_{sp} (\text{Mg(OH)}_2) = 2.06 \times 10^{-13}\)

Conceptual Plan: For pure water:

The expression of the solubility product constant of \(A_mX_n\) is

\[K_{sp} = [A_n^+][X_m^-].\]

The molar solubility of a compound, \(A_mX_n\), can be computed directly from \(K_{sp}\) by solving for \(S\) in the expression

\[K_{sp} = (mS)^m (nS)^n = m^n n^m S^{m+n}.\]

Then \(ml \rightarrow L\) then \(S, L \rightarrow \text{mol Mg(OH)}_2 \rightarrow \text{g Mg(OH)}_2\).

For buffer solution: pH \(\rightarrow [H_3O^+] \rightarrow [OH^-]\) then

\[\frac{\text{mol}}{1 \text{L}} \times \frac{58.33 \text{ g Mg(OH)}_2}{1 \text{ mol Mg(OH)}_2} = \frac{\text{g Mg(OH)}_2}{1 \text{L}}\]

Check: The units (M) are correct. The solubility of the \(\text{Mg(OH)}_2\) decreases as the pH increases (and the hydroxide ion concentration increases).

16.99 (a) \(\text{BaCO}_3\) will be more soluble in acidic solutions because \(\text{CO}_3^{2-}\) is basic. In acidic solutions it can be converted to \(\text{HCO}_3^-\) and \(\text{H}_2\text{CO}_3^2^-\). These species are not \(\text{CO}_3^{2-}\) so they do not appear in the \(K_{sp}\) expression.

(b) \(\text{CuS}\) will be more soluble in acidic solutions because \(\text{S}^2^-\) is basic. In acidic solutions it can be converted to \(\text{HS}^-\) and \(\text{H}_2\text{S}^2^-\). These species are not \(\text{S}^2^-\) so they do not appear in the \(K_{sp}\) expression.

(c) \(\text{AgCl}\) will not be more soluble in acidic solutions because \(\text{Cl}^-\) will not react with acidic solutions, because \(\text{HCl}\) is a strong acid.
16.103 Given: 75.0 mL of NaOH with pOH = 2.58 and 125.0 mL of 0.0018 M MgCl₂
Find: Will a precipitate form?

(d) PbI₂ will not be more soluble in acidic solutions because I⁻ will not react with acidic solutions, because HI is a strong acid.

16.100 (a) Hg₂Br₂ will not be more soluble in acidic solutions because Br⁻ will not react with acidic solutions, because HBr is a strong acid.
(b) Mg(OH)₂ will be more soluble in acidic solutions because OH⁻ is basic. In acidic solutions it can be converted to H₂O. This species is not OH⁻ and so it does not appear in the Ksp expression.
(c) CaCO₃ will be more soluble in acidic solutions because CO₃²⁻ is basic. In acidic solutions it can be converted to HCO₃⁻ and H₂CO₃. These species are not CO₃²⁻ so they do not appear in the Ksp expression.
(d) AgI will not be more soluble in acidic solutions because I⁻ will not react with acidic solutions, because HI is a strong acid.

Precipitation and Qualitative Analysis

16.107 Given: 0.015 M NaF and 0.010 M Ca(NO₃)₂
Find: Will a precipitate form? If so, identify it.

Other: Ksp [CaF₂] = 1.46 x 10⁻¹⁰

Conceptual Plan: Look at all possible combinations and consider the solubility rules from Chapter 4. Salts of alkali metals (Na) are very soluble, so NaF and NaNO₃ will be very soluble. Nitrate compounds are very soluble so NaNO₃ will be very soluble. The only possibility for a precipitate is CaF₂. Determine if a precipitate will form by determining the concentration of the Ca²⁺ and F⁻ in solution. Then compute the reaction quotient, Q. If Q > Ksp then a precipitate will form.

Solution: Since the only possible precipitate is CaF₂, calculate the concentrations of Ca²⁺ and F⁻. NaF (s) → Na⁺ (aq) + F⁻ (aq). Since 1 F⁻ ion is generated for each NaF, [F⁻] = 0.015 M.
Ca(NO₃)₂ (s) → Ca²⁺ (aq) + 2 NO₃⁻ (aq). Since 1 Ca²⁺ ion is generated for each Ca(NO₃)₂, [Ca²⁺] = 0.010 M.
Then calculate Q (CaF₂) = [Ca²⁺] [F⁻]² = (0.010) (0.015)² = 2.3 x 10⁻⁶ > 1.46 x 10⁻¹⁰ = Ksp (CaF₂), so a precipitate will form.

