COMMON ION EFFECT

- Common ion effect is the shift in equilibrium caused by the addition of an ion that takes part in the equilibrium.

- What is effect of adding HCl (hydrochloric acid) to a solution of HC₂H₃O₂ (acetic acid)?

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

Complete ionization of the strong acid

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

Weak acid

**Stress:** \(\text{H}_3\text{O}^+ (aq)\) added (from HCl)

**Response:** Equilibrium shifts

**New Equil:** \(\text{HC}_2\text{H}_3\text{O}_2 (aq) + \text{H}_2\text{O (l)} \rightarrow \text{H}_3\text{O}^+ (aq) + \text{C}_2\text{H}_3\text{O}_2^- (aq)\)

\[[\text{HC}_2\text{H}_3\text{O}_2(aq)] \text{ increases}\]

\[[\text{C}_2\text{H}_3\text{O}_2^-(aq)] \text{ decreases}\]

- Net Result: Degree of ionization of acetic acid (HC₂H₃O₂) decreases
Examples:
1. Calculate the degree of ionization of benzoic acid, \( \text{HC}_7\text{H}_5\text{O}_2 \), in a 0.15 M solution to which sufficient HCl is added to make it 0.010 M. Compare the degree of ionization to that of 0.15 M benzoic acid with no HCl added (\( K_a \) of benzoic acid = \( 6.3 \times 10^{-5} \))

Calculate the degree of ionization of benzoic acid (\( \text{HC}_7\text{H}_5\text{O}_2 \)) with no HCl added

\[
\text{HC}_7\text{H}_5\text{O}_2 (\text{aq}) \quad + \quad \text{H}_2\text{O} (\text{l}) \quad \rightleftharpoons \quad \text{H}_3\text{O}^+ (\text{aq}) \quad + \quad \text{C}_7\text{H}_5\text{O}_2^- (\text{aq})
\]

<table>
<thead>
<tr>
<th></th>
<th>( \text{HC}_7\text{H}_5\text{O}_2 ) (aq)</th>
<th>( \text{H}_2\text{O} ) (l)</th>
<th>( \text{H}_3\text{O}^+ ) (aq)</th>
<th>( \text{C}_7\text{H}_5\text{O}_2^- ) (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.15</td>
<td>----</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( \Delta )</td>
<td>( -x )</td>
<td>----</td>
<td>( +x )</td>
<td>( +x )</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.15–( x )</td>
<td>-----</td>
<td>( x )</td>
<td>( x )</td>
</tr>
</tbody>
</table>

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_7\text{H}_5\text{O}_2^-]}{[\text{HC}_7\text{H}_5\text{O}_2]} = \frac{x^2}{0.15-x} \approx \frac{x^2}{0.15} = 6.3 \times 10^{-5}
\]

\[
x = [\text{C}_7\text{H}_5\text{O}_2^-] = 3.07 \times 10^{-3}
\]

\[
\text{Degree of Ionization}% = \frac{[\text{C}_7\text{H}_5\text{O}_2^-]}{[\text{HC}_7\text{H}_5\text{O}_2]} \times 100 = \frac{3.07 \times 10^{-3}}{0.15} \times 100 = 2.0\%
\]

Calculate the degree of ionization of benzoic acid (\( \text{HC}_7\text{H}_5\text{O}_2 \)) with HCl added (0.010 M)

\[
\text{HC}_7\text{H}_5\text{O}_2 (\text{aq}) \quad + \quad \text{H}_2\text{O} (\text{l}) \quad \rightleftharpoons \quad \text{H}_3\text{O}^+ (\text{aq}) \quad + \quad \text{C}_7\text{H}_5\text{O}_2^- (\text{aq})
\]

<table>
<thead>
<tr>
<th></th>
<th>( \text{HC}_7\text{H}_5\text{O}_2 ) (aq)</th>
<th>( \text{H}_2\text{O} ) (l)</th>
<th>( \text{H}_3\text{O}^+ ) (aq)</th>
<th>( \text{C}_7\text{H}_5\text{O}_2^- ) (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.15</td>
<td>----</td>
<td>0.010</td>
<td>0</td>
</tr>
<tr>
<td>( \Delta )</td>
<td>( -x )</td>
<td>----</td>
<td>( +x )</td>
<td>( +x )</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.15–( x )</td>
<td>-----</td>
<td>( x )</td>
<td>( x )</td>
</tr>
</tbody>
</table>

Note: Since HCl is a strong acid, the initial concentration of \( \text{H}_3\text{O}^+ \) ions is the same as the concentration of HCl.

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_7\text{H}_5\text{O}_2^-]}{[\text{HC}_7\text{H}_5\text{O}_2]} = \frac{(0.010+x) x}{0.15-x}
\]

Assumptions: \( 0.010 + x \approx 0.010 \quad 0.15 - x \approx 0.15 \)

\[
K_a = \frac{0.010 x}{0.15} = 6.3 \times 10^{-5} \quad x = [\text{C}_7\text{H}_5\text{O}_2^-] = 9.45 \times 10^{-4}
\]
Degree of Ionization = \frac{[C_7H_5O_2^-]}{[HC_7H_5O_2]} \times 100 = \frac{9.45 \times 10^{-4}}{0.15 \text{ M}} \times 100 = 0.63 \%

NOTE:  
0.63 \% <<<<< 2.0\% 
(with HCl)  (without HCl)

2. Calculate the pH of a 0.10 M solution of hydrofluoric acid (HF) to which sufficient NaF is added to make the concentration of NaF 0.20 M. (K_a of HF = 6.8 \times 10^{-4})

<table>
<thead>
<tr>
<th></th>
<th>HF (aq) + H_2O (l) \rightleftharpoons H_3O^+(aq) + F^- (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>----</td>
</tr>
<tr>
<td>\Delta</td>
<td>----</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>-----</td>
</tr>
</tbody>
</table>

Assume x is small. Therefore,

[F^-] =

[HF] =

K_a = \frac{[H_3O^+][F^-]}{[HF]} =

x = [H_3O^+] =

pH = - \log (H_3O^+) =
Buffers are solutions that have the ability to resist changes in pH when limited amounts of acid or bases are added to it.