Check: The units (none) are correct. The solubility of the CaF₂ is low, and the concentration of ions are extremely large compared to the Ksp, so a precipitate will form.

16.102 Given: 0.013 M KBr and 0.0035 M Pb(C₂H₃O₂)₂
Find: Will a precipitate form? If so, identify it.

Other: Ksp (PbBr₂) = 4.67 x 10⁻⁶

Conceptual Plan: Look at all possible combinations and consider the solubility rules from Chapter 4. Salts of alkali metals (K) are very soluble, so KBr and KC₂H₃O₂ will be very soluble. Acetate compounds are very soluble so Pb(C₂H₃O₂)₂ and KC₂H₃O₂ will be very soluble. The only possibility for a precipitate is PbBr₂. Determine if a precipitate will form by determining the concentration of the Pb²⁺ and Br⁻ in solution. Then compute the reaction quotient, Q. If Q > Ksp then a precipitate will form.

Solution: Since the only possible precipitate is PbBr₂, calculate the concentrations of Pb²⁺ and Br⁻. KBr (s) → K⁺ (aq) + Br⁻ (aq). Since 1 Br⁻ ion is generated for each KBr, [Br⁻] = 0.013 M. Pb(C₂H₃O₂)₂ (s) → Pb²⁺ (aq) + 2 C₂H₃O₂⁻ (aq). Since 1 Pb²⁺ ion is generated for each Pb(C₂H₃O₂)₂, [Pb²⁺] = 0.0035 M. Then calculate Q (PbBr₂) = [Pb²⁺] [Br⁻] = (0.013)(0.0035) = 6.0 x 10⁻⁶ < 4.67 x 10⁻⁶ = Ksp (PbBr₂), so a precipitate will not form.

Check: The units (none) are correct. The Ksp of the PbBr₂ is not too low compared to the solution ion concentrations, so a precipitate will not form.

16.103 Given: 75.0 mL of NaOH with pOH = 2.58 and 125.0 mL of 0.0018 M MgCl₂
Find: Will a precipitate form?

If so, identify it. Other: Ksp (Mg(OH)₂) = 2.06 x 10⁻¹¹

Conceptual Plan: Look at all possible combinations and consider the solubility rules from Chapter 4. Salts of alkali metals (Na) are very soluble, so NaOH and NaCl will be very soluble. Chloride compounds are generally very soluble so MgCl₂ and NaCl will be very soluble. The only possibility for a precipitate is Mg(OH)₂. Determine if a precipitate will form by determining the concentration of the Mg²⁺ and OH⁻ in solution. Since pH, not NaOH concentration, is given pOH → [OH⁻] then [OH⁻] = 10⁻¹⁰
Given: KOH as precipitation agent in a) 0.015 M CaCl\textsubscript{2},
and c) 0.0018 M MgBr\textsubscript{2}.
b) 0.0025 M Fe(NO\textsubscript{3})\textsubscript{2}.

Find: concentration of KOH necessary to form a precipitate.

Solution:
Since the only possible precipitate is Mg(OH)\textsubscript{2}, calculate the concentrations of Mg\textsuperscript{2+} and OH\textsuperscript{-}.

For NaOH at pOH = 2.58, so \[\text{[OH}^-\text{]} = 10^{-2.58} = 2.63027 \times 10^{-3}\text{ M}\] and
MgCl\textsubscript{2} (s) \rightarrow Mg\textsuperscript{2+} (aq) + 2 Cl\textsuperscript{-} (aq). Since 1 Mg\textsuperscript{2+} ion is generated for each MgCl\textsubscript{2}, \text{[Mg}^2\text{]} = 0.0018 M.

Then total mL = mL NaOH + mL MgCl\textsubscript{2} = 75.0 mL + 125.0 mL = 200.0 mL. Then \(M_1 = \frac{V_1}{V_2}\).

\[M_2 = \frac{M_1 V_1}{V_2} = \frac{0.0018 \text{ M Mg}^2\text{+} \times 125.0 \text{ mL}}{200.0 \text{ mL}} = 0.018 \text{ M KOH}\.

Check: The units (none) are correct. The solubility of the Mg(OH)\textsubscript{2} is low, and the NaOH (a base) is high enough that the product of the concentration of ions is large compared to the \(K\text{sp}\), so a precipitate will form.

16.104
Given: 175.0 mL of 0.0055 M KCl and 145.0 mL of 0.0015 M AgNO\textsubscript{3}.
Find: Will a precipitate form? If so, identify it. Other: \(K\text{sp} (\text{AgCl}) = 1.77 \times 10^{-10}\).

Conceptual Plan: Look at all possible combinations and consider the solubility rules from Chapter 4.

Salts of alkali metals (K) are very soluble, so KCl and KNO\textsubscript{3} will be very soluble. Nitrate compounds are very soluble so KNO\textsubscript{3} and Ag NO\textsubscript{3} will be very soluble. The only possibility for a precipitate is AgCl.

Determine if a precipitate will form by determining the concentration of the Ag\textsuperscript{+} and Cl\textsuperscript{-} in solution.

Mix solutions and calculate diluted concentrations mL KCl, mL AgNO\textsubscript{3} \rightarrow mL total then

\[\text{ml KCl} + \text{ml AgNO}_3 = \text{ml total}\]

\[M_1 = \frac{V_1}{V_2}\]

Solution: Since the only possible precipitate is AgCl, calculate the concentrations of Ag\textsuperscript{+} and Cl\textsuperscript{-}.

KCl (s) \rightarrow K\textsuperscript{+} (aq) + Cl\textsuperscript{-} (aq). Since 1 Cl\textsuperscript{-} ion is generated for each AgCl, \text{[Cl}^-\text{]} = 0.0055 M and AgNO\textsubscript{3} (s) \rightarrow Ag\textsuperscript{+} (aq) + NO\textsubscript{3}^- (aq). Since 1 Ag\textsuperscript{+} ion is generated for each AgNO\textsubscript{3}, \text{[Ag}^+\text{]} = 0.0015 M.

Then total mL = mL KCl + mL AgNO\textsubscript{3} = 175.0 mL + 145.0 mL = 320.0 mL. Then \(M_1 = \frac{V_1}{V_2}\).

\[M_2 = \frac{M_1 V_1}{V_2} = \frac{0.0055 \text{ M Cl}^- \times 175.0 \text{ mL}}{320.0 \text{ mL}} = 0.00300781 \text{ M Cl}^-\text{ of KCl}\] and
\[M_2 = \frac{M_1 V_1}{V_2} = \frac{0.0015 \text{ M Ag}^+ \times 145.0 \text{ mL}}{320.0 \text{ mL}} = 0.00067969 \text{ M Ag}^+\text{ of AgNO}_3.

Calculate Q (AgCl), \(A = Ag^+\), \(n = 1, X = Cl^-\), and \(m = 2\). Since \(Q = [A^n]^+ [X^m]^- = (1.125 \times 10^{-3})(9.8635 \times 10^{-6})^2 = 1.1 \times 10^{-9} > 2.06 \times 10^{-13} = K\text{sp} (\text{AgCl})\), so a precipitate will form.

Check: The units (none) are correct. The solubility of the AgCl is low, and the product of the concentration of ions is high enough that the product of the concentration of ions is very large compared to the \(K\text{sp}\), so a precipitate will form.

16.105
Given: KOH as precipitation agent in a) 0.015 M CaCl\textsubscript{2}, b) 0.0025 M Fe(NO\textsubscript{3})\textsubscript{2}, and c) 0.0018 M MgBr\textsubscript{2}.
Find: concentration of KOH necessary to form a precipitate.

Other: \(K\text{sp} (\text{Ca(OH})_2) = 4.68 \times 10^{-6}\), \(K\text{sp} (\text{Fe(OH})_2) = 4.87 \times 10^{-17}\), \(K\text{sp} (\text{Mg(OH})_2) = 2.06 \times 10^{-13}\)

Conceptual Plan: The solubility rules from Chapter 4 state that most hydroxides are insoluble, so all precipitates will be hydroxides. Determine the concentration of the cation in solution. Since all metals have an oxidation state of +2 and [OH\textsuperscript{-} = K\text{OH}], all of the \(K\text{sp} = [\text{cation}] [\text{KOH}]^2\) and so \([\text{KOH}] = \sqrt{\frac{K\text{sp}}{[\text{cation}]}\] (solution).