**What does a buffer do?**

Consider:

<table>
<thead>
<tr>
<th>Solution</th>
<th>1 L pure water</th>
<th>pH = 7.00</th>
<th>IL buffered solution</th>
<th>pH = 9.43</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Addition</strong></td>
<td>0.01 mol HCl</td>
<td>pH changes to 2.00</td>
<td>0.01 mol HCl</td>
<td>pH changes to 9.33</td>
</tr>
<tr>
<td><strong>Change in pH</strong></td>
<td>7.00–2.00 = 5.00</td>
<td></td>
<td>9.43–9.33 = 0.10</td>
<td></td>
</tr>
</tbody>
</table>

**Types of buffer solutions**

There are two types of buffer solutions:

1. Solution of a weak acid and its conjugate base
   
   \[ \text{HC}_2\text{H}_3\text{O}_2 \text{ and NaC}_2\text{H}_3\text{O}_2 \]

2. Solution of a weak base and its conjugate acid
   
   \[ \text{NH}_3 \text{ and NH}_4\text{Cl} \]

**How do buffers function?**

I. A mixture of a weak acid (HA) and its conjugate base (A\(^-\))

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

Results:

> \(\text{H}_3\text{O}^+\) is used up
> little change in pH
\[ \text{OH}^- (aq) + \text{HA}(aq) \rightarrow \text{A}^- (aq) + \text{H}_2\text{O}(l) \]

Results:
- \text{OH}^- is used up
- little change in pH

II. A mixture of a weak base (B) and its conjugate acid (HB\(^+\))

\[ \text{H}_3\text{O}^+ (aq) + \text{B} (aq) \rightarrow \text{HB}^+ (aq) + \text{H}_2\text{O} (l) \]

Results:
- \text{H}_3\text{O}^+ is used up
- little change in pH

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

Results:
- \text{OH}^- is used up
- little change in pH

**CONCLUSION:**
- A buffer system (solution) resists changes in pH through its ability to combine with both \text{H}_3\text{O}^+ ions and \text{OH}^- ions.
PROPERTIES OF BUFFERS

Uses & Importance of Buffers:

1. In biological fluids
   • Blood is a buffer solution (containing H₂CO₃, weak acid and HCO₃⁻ as its conjugate base and several other buffer systems) with a pH = 7.4.
   • A change in more than 0.1 in the pH of blood would cause blood to lose its capacity to carry oxygen to the cells.

2. Commercial applications
   • Fruit juice mixes contain citric acid (a weak acid) and sodium citrate (the citrate anion is the conjugate base of citric acid) which ensure that the pH is maintained (“the tartness is regulated”)

Characteristics of Buffers

1. pH

2. Buffer Capacity
   • The amount of acid or base the buffer can react with before giving a significant pH change depends on:
     • amount of weak acid (HA) and its conjugate base (A⁻) in solution
     • amount of weak base (B) and its conjugate acid (HB⁺) in solution
   • This dependence is usually expressed as a ratio:

     \[
     \frac{HA}{A^-} \quad \text{or} \quad \frac{HB^+}{B} \quad \text{(should be close to 1)}
     \]

     \[
     \frac{1}{10} < \frac{HA}{A^-} \quad \text{or} \quad \frac{HB^+}{B} < \frac{10}{1}
     \]

     Or simply:

     \[
     0.1 < \frac{HA}{A^-} \quad \text{or} \quad \frac{HB^+}{B} < 10
     \]
MILLIMOLE CALCULATIONS

- When working with solutions, we often express the \textit{volume in milliliters} (mL) rather than in liters.
- Likewise, we may express the amount of \textit{solute in millimoles} (mmol) rather than in moles.
- Because mL is 1/1000 of a Liter and mmol is 1/1000 of a mole, molarity can also be expressed in mmol of solute in mL of solution:

\[
molarity = \frac{\text{mol solute}}{L \text{ of solution}} = \frac{\text{mmol of solute}}{mL \text{ of solution}}
\]

- For problems that involve volume and concentration, solving in terms of millimoles and milliliters often involves more convenient numbers that using moles and Liters.
- It should also be noted that the reactions coefficients in a balanced chemical equation are exactly the same whether we express the amounts in moles or millimoles.
- When solving solution problems, the millimoles of solute can be easily obtained from given data as shown in the examples below.

\textbf{Examples:}

1. How many mmoles of solute are present in 125 mL of 0.100 M HCl solution?

\[
125 \text{ mL} \times \frac{0.100 \text{ mmol}}{1 \text{ mL}} = 12.5 \text{ mmol HCl}
\]

2. If 100. mL of 1.00 M HCl is added to 100. mL of 0.80 M NaOH, what are the molarities of the solutes in the solution after all reaction has completed?

<table>
<thead>
<tr>
<th></th>
<th>HCl</th>
<th>+</th>
<th>NaOH</th>
<th>→</th>
<th>NaCl</th>
<th>+</th>
<th>H\textsubscript{2}O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\Delta)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>End</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**BUFFER CALCULATIONS**

**Examples:**
1. A buffer solution is prepared to be 0.10 M acetic acid (HC\(_2\)H\(_3\)O\(_2\)) and 0.20 M sodium acetate (NaC\(_2\)H\(_3\)O\(_2\)). What is the pH of this buffer system at 25°C (\(K_a\) of acetic acid = 1.7 x 10\(^{-5}\))