Solution:
(a) CaCl\textsubscript{2} (s) \rightarrow Ca\textsuperscript{2+} (aq) + 2 Cl\textsuperscript{-} (aq). Since 1 Ca\textsuperscript{2+} ion is generated for each CaCl\textsubscript{2}, \text{[Ca}^{2+}\text{]} = 0.015 M.

Then \([\text{KOH}] = \sqrt{\frac{K\text{sp}}{[\text{cation}]} = \sqrt{4.68 \times 10^{-6} \times \frac{0.015}{0.015}} = 0.018 \text{ M KOH}.\]
Given: solution with 0.010 M Ba\(^{2+}\) and 0.020 M Ca\(^{2+}\) to form precipitates

\[
16.106 \text{ Given: solution and precipitation agent pairs a) } 0.035 \text{ M Ba(NO}_3\text{)}_2: \text{NaF, b) } 0.085 \text{ M CaI}_2: \text{K}_2\text{SO}_4, \text{ and c) } 0.0018 \text{ M CaBr}_2: \text{RbCl} \]

Conceptual Plan: Determine the concentration of the cation in solution. The solubility product constant \((K_{sp})\) is the equilibrium expression for a chemical equation representing the dissolution of an ionic compound. The expression of the solubility product constant of \(A_mX_n\) is \(K_{sp} = [A^{m+}]^m[\ X^{n-}]^n\). Substitute in concentration of cation and solve for concentration of anion.

Solution:

(a) The precipitate is \(\text{BaF}_2\). \(\text{Ba(NO}_3\text{)}_2(s) \rightarrow \text{Ba}^{2+}(aq) + 2 \text{NO}_3^- (aq)\). Since 1 \(\text{Ba}^{2+}\) ion is generated for each \(\text{Ba(NO}_3\text{)}_2\), \(A = \text{Ba}^{2+}, m = 1, X = \text{F}\), and \(n = 2\) since \(K_{sp} = [\text{Ba}^{2+}]^1[\text{F}^-]^2\), then \(K_{sp}(\text{BaF}_2) = 2.45 \times 10^{-5}\). Solve for \([\text{F}^-]\). \([\text{F}^-] = 0.026 \text{ M}\). Since \(\text{NaF}(s) \rightarrow \text{Na}^+(aq) + \text{F}^-(aq)\), 1 \(\text{F}^-\) ion is generated for each \(\text{NaF}\); \([\text{NaF}] = 0.026 \text{ M}\). NaF.

(b) The precipitate is \(\text{CaSO}_4\). \(\text{CaCl}_2(s) \rightarrow \text{Ca}^{2+}(aq) + 2 \text{Cl}^- (aq)\). Since 1 \(\text{Ca}^{2+}\) ion is generated for each \(\text{CaCl}_2\), \([\text{Ca}^{2+}] = 0.085 \text{ M}\). Then derive expression for \(K_{sp}(\text{CaSO}_4)\), \(A = \text{Ca}^{2+}, m = 1, X = \text{SO}_4^{2-}\), and \(n = 1\) since \(K_{sp} = [\text{Ca}^{2+}]^1[\text{SO}_4^{2-}]^1\), then \(K_{sp}(\text{CaSO}_4) = 7.10 \times 10^{-5}\). Solve for \([\text{SO}_4^{2-}]\). \([\text{SO}_4^{2-}] = 0.0085 \text{ M}\). Since \(\text{K}_2\text{SO}_4(s) \rightarrow 2 \text{K}^+(aq) + \text{SO}_4^{2-}(aq)\), 1 \(\text{SO}_4^{2-}\) ion is generated for each \(\text{K}_2\text{SO}_4\); \([\text{K}_2\text{SO}_4] = 0.00084 \text{ M}\). K\text{SO}_4.

(c) The precipitate is \(\text{AgCl}\). \(\text{AgNO}_3(s) \rightarrow \text{Ag}^+(aq) + \text{NO}_3^- (aq)\). Since 1 \(\text{NO}_3^-\) ion is generated for each \(\text{AgNO}_3\), \([\text{Ag}^+] = 0.0018 \text{ M}\). Then derive expression for \(K_{sp}(\text{AgCl})\), \(A = \text{Ag}^+, m = 1, X = \text{Cl}\), and \(n = 1\) since \(K_{sp} = [\text{Ag}^+]^1[\text{Cl}]^1\), then \(K_{sp}(\text{AgCl}) = 1.77 \times 10^{-10}\). Solve for \([\text{Cl}^-]\). \([\text{Cl}^-] = 0.0018 \text{ M}\). Since \(\text{RbCl}(s) \rightarrow \text{Rb}^+(aq) + \text{Cl}^- (aq)\), 1 \(\text{Cl}^-\) ion is generated for each \(\text{RbCl}\); \([\text{RbCl}] = 9.8 \times 10^{-8} \text{ M}\). RbCl.

Check: The units (none) are correct. Comparing part (a) and part (b) the effect of the stoichiometry of the precipitate is seen and the concentration of the precipitation agent is much lower. Looking at part (c) the concentration of the precipitation agent is so low because the \(K_{sp}\) is so small.

16.107 Given: solution with 0.010 M \(\text{Ba}^{2+}\) and 0.020 M \(\text{Ca}^{2+}\) to form precipitates

Find: (a) which ion precipitates first and minimum \([\text{Na}_2\text{SO}_4]\) needed; and (b) [first cation] when second cation precipitates

Other: \(K_{sp}(\text{BaSO}_4) = 1.07 \times 10^{-10}\), \(K_{sp}(\text{CaSO}_4) = 7.10 \times 10^{-5}\)

Conceptual Plan: (a) The precipitates that will form are \(\text{BaSO}_4\) and \(\text{CaSO}_4\). Use the equation derived in Problem 19 to define \(K_{sp}\). Substitute in concentration of cation and solve for concentration of anion to form precipitate. The cation with the lower anion concentration will precipitate first.

(b) Substitute the higher anion concentration into the \(K_{sp}\) expression for the first cation to precipitate and calculate the amount of this first cation to remain in solution.

Solution:

(a) Derive expression for \(K_{sp}(\text{BaSO}_4)\), \(A = \text{Ba}^{2+}, m = 1, X = \text{SO}_4^{2-}\), and \(n = 1\) since \(K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]\), then \(K_{sp}(\text{BaSO}_4) = 1.07 \times 10^{-10}\). Solve for \([\text{SO}_4^{2-}]\). \([\text{SO}_4^{2-}] = 0.010 \text{ M}\). Since \(\text{Na}_2\text{SO}_4(s) \rightarrow 2 \text{Na}^+(aq) + \text{SO}_4^{2-}(aq)\), 1 \(\text{SO}_4^{2-}\) ion is generated for each \(\text{Na}_2\text{SO}_4\); \([\text{Na}_2\text{SO}_4] = 1.1 \times 10^{-8} \text{ M}\) to precipitate \(\text{BaSO}_4\). Derive expression for \(K_{sp}(\text{CaSO}_4)\), \(A = \text{Ca}^{2+}, m = 1, X = \text{SO}_4^{2-}\), and \(n = 1\) since \(K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}]\), then \(K_{sp}(\text{CaSO}_4) = 7.10 \times 10^{-5}\). Solve for \([\text{SO}_4^{2-}]\).
[SO$_4^{2-}$] = 0.0036 M SO$_4^{2-}$ = 0.0036 M Na$_2$SO$_4$ = [Na$_2$SO$_4$] to precipitate CaSO$_4$. Since 1.1 x $10^{-8}$ M Na$_2$SO$_4$ < < 0.0036 M Na$_2$SO$_4$, the Ba$^{2+}$ will precipitate first.

(b) Since Ca$^{2+}$ will not precipitate until [Na$_2$SO$_4$] = 0.00355 M Na$_2$SO$_4$, substitute this value into the $K_{sp}$ expression for BaSO$_4$. So $K_{sp}$ (BaSO$_4$) = [Ba$^{2+}$] [SO$_4^{2-}$] = 1.07 x $10^{-10}$ = [Ba$^{2+}$] = 0.0035. Solve for [Ba$^{2+}$] = 3.0 x $10^{-8}$ M Ba$^{2+}$.

Check: The units (none, M, and M) are correct. Comparing the two $K_{sp}$ values, it can be seen that the Ba$^{2+}$ will precipitate first since the solubility product is so much lower. Since the $K_{sp}$ value is so low, the concentration of precipitating agent is very low. Since the Ca$_2$SO$_4$ $K_{sp}$ value is so much higher, the higher [SO$_4^{2-}$] will precipitate Ca$^{2+}$ will force the concentration of Ba$^{2+}$ to very low levels.