<table>
<thead>
<tr>
<th></th>
<th>HC(_2)H(_3)O(_2) (aq)</th>
<th>H(_2)O (l)</th>
<th>H(_3)O(^+) (aq)</th>
<th>C(_2)H(_3)O(_2)^(-) (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.10</td>
<td></td>
<td>0</td>
<td>0.20</td>
</tr>
<tr>
<td>(\Delta)</td>
<td>(-x)</td>
<td></td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.10–x</td>
<td></td>
<td>x</td>
<td>0.20 + x</td>
</tr>
</tbody>
</table>

\[K_a = \frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{x(0.20 + x)}{(0.10–x)} \approx \frac{0.20 x}{0.10} = 1.7 \times 10^{-5}\]

\(x = [H_3O^+] = 8.5 \times 10^{-6}\)

pH = - log (8.5 x 10\(^{-6}\)) = 5.07

2. Calculate the pH of a buffer that is 1.00 M in NH\(_3\) and 0.80 M in NH\(_4\)Cl. (\(K_b\) for NH\(_3\) = 1.8x10\(^{-5}\))

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td></td>
</tr>
<tr>
<td>(\Delta)</td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td></td>
</tr>
</tbody>
</table>
PREPARATION OF BUFFER SOLUTIONS

- Many buffer problems can be solved by using the following stepwise procedure:

  1. Calculate the initial molarities of solutions
  2. Calculate the equilibrium concentrations of common species
  3. Calculate \([H_3O^+]\) and pH of solution from \(K_a\)

Examples:
1. What is the pH of a buffer made by mixing 1.00 L of 0.020 M benzoic acid (HC\(_7\)H\(_5\)O\(_2\)) with 3.00 L of 0.060 M sodium benzoate (NaC\(_7\)H\(_5\)O\(_2\))? \(K_a\) of benzoic acid = 6.3 x 10\(^{-5}\)

**Step 1:** Calculate the initial molarities of solutions:

- Initial molarity HC\(_7\)H\(_5\)O\(_2\) = 1.00 L x \(\frac{0.020 \text{ mol}}{1.00 \text{ L}}\) x \(\frac{1}{4.00 \text{ L}}\) = 0.0050 M
- Initial molarity of NaC\(_7\)H\(_5\)O\(_2\) = 3.00 L x \(\frac{0.060 \text{ mol}}{1.00 \text{ L}}\) x \(\frac{1}{4.00 \text{ L}}\) = 0.045 M

**Step 2:** Calculate the equilibrium concentrations of common species

<table>
<thead>
<tr>
<th></th>
<th>HC(_7)H(_5)O(_2) (aq) + H(_2)O (l) (\rightleftharpoons) H(_3)O(^+)(aq) + C(_7)H(_5)O(_2)^(-) (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.0050                                                             ----                      0                    0.045</td>
</tr>
<tr>
<td>(\Delta)</td>
<td>(-x)                                                             ----                      (+x)               (+x)</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.0050–x                                                           ----                      (x)                  0.045 + (x)</td>
</tr>
</tbody>
</table>

**Step 3:** Calculate \([H_3O^+]\) and pH from \(K_a\)

\[
K_a = \left[\frac{[H_3O^+][C_7H_5O_2^-]}{[HC_7H_5O_2]}\right] = \frac{x (0.045 + x)}{(0.0050 - x)} \approx \frac{0.045 x}{0.0050} = 6.3 \times 10^{-5}
\]

\[
x = [H_3O^+] = 7.0 \times 10^{-6} \text{ M}
\]

\[
pH = - \log (7.0 \times 10^{-6}) = 5.15
\]
2. A buffer is prepared by adding 115 mL of 0.30 M NH₃ to 145 mL of 0.15 M NH₄NO₃. What is the pH of the final solution? (K_b of ammonia = 1.8 x 10⁻⁵)

**Step 1:** Calculate the initial molarities of solutions:

Total Volume of Solution =

Initial molarity of NH₃ =

Initial molarity of NH₄NO₃ =

**Step 2:** Calculate the equilibrium concentrations of common species

<table>
<thead>
<tr>
<th></th>
<th>NH₃</th>
<th>+</th>
<th>H₂O (l)</th>
<th>NH₄⁺</th>
<th>+</th>
<th>OH⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>----</td>
<td></td>
<td>----</td>
<td>----</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Δ</td>
<td>----</td>
<td></td>
<td>----</td>
<td>----</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>-----</td>
<td></td>
<td>----</td>
<td>----</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Step 3:** Calculate [H₃O⁺] and pH from K_b

K_b =

x =

pOH =

pH =
3. Calculate the pH of a solution prepared by mixing 400. mL of a 0.200 M acetic acid solution and 100. mL of a 0.300 M sodium hydroxide solution. \( \text{K}_a \text{acetic acid} = 1.7 \times 10^{-5} \)

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

**NOTE:**
NaOH is a strong base, and reacts with acetic acid to form sodium acetate. If an appreciable amount of excess acetic acid is still present after the NaOH has reacted, the excess acetic acid and the newly formed sodium acetate form a buffer solution.

**Step 1:** Calculate the amount of acetic acid neutralized:

\[
\text{mmol of acetic acid} = 400. \text{ mL} \times \frac{0.200 \text{ mol}}{1.00 \text{ L}} = 80.0 \text{ mmol}
\]

\[
\text{mmol of NaOH} = 100. \text{ mL} \times \frac{0.300 \text{ mol}}{1.00 \text{ L}} = 30.0 \text{ mmol}
\]

<table>
<thead>
<tr>
<th></th>
<th>HC(_2)H(_3)O(_2)</th>
<th>+</th>
<th>NaOH</th>
<th>→</th>
<th>NaC(_2)H(_3)O(_2)</th>
<th>+</th>
<th>H(_2)O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>80.0</td>
<td></td>
<td>30.0</td>
<td></td>
<td>0</td>
<td></td>
<td>----</td>
</tr>
<tr>
<td></td>
<td>(\Delta)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>----</td>
</tr>
<tr>
<td>End</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>----</td>
</tr>
</tbody>
</table>

**Step 2:** Calculate the concentration of species present after neutralization:

\[
\text{Conc. of HC}_2\text{H}_3\text{O}_2 = \frac{\text{mmol HC}_2\text{H}_3\text{O}_2}{\text{mL solution}} = \]

\[
\text{Conc. of NaC}_2\text{H}_3\text{O}_2 = \frac{\text{mmol NaC}_2\text{H}_3\text{O}_2}{\text{mL solution}} = \]
Step 3: Calculate the equilibrium concentrations of common species

$$\text{HC}_2\text{H}_3\text{O}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{C}_2\text{H}_3\text{O}_2^-$$

<table>
<thead>
<tr>
<th></th>
<th>\text{HC}_2\text{H}_3\text{O}_2</th>
<th>\text{H}_2\text{O}</th>
<th>\text{H}_3\text{O}^+</th>
<th>\text{C}_2\text{H}_3\text{O}_2^-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>----</td>
<td>----</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta$</td>
<td>----</td>
<td>----</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>-----</td>
<td>-----</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Step 3: Calculate $[\text{H}_3\text{O}^+]$ and pH from $K_a$

$$K_a =$$

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

$$\text{pH} =$$
ADDITION OF ACID OR BASE TO A BUFFER

- Addition of acid or base to a buffer will cause a slight change in pH
- This change in pH can be calculated.

A buffer is prepared by mixing 525 mL of 0.50 M formic acid, HCHO₂, and 475 mL of 0.50 M sodium formate, NaCHO₂. (Kᵢ for formic acid = 1.7 x 10⁻⁴)
1. Calculate the pH of the buffer solution.
2. What would be the pH of 85 mL of the buffer to which 8.5 mL of 0.15 M hydrochloric has been added?

I. Calculate the pH of the buffer solution

Step 1: Calculate the initial molarities of solutions:

Total Volume of Solution = 525 mL + 475 mL = 1000 mL = 1.00 L

Initial molarity HCHO₂ = 525 mL x \( \frac{0.50 \text{ mol}}{1000 \text{ mL}} \times \frac{1}{1.00 \text{ L}} = 0.263 \text{ M} \)

Initial molarity of NaCHO₂ = 475 mL x \( \frac{0.50 \text{ mol}}{1000 \text{ mL}} \times \frac{1}{1.00 \text{ L}} = 0.238 \text{ M} \)

Step 2: Calculate the equilibrium concentrations of the common species:

\[
\begin{array}{|c|c|c|c|c|}
\hline
 & \text{HCHO}_2 (aq) & \text{H}_2\text{O} (l) & \text{H}_3\text{O}^+ (aq) & \text{CHO}_2^- (aq) \\
\hline
\text{Initial} & 0.263 & ---- & 0 & 0.238 \\
\Delta & -x & ---- & +x & +x \\
\text{Equilibrium} & 0.263 - x & ---- & x & 0.238 + x \\
\hline
\end{array}
\]

Assume x is small:

\[
[\text{HCHO}_2] (\text{total}) = 0.263 \text{ M} - x \approx 0.263 \\
[\text{CHO}_2^-] (\text{total}) = 0.238 \text{ M} + x \approx 0.238
\]

Step 4: Calculate [H₃O⁺] and pH from Kᵢ

\[
Kᵢ = \frac{[\text{H}_3\text{O}^+][\text{CHO}_2^-]}{[\text{HCHO}_2]} = \frac{0.238 x}{0.263} = 1.7 \times 10^{-4}
\]

\[
x = [\text{H}_3\text{O}^+] = 1.88 \times 10^{-4} \text{ M} \\
pH = - \log (1.88 \times 10^{-4}) = 3.73
\]
II. Calculate the pH of the solution after 8.5 mL of 0.15 M hydrochloric acid added to 85 mL of the buffer

Data: 8.5 mL HCl, 0.15 M  
85 mL formic acid, HCHO₂, 0.263 M  
85 mL formate ion, CHO₂⁻, 0.238 M

Step 1: Calculate the mmol of the species involved before addition:

\[
m\text{moles HCl} = 8.5 \text{ mL} \times \frac{0.15 \text{ mol}}{1 \text{ L}} = 1.28 \text{ mmol} \\
m\text{moles HCHO}_2 = 85 \text{ mL} \times \frac{0.263 \text{ mol}}{1 \text{ L}} = 22.4 \text{ mol} \\
m\text{moles CHO}_2^- = 85 \text{ mL} \times \frac{0.238 \text{ mol}}{1 \text{ L}} = 20.2 \text{ mol} 
\]

Step 2: Calculate the mmol of the species involved after addition:

\[
\text{HCl (aq) + H}_2\text{O (l)} \rightarrow \text{H}_3\text{O}^+ (aq) + \text{Cl}^- (aq) \\
1.28 \text{ mmol} \quad 1.28 \text{ mmol}
\]

All of the H₃O⁺ reacts with the CHO₂⁻ ion:

<table>
<thead>
<tr>
<th></th>
<th>H₃O⁺ (aq)</th>
<th>CHO₂⁻</th>
<th>HCHO₂ (aq)</th>
<th>H₂O (l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>1.28 mmol</td>
<td>20.2 mmol excess</td>
<td>22.4 mmol</td>
<td>-----</td>
</tr>
<tr>
<td>Change (Δ)</td>
<td>-1.28</td>
<td>-1.28</td>
<td>+1.28</td>
<td>-----</td>
</tr>
<tr>
<td>End</td>
<td>0</td>
<td>18.9</td>
<td>23.7</td>
<td>-----</td>
</tr>
</tbody>
</table>
Step 3: Find the starting concentrations (molarities) of the species involved

Total Volume of Solution = 85 mL buffer + 8.5 mL HCl = 93.5 mL

mmol HCHO₂⁻/mL solution = \[\frac{23.7 \text{ mmol}}{93.5 \text{ mL}} = 0.253 \text{ M}\]

mmol CHO₂⁻/mL solution = \[\frac{18.9 \text{ mmol}}{93.5 \text{ mL}} = 0.202 \text{ M}\]