16.108 Given: solution with 0.022 M Fe$^{2+}$ and 0.014 M Mg$^{2+}$, add K$_2$CO$_3$ to form precipitates.

Find: (a) which ion precipitates first and minimum [K$^+$] needed; and (b) [first cation] when second cation precipitates

Other: $K_{sp}$ (FeCO$_3$) = 3.07 x $10^{-11}$, $K_{sp}$ (MgCO$_3$) = 6.82 x $10^{-6}$.

Conceptual Plan: (a) The precipitates that will form are FeCO$_3$ and MgCO$_3$.

Use the equation derived in Problem 19 to define $K_{sp}$. Substitute in concentration of cation and solve for $K_{sp}$ as a function of precipitation and cation (and for anion, too). The lowest concentration of anion to form precipitate. The cation with the lower anion concentration will precipitate first.

(b) Substitute the higher anion concentration into the $K_{sp}$ expression for the first cation to precipitate and calculate the amount of this first cation to remain in solution.

Solution:

(a) Derive expression for $K_{sp}$ (FeCO$_3$), $A = Fe^{2+}$, $m = 1$, $X = CO_3^{2-}$, and $n = 1$. Since $K_{sp}$ = [Fe$^{2+}$] [CO$_3^{2-}$], then

$K_{sp}$ (FeCO$_3$) = 3.07 x $10^{-11}$ = [Fe$^{2+}$] [CO$_3^{2-}$]. Solve for [CO$_3^{2-}$].

(b) Since Mg$^{2+}$ will not precipitate until [K$^+$] = 4.9 x $10^{-4}$ M K$_2$CO$_3$, substitute this value into the $K_{sp}$ expression for FeCO$_3$. So $K_{sp}$ (FeCO$_3$) = [Fe$^{2+}$] [CO$_3^{2-}$] = 3.07 x $10^{-11}$ = [Fe$^{2+}$] [CO$_3^{2-}$]. Solve for [Fe$^{2+}$] = 6.3 x $10^{-8}$ M Fe$^{2+}$.

Check: The units (none, M, and M) are correct. Comparing the two $K_{sp}$ values, it can be seen that the Fe$^{2+}$ will precipitate first since the solubility product is so much lower. Since the $K_{sp}$ value is so low, the concentration of precipitating agent is very low. Since the Mg$_2$CO$_3$ $K_{sp}$ value is so much higher, the higher [CO$_3^{2-}$] to precipitate Mg will force the concentration of Fe$^{2+}$ to very low levels.

Complex Ion Equilibria

16.109 Given: solution with 1.1 x $10^{-3}$ M Zn(NO$_3$)$_2$ and 0.150 M NH$_3$.

Find: [Zn$^{2+}$] at equilibrium.

Other: $K_f$ (Zn(NH$_3$)$_2^{2+}$) = 2.8 x $10^9$.

Conceptual Plan: Write a balanced equation and expression for $K_f$. Use initial concentrations to set up an ICE table. Since the $K_f$ is so large, assume that reaction essentially goes to completion. Solve for [Zn$^{2+}$] at equilibrium.

Solution: Zn(NO$_3$)$_2$ (s) $\rightarrow$ Zn$^{2+}$ (aq) + 2 NO$_3^-$ (aq). Since 1 Zn$^{2+}$ ion is generated for each Zn(NO$_3$)$_2$, [Zn$^{2+}$] = 1.1 x $10^{-3}$ M. Balanced equation is:

Zn$^{2+}$ (aq) + 4 NH$_3$ (aq) $\rightleftharpoons$ Zn(NH$_3$)$_2^{2+}$ (aq)

Set up an ICE table with initial concentrations.

Since $K_f$ is so large and since initially [NH$_3$] > 4 [Zn$^{2+}$] the reaction essentially goes to completion then write equilibrium expression and solve for x.
Chapter 16 Aqueous Ionic Equilibrium

\[
K_f = \frac{[\text{Zn(NH}_3^\text{4+})][\text{NH}_3]}{[\text{Zn}^2+]^4} = 2.8 \times 10^9 = \frac{1.1 \times 10^{-3}}{x(0.1456)^4}
\]

so \( x = 8.7 \times 10^{-10} \) M \( \text{Zn}^{2+} \). Since \( x \) is insignificant compared to the initial concentration, the assumption is valid.

Check: The units (M) are correct. Since \( K_f \) is so large, the reaction essentially goes to completion and \([\text{Zn}^{2+}]\) is extremely small.