Step 4: Calculate [H₃O⁺] and pH from Kᵦ and equilibrium concentrations

<table>
<thead>
<tr>
<th></th>
<th>HCHO₂ (aq)</th>
<th>H₂O (l)</th>
<th>H₃O⁺(aq)</th>
<th>CHO₂⁻ (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.253</td>
<td>----</td>
<td>0</td>
<td>0.202</td>
</tr>
<tr>
<td>Δ</td>
<td>–x</td>
<td>----</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.253 – x</td>
<td>----</td>
<td>x</td>
<td>0.202 + x</td>
</tr>
</tbody>
</table>

\[Kᵦ = \frac{[H₃O⁺][CHO₂⁻]}{[HCHO₂⁻]} = \frac{x (0.202 + x)}{(0.253 – x)} \approx \frac{0.202 x}{0.253} = 1.7 \times 10^{-4}\]

\[x = [H₃O⁺] = 2.13 \times 10^{-4} \text{ M}\]

\[\text{pH} = – \log (2.13 \times 10^{-4}) = 3.67 \text{ (with HCl added)}\]

Compare: \(\text{pH} = 3.73 \text{ (without HCl added)}\)

CONCLUSION:
- pH was lowered by 0.06 upon addition of HCl (minimal change)

FOLLOW-UP:
What is the pH of the solution if 8.5 mL of 0.15 NaOH were added to 85 mL of the buffer solution?
How do you prepare a buffer of a desired pH?

Consider the following buffer: \( \text{HA(aq)} + \text{A}^- (\text{aq}) \)

denotes a weak acid and \( \text{its conjugate base} \)

\[
\begin{align*}
\text{HA(aq)} + \text{H}_2\text{O} & \rightleftharpoons \text{H}_3\text{O}^+ (\text{aq}) + \text{A}^- (\text{aq}) \\
\end{align*}
\]

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

\([\text{HA}], [\text{A}^-]\):

- should be equilibrium concentrations
- are not exactly equilibrium concentrations, since there is excess of \( [\text{A}^-] \) in the buffer solution
- they do not differ significantly from the equilibrium concentrations, since \( \text{A}^- \) represses the ionization of \( \text{HA} \)

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

NOTE: If \( [\text{HA}] \approx [\text{A}^-] \)
then \( [\text{H}_3\text{O}^+] \approx K_a \)

- Take negative logs of both parts of the equation:

\[
\begin{align*}
-log [\text{H}_3\text{O}^+] &= -log \left( K_a \times \frac{[\text{HA}]}{[\text{A}^-]} \right) = -log K_a -log \frac{[\text{HA}]}{[\text{A}^-]} \\
-log [\text{H}_3\text{O}^+] &= pH \\
-log K_a &= pK_a
\end{align*}
\]

\[
\begin{align*}
\text{pH} &= pK_a - log \frac{[\text{A}^-]}{[\text{HA}]} \\
\text{pH} &= pK_a + log \frac{[\text{HA}]}{[\text{A}^-]}
\end{align*}
\]

**Henderson-Hasselbalch Equation**
• The Henderson-Hasselbalch Equation can be used for both type of buffers.

• To prepare a buffer with a specific pH:
  - A weak acid and its conjugate base must be found for which the pKₐ of the weak acid is close to the desired pH.
  - The pH value is fine tuned using the acid-base ratio

Examples:
1. A buffer with a pH of 4.90 is desired. Would HC₂H₃O₂⁻/C₂H₃O₂⁻ be a suitable buffer system?

\[
K_a(HC_2H_3O_2) = 1.7 \times 10^{-5}
\]

\[
pK_a = -\log (1.7 \times 10^{-5}) = 4.77
\]

This is relatively close to the desired pH (4.77 versus 4.90)

The pH may be increased by increasing the ratio: \[ \frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} \]

1. Calculate the pH of a buffer containing 0.10 M NH₃ and 0.2 M NH₄⁺. \( K_b(NH_3) = 1.8 \times 10^{-5} \)

\[
K_a(NH_4^+) = \frac{K_w}{K_b(NH_3)} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}
\]

\[
pK_a = -\log (5.56 \times 10^{-10}) = 9.25
\]

\[
pH = pK_a + \log \frac{[NH_3]}{[NH_4^+]} = 9.25 + \log \frac{0.10}{0.20} = 8.95
\]
3. 1.5 mL of 1 M HCl is added to each of the following solutions. Which one will show the least change in pH?

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>a) 15 mL of 0.1M NaOH</td>
<td>The solution is a strong base. The addition of a strong acid will lower the pH considerably.</td>
</tr>
<tr>
<td>b) 15 mL of 0.1M HC$_2$H$_3$O$_2$</td>
<td>The solution is a weak acid. The addition of a strong acid will lower the pH considerably.</td>
</tr>
<tr>
<td>c) 30 mL of 0.1M NaOH and 30 mL of 0.1M HC$_2$H$_3$O$_2$</td>
<td>After mixing, the solution is 0.05 M NaC$_2$H$_3$O$_2$, a basic salt, not a buffer. The addition of a strong acid will lower the pH considerably.</td>
</tr>
</tbody>
</table>
| d) 30 mL of 0.1M NaOH and 60 mL of 0.1M HC$_2$H$_3$O$_2$ | After mixing, the solution contains:  
\[
[\text{NaC}_2\text{H}_3\text{O}_2] = \frac{0.0030 \text{ moles}}{0.090 \text{ L}} = 0.033 \text{ M} \\
[\text{HC}_2\text{H}_3\text{O}_2] = \frac{0.0030 \text{ moles}}{0.090 \text{ L}} = 0.033 \text{ M}
\]  
This solution is a buffer and as such the addition of a strong acid will show the least change in pH.
ACID–BASE TITRATION CURVES

- Titration is a procedure for determining the amount of acid (or base) in a solution by determining the volume of base (or acid) of known concentration that will completely react with it.