16.110 Given: 120.0 mL of \( 2.8 \times 10^{-3} \) M \( \text{AgNO}_3 \) mixed with 225.0 mL of 0.10 M \( \text{NaCN} \)

Find: \([\text{Ag}^+]\) at equilibrium

Other: \( K_f (\text{Ag(CN)}_2^-) = 1 \times 10^{-21} \)

Conceptual Plan: Mix solutions and calculate diluted concentrations mL \( \text{AgNO}_3 \), mL \( \text{NaCN} \) \( \rightarrow \) mL total

\[ \text{ml} \text{AgNO}_3 + \text{ml} \text{NaCN} = \text{total ml} \]

Then \( \text{ml} \text{total} = \text{ml} \text{AgNO}_3 + \text{ml} \text{NaCN} = 120.0 \text{ ml} + 225.0 \text{ ml} = 345.0 \text{ ml} \).

Then \( M_1 V_1 = M_2 V_2 \) \( \rightarrow \) solve for \( M_2 \).

\[ M_2 = \frac{M_1 V_1}{V_2} = 0.10 \text{ M} \text{CN}^- x \frac{225.0 \text{ ml}}{345.0 \text{ ml}} = 0.065217 \text{ M} \text{CN}^- \] and \( 0.0097391 \text{ M} \text{Ag}^+ \) and

\[ [\text{Ag}^+] = 2.8 \times 10^{-3} \text{ M} Ag^+ \times 120.0 \text{ ml} \]

Check: The units (M) are correct. Since \( K_f \) is so large, the reaction essentially goes to completion and \([\text{Ag}^+]\) is extremely small.

16.111 Given: \( \text{FeS} (s) + 6 \text{CN}^- (aq) \leftrightarrow \text{Fe(CN)}_6^{4-} (aq) + \text{S}^{2-} (aq) \)

Use \( K_{sp} \) and \( K_f \) values

Find: \( K \)

Other: \( K_f (\text{Fe(CN)}_6^{4-}) = 1.5 \times 10^{35} \), \( K_{sp} (\text{FeS}) = 3.72 \times 10^{-19} \)

Conceptual Plan: Identify the appropriate solid and complex ion. Write balanced equations for dissolving the solid and forming the complex ion. Add these two reactions to get the desired overall reaction. Using the rules from Chapter 14, multiply the individual reaction \( K_s \) to get the overall \( K \) for the sum of these reactions.

Solution: Identify the solid as \( \text{FeS} \) and the complex ion as \( \text{Fe(CN)}_6^{4-} \). Write the individual reactions and add them together.

\[ \text{FeS} (s) \rightarrow \text{Fe}^{2+} (aq) + \text{S}^{2-} (aq) \]

\[ \text{Fe}^{2+} (aq) + 6 \text{CN}^- (aq) \rightarrow \text{Fe(CN)}_6^{4-} (aq) \]

Since the overall reaction is the simple sum of the two reactions, the overall reaction \( K = K_f \times K_{sp} = (1.5 \times 10^{35}) \times (3.72 \times 10^{-19}) = 5.6 \times 10^{16} \).

Check: The units (none) are correct. Since \( K \) is so large, it overwhelms the \( K_{sp} \) and the overall reaction is very spontaneous.

16.112 Given: \( \text{PbCl}_2 (s) + 3 \text{OH}^- (aq) \rightarrow \text{Pb(OH)}_3^- (aq) + 2 \text{Cl}^- (aq) \)

Use \( K_{sp} \) and \( K_f \) values

Find: \( K \)

Other: \( K_f (\text{Pb(OH)}_3^\text{4+}) = 8 \times 10^{13} \), \( K_{sp} (\text{PbCl}_2) = 1.17 \times 10^{-5} \)
Conceptual Plan: Identify the appropriate solid and complex ion. Write balanced equations for dissolving the solid and forming the complex ion. Add these two reactions to get the desired overall reaction. Using the rules from Chapter 14, multiply the individual reaction $K_s$ to get the overall $K$ for the sum of these reactions.

Solution: Identify the solid as PbCl$_2$ and the complex ion as Pb(OH)$_3$~. Write the individual reactions and add them together.

\[
PbCl_2(s) \rightleftharpoons Pb^{2+}^{(aq)} + 2Cl^-^{(aq)} \quad K_{sp} = 1.17 \times 10^{-5}
\]

\[
Pb^{2+}^{(aq)} + 3OH^-^{(aq)} \rightleftharpoons Pb(OH)_3^{~(aq)} \quad K_f = 8 \times 10^{13}
\]

\[
PbCl_2(s) + 3OH^-^{(aq)} \rightleftharpoons Pb(OH)_3^{~(aq)} + 2Cl^-^{(aq)}
\]

Since the overall reaction is the simple sum of the two reactions, the overall reaction $K = K_f \times K_{sp} = (8 \times 10^{13}) \times (1.17 \times 10^{-5}) = 9 \times 10^{8}$.

Check: The units (none) are correct. Since $K_f$ is so large, it overwhelms the $K_{sp}$ and the overall reaction is very spontaneous.

Cumulative Problems

16.113 Given: 150.0 mL solution of 2.05 g sodium benzoate and 2.47 g benzoic acid Find: pH

Other: $K_a$ (HC$_7$H$_5$O$_2$) = 6.5 \times 10^{-5}

Conceptual Plan: g NaC$_7$H$_5$O$_2$ $\rightarrow$ mol NaC$_7$H$_5$O$_2$ and g HC$_7$H$_5$O$_2$ $\rightarrow$ mol HC$_7$H$_5$O$_2$

\[
\frac{1 \text{ mol NaC}_7\text{H}_5\text{O}_2}{144.11 \text{ g NaC}_7\text{H}_5\text{O}_2} \times \frac{1 \text{ mol HC}_7\text{H}_5\text{O}_2}{122.13 \text{ g HC}_7\text{H}_5\text{O}_2}
\]

Since the two components are in the same solution, the ratio of [base]/[acid] = (mol base)/(mol acid). Then $K_a$, mol NaC$_7$H$_5$O$_2$ mol HC$_7$H$_5$O$_2$, $\rightarrow$ pH

\[
\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}
\]

Solution: 2.05 g NaC$_7$H$_5$O$_2$ x $\frac{1 \text{ mol NaC}_7\text{H}_5\text{O}_2}{144.11 \text{ g NaC}_7\text{H}_5\text{O}_2}$ = 0.0142252 mol NaC$_7$H$_5$O$_2$ and 2.47 g HC$_7$H$_5$O$_2$ x $\frac{1 \text{ mol HC}_7\text{H}_5\text{O}_2}{122.13 \text{ g HC}_7\text{H}_5\text{O}_2}$ = 0.0202244 mol HC$_7$H$_5$O$_2$ then

\[
\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}
\]

Check: The units (none) are correct. The magnitude of the answer makes physical sense because the pH is a little lower than the $pK_a$ of the acid because there is more acid than base in the buffer solution.

16.114 Given: 10.0 mL of 17.5 M acetic acid and 5.54 g sodium acetate diluted to 1.50 L Find: pH

Other: $K_a$ (HC$_2$H$_3$O$_2$) = 1.8 \times 10^{-5}

Conceptual Plan: mL $\rightarrow$ L then L, initial HC$_2$H$_3$O$_2$ M $\rightarrow$ mol HC$_2$H$_3$O$_2$ then

\[
\frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{1 \text{ mol NaC}_7\text{H}_5\text{O}_2}{83.04 \text{ g NaC}_7\text{H}_5\text{O}_2}
\]

g NaC$_7$H$_5$O$_2$ $\rightarrow$ mol NaC$_7$H$_5$O$_2$ then since the two components are in the same solution, the ratio of [base]/[acid] = (mol base)/(mol acid). Then $K_a$, mol NaC$_7$H$_5$O$_2$ mol HC$_2$H$_3$O$_2$, $\rightarrow$ pH

\[
\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}
\]

Solution: 10.0 mL x $\frac{1 \text{ L}}{1000 \text{ mL}}$ = 0.0100 L then

0.0100 L HC$_2$H$_3$O$_2$ x $\frac{17.5 \text{ mol HC}_2\text{H}_3\text{O}_2}{1 \text{ L HC}_2\text{H}_3\text{O}_2}$ = 0.175 mol HC$_2$H$_3$O$_2$ then

5.54 g NaC$_2$H$_3$O$_2$ x $\frac{1 \text{ mol NaC}_2\text{H}_3\text{O}_2}{82.04 \text{ g NaC}_2\text{H}_3\text{O}_2}$ = 0.06752803 mol NaC$_2$H$_3$O$_2$ then

\[
\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}
\]

Check: The units (none) are correct. The magnitude of the answer makes physical sense because the pH is a little lower than the $pK_a$ of the acid because there is more acid than base in the buffer solution.