- Acid–base titration curve is a plot of the pH of a solution of acid (or base) against the volume of added base (or acid)

- These curves can be used to choose an indicator that will show when the titration is complete.
TITRATION OF A STRONG ACID BY A STRONG BASE

HCl (aq) + NaOH (aq) → NaCl (aq) + H₂O (aq)

0.100 M  0.100 M
25.00 mL  ? mL

First Part of Titration:
The pH changes slowly until about 24 mL of base is added (until the titration is near the equivalence point)

Second Part of Titration:
The pH changes rapidly from pH = 3 to pH = 11

At pH = 7:
- the solution contains NaCl, a salt that does not hydrolyze
- the equivalence point is reached

- Equivalence point: the point in a titration when a stoichiometric amount of reactant has been added
**Choice of Indicator to detect equivalence point:**

- The indicator should change color within the pH range **3 – 11**
- Which indicators change color within the **pH range of 3-11**?

<table>
<thead>
<tr>
<th>Indicator name</th>
<th>pH range for color change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl violet</td>
<td>yellow → violet</td>
</tr>
<tr>
<td>Thymol blue (acidic range)</td>
<td>red → yellow</td>
</tr>
<tr>
<td>Bromphenol blue</td>
<td>yellow → blue</td>
</tr>
<tr>
<td>Methyl orange</td>
<td>red → yellow</td>
</tr>
<tr>
<td>Bromcresol green</td>
<td>yellow → blue</td>
</tr>
<tr>
<td>Methyl red</td>
<td>red → yellow</td>
</tr>
<tr>
<td>Bromthymol blue</td>
<td>yellow → blue</td>
</tr>
<tr>
<td>Thymol blue (basic range)</td>
<td>yellow → blue</td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>colorless → pink</td>
</tr>
<tr>
<td>Alizarin yellow R</td>
<td>yellow → red</td>
</tr>
</tbody>
</table>
CALCULATING THE PH OF A SOLUTION OF A STRONG ACID AND A STRONG BASE

Examples:
1. Calculate the pH of a solution in which 10.0 mL of 0.100 M HCl is added to 25.0 mL of 0.100 M NaOH.

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

<table>
<thead>
<tr>
<th></th>
<th>HCl</th>
<th>NaOH</th>
<th>NaCl</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start</td>
<td>1.00 mmol</td>
<td>2.50 mmol</td>
<td>0</td>
<td>----</td>
</tr>
<tr>
<td>Δ</td>
<td>–1.00 mmol</td>
<td>–1.00 mmol</td>
<td>+1.00 mmol</td>
<td>----</td>
</tr>
<tr>
<td>End</td>
<td>0</td>
<td>1.50 mmol</td>
<td>1.00 mmol</td>
<td>----</td>
</tr>
</tbody>
</table>

\[
[\text{OH}^-] = \frac{1.50 \text{ mmoles}}{35.0 \text{ mL solution}} = \frac{1.50 \text{ mmoles OH}^-}{10.0 \text{ mL acid} + 25.0 \text{ mL base}} = \frac{1.50 \text{ mmoles OH}^-}{35.0 \text{ mL solution}}
\]

\[
[\text{OH}^-] = 4.286 \times 10^{-2} \text{ M} \quad \text{pOH} = – \log (4.286 \times 10^{-2}) = 1.368
\]

\[
\text{pH} = 14.000 – 1.368 = \boxed{12.632} \quad \text{(strongly basic)}
\]

2. Calculate the pH of a solution in which 30.0 mL of 0.100 M HCl is added to 25.0 mL of 0.100 NaOH.
TITRATION OF A WEAK ACID BY A STRONG BASE

\[
\text{HC}_2\text{H}_3\text{O}_2(aq) + \text{NaOH}(aq) \rightarrow \text{NaC}_2\text{H}_3\text{O}_2(aq) + \text{H}_2\text{O}(aq)
\]

0.100 M \hspace{1cm} 0.100 M

25.00 mL \hspace{1cm} ? mL

First Part of Titration:
pH changes slowly at first (from about 3 to about 7)

NOTE:
- The titration starts at a higher pH (pH = 3) than HCl because HC\(_2\)H\(_3\)O\(_2\) is a weak acid

Second Part of Titration:
pH changes rapidly from pH = 7 to pH = 11

NOTE:
- This is a shorter range than that for a strong acid by a a strong base (from 3 to 11)
- The equivalence point occurs on the basic side; this is the pH of the NaC\(_2\)H\(_3\)O\(_2\)(aq)
Choice of Indicator to detect equivalence point:

- The indicator should change color within the pH range 7 – 11
- Which indicators change color within the pH range of 7-11?

![Indicator Chart]

**NOTE:**
- Because the range in which the rapid change of pH occurs is narrower (7 to 11), the choice of an indicator is more limited.
- The following indicators can be used:
  1. Thymol blue (basic range)
  2. Phenolphtalein
Calculating the pH at the Equivalence Point in the Titration of a Weak Acid by a Strong Base

Examples:
1. Calculate the pH at the equivalence point for the titration of 500. mL of 0.10 M acetic acid with 0.050 M sodium hydroxide. \( (K_a = 1.7 \times 10^{-5}) \)

First: Stoichiometry

\[
\text{HC}_2\text{H}_3\text{O}_2\text{(aq)} + \text{NaOH(aq)} \rightarrow \text{NaC}_2\text{H}_3\text{O}_2\text{(aq)} + \text{H}_2\text{O(l)}
\]

At the equivalence point:

\[
\text{# mmoles of HC}_2\text{H}_3\text{O}_2\text{(aq)} \text{ reacted} = \text{# mmoles of NaOH(aq)} \text{ reacted}
\]

<table>
<thead>
<tr>
<th>500. mL</th>
<th>0.10 M</th>
<th>( ? ) mL</th>
<th>0.050 M</th>
</tr>
</thead>
</table>

\[
0.10 \text{ moles HC}_2\text{H}_3\text{O}_2 \times \frac{1 \text{ mmol NaOH}}{1 \text{ L NaOH}} = 1000 \text{ mL}
\]

\[
\text{HC}_2\text{H}_3\text{O}_2\text{(aq)} + \text{NaOH(aq)} \rightarrow \text{NaC}_2\text{H}_3\text{O}_2\text{(aq)} + \text{H}_2\text{O(l)}
\]

<table>
<thead>
<tr>
<th>500. mL</th>
<th>1000 mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10 M</td>
<td>0.050 M</td>
</tr>
</tbody>
</table>

|  | HC\(_2\)H\(_3\)O\(_2\) + NaOH \rightarrow NaC\(_2\)H\(_3\)O\(_2\) + H\(_2\)O |
|---|------------------|--|--|--|
| Start | 50. mmol | 50. mmol | 0 | ---- |
| \( \Delta \) | -50. mmol | -50. mmol | 50. mmol | ---- |
| End | 0 | 0 mmol | 50. mmol | ---- |

\[
\text{NaC}_2\text{H}_3\text{O}_2\text{(aq)} \rightarrow \text{Na}^+(aq) + \text{C}_2\text{H}_3\text{O}_2^-\text{(aq)}
\]

Note: \# mmoles NaC\(_2\)H\(_3\)O\(_2\) = \# mmoles C\(_2\)H\(_3\)O\(_2\)\(^-\) = 50. mmol

\[
[C_2\text{H}_3\text{O}_2^-] = \frac{50. \text{ mmol}}{500. \text{ mL acid} + 1000 \text{ mL base}} = 0.0333 \text{ M}
\]
Second: Hydrolysis of the acetate ion

\[
\text{C}_2\text{H}_3\text{O}_2^{-} (\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{HC}_2\text{H}_3\text{O}_2 (\text{aq}) + \text{OH}^{-} (\text{aq})
\]

\[K_b = ?\]

Recall: \(K_a(\text{HC}_2\text{H}_3\text{O}_2) \times K_b(\text{C}_2\text{H}_3\text{O}_2^-) = K_w\)

\[
K_b(\text{C}_2\text{H}_3\text{O}_2^-) = \frac{K_w}{K_a(\text{HC}_2\text{H}_3\text{O}_2)} = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-5}} = 5.88 \times 10^{-10}
\]

<table>
<thead>
<tr>
<th></th>
<th>C\textsubscript{2}H\textsubscript{3}O\textsubscript{2\textsuperscript{-}} (aq) + H\textsubscript{2}O (l) \rightleftharpoons HC\textsubscript{2}H\textsubscript{3}O\textsubscript{2} (aq) + OH\textsuperscript{-} (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.03(\frac{3}{3}) M</td>
</tr>
<tr>
<td>(\Delta)</td>
<td>(-x)</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.03(\frac{3}{3})(-x)</td>
</tr>
</tbody>
</table>

\[
K_b = \frac{[\text{HC}_2\text{H}_3\text{O}_2] [\text{OH}^{-}]}{[\text{C}_2\text{H}_3\text{O}_2^-]} \approx \frac{x^2}{0.03\frac{3}{3} - x} = 5.88 \times 10^{-10}
\]

\[
x = [\text{OH}^{-}] = 4.43 \times 10^{-6} \text{ M}
\]

\[
pOH = -\log (4.43 \times 10^{-6}) = 5.35
\]

\[
pH = 14.00 - 5.35 = 8.65 \quad \text{(basic, as expected)}
\]

2. Calculate the pH at the equivalence point for the titration of 100. mL of 0.10 M acetic acid with 0.100 M sodium hydroxide. (\(K_a = 1.7 \times 10^{-5}\))
TITRATION OF A WEAK BASE BY A STRONG ACID

\[ \text{NH}_3 + \text{HCl(aq)} \rightarrow \text{NH}_4\text{Cl(aq)} \]

0.100 M 0.100 M
25.0 mL ?

**First Part of Titration:**
pH changes slowly at first (from about 11 to about 7)

**Second Part of Titration:**
pH changes rapidly from pH = 7 to pH = 3

- This range of pH change (7 to 3) is about the same as that of a titration of a Weak Acid by a Strong Base (7 to 11)
- The equivalence point occurs on the acidic side; the pH at the equivalence point is the pH of NH₄Cl(aq)
**Choice of Indicator to detect equivalence point**

- The indicator should change color within the pH range **3-7**
- Which indicators change color within the **pH range of 3-7**?

![Table of indicators and pH ranges](image)

**Note:**
- Because the range in which the rapid change of pH occurs is narrow (3 to 7), the choice of an indicator is more limited.

- The following indicators can be used:
  1. Bromphenol Blue
  2. Methyl Orange
  3. Bromcresol Green
  4. Methyl Red
CALCULATING THE PH AT THE EQUIVALENCE POINT IN THE TITRATION OF A WEAK BASE BY A STRONG ACID

**Examples:**
1. What is the pH at the equivalence point when 35 mL of 0.20 M ammonia is titrated by 0.12 M hydrochloric acid? (K_b for NH_3 is 1.8 x 10^{-5})

**First: Stoichiometry**

\[
\text{HCl (aq) + NH}_3 \text{ (aq)} \rightarrow \text{NH}_4\text{Cl (aq)}
\]

At the equivalence point:

# mmoles of NH_3 reacted = # mmoles of HCl reacted

\[
\text{HCl (aq) + NH}_3 \text{ (aq)} \rightarrow \text{NH}_4\text{Cl (aq)}
\]

\[
? \text{ mL} \quad 35 \text{ mL} \\
0.12 \text{ M} \quad 0.20 \text{ M}
\]

\[
\frac{0.20 \text{ mmol NH}_3}{1 \text{ mL}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NH}_3} \times \frac{1 \text{ mL HCl}}{0.12 \text{ mmol HCl}} = 58.3 \text{ mL HCl}
\]

\[
\text{HCl (aq) + NH}_3 \text{ (aq)} \rightarrow \text{NH}_4\text{Cl (aq)}
\]

\[
58.3 \text{ mL} \quad 35 \text{ mL} \\
0.12 \text{ M} \quad 0.20 \text{ M}
\]

<table>
<thead>
<tr>
<th></th>
<th>HCl</th>
<th>NH_3</th>
<th>\rightarrow</th>
<th>NH_4Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start</td>
<td>70. mmol</td>
<td>70. mmol</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>(\Delta)</td>
<td>-70. mmol</td>
<td>-70. mmol</td>
<td>+70. mmol</td>
<td></td>
</tr>
<tr>
<td>End</td>
<td>0</td>
<td>0 mmol</td>
<td>70. mmol</td>
<td></td>
</tr>
</tbody>
</table>

\[
\text{NH}_4\text{C l(aq)} \rightarrow \text{NH}_4^+ \text{(aq)} + \text{Cl}^- \text{(aq)}
\]

Note: # mmoles NH_4Cl = # mmoles NH_4^+ = 70. mmol

\[
[\text{NH}_4^+] = \frac{70. \text{ mmol}}{35 \text{ mL base} + 58.3 \text{ mL acid}} = 0.075 \text{ M}
\]
Second: Hydrolysis of the ammonium ion

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

\[ K_a(\text{NH}_4^+) = ? \]

Recall: \[ K_a(\text{NH}_4^+) \times K_b(\text{NH}_3) = K_w \]

\[ K_a(\text{NH}_4^+) = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10} \]

<table>
<thead>
<tr>
<th></th>
<th>\text{NH}_4^+ (aq)</th>
<th>\text{H}_2\text{O} (l)</th>
<th>\rightleftharpoons</th>
<th>\text{NH}_3 (aq)</th>
<th>\text{H}_3\text{O}^+ (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.075 M</td>
<td>-----</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>\Delta</td>
<td>-x</td>
<td>-----</td>
<td>+x</td>
<td>+x</td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.075\text{--}x</td>
<td>-----</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

\[ K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{x^2}{0.075 - x} \approx \frac{x^2}{0.075} = 5.56 \times 10^{-10} \]

\[ x = [\text{H}_3\text{O}^+] = 6.46 \times 10^{-6} \quad \text{pH} = -\log(6.46 \times 10^{-6}) = 5.19 \quad \text{(acidic, as expected)} \]

2. What is the pH at the equivalence point when 50 mL of 0.10 M ammonia is titrated by 0.25 M hydrochloric acid? (\(K_b\) for \(\text{NH}_3\) is 1.8 \times 10^{-5})
ACID-BASE TITRATIONS (SUMMARY)

HCl (aq) + NaOH (aq) \rightarrow NaCl(aq)

Solution is neutral at Equivalence Point
(Rapid Change of pH = 3-11)

HC₂H₃O₂ (aq) + NaOH (aq) \rightarrow NaC₂H₃O₂(aq)

Solution is basic at Equivalence Point
(Rapid Change of pH = 7-11)
ACID-BASE TITRATIONS (SUMMARY)

\[
\text{NH}_3 \text{(aq)} + \text{HCl} \text{(aq)} \rightarrow \text{NH}_4\text{Cl}
\]

Solution is **acidic** at Equivalence Point

**Rapid Change of pH=3.7**
SLIGHTLY SOLUBLE SOLIDS

- When a slightly soluble ionic compound is mixed with water, one of the following two phenomena may occur:

1. The amount of ionic compound is very small. As such:
   - it completely dissolves (completely dissociates into ions)
   - an unsaturated solution is formed
   - no undissolved solid remains

\[
\begin{align*}
H_2O & \rightarrow \\
\text{CaCO}_3 \text{ (s)} & \rightarrow \text{Ca}^{2+} \text{ (aq)} + \text{CO}_3^{2-} \text{ (aq)}
\end{align*}
\]

2. The amount of ionic compound is relatively large. As such:
   - it partially dissolves in water (partially dissociates into ions)
   - a saturated solution is formed
   - some of the solid remains undissolved
   - an equilibrium occurs between the undissolved solid and the ions in the solution

\[
\begin{align*}
H_2O & \rightarrow \\
\text{CaCO}_3 \text{ (s)} & \rightleftharpoons \text{Ca}^{2+} \text{ (aq)} + \text{CO}_3^{2-} \text{ (aq)}
\end{align*}
\]

Solubility Equilibrium

- The equilibrium constant for the solubility process is called the Solubility Product Constant of CaCO₃ (K_{sp})

\[
K_{sp} = [\text{Ca}^{2+}] \cdot [\text{CO}_3^{2-}]
\]
THE SOLUBILITY PRODUCT CONSTANT (K_{sp})

- K_{sp} is the equilibrium constant for the solubility equilibrium of a slightly soluble (or nearly insoluble) ionic compound.
- K_{sp} equals the product of the equilibrium concentrations of the ions, raised to a power equal to the number of the ions in the formula of the compound.
- K_{sp} depends on the concentration of the ions and is temperature dependent (constant at a given temperature).

**Examples:**
Write the solubility product expressions for the following compounds:

1) Mg(OH)_{2}

\[
\text{Mg(OH)}_2 (s) \rightleftharpoons \text{Mg}^{2+} (aq) + 2 \text{OH}^- (aq)
\]

\[K_{sp} = [\text{Mg}^{2+}] [\text{OH}^-]^2\]

2) Ca_{3}(PO_{4})_{2}

\[
\text{Ca}_3\text{(PO}_4\text{)}_2 (s) \rightleftharpoons 3 \text{Ca}^{2+} (aq) + 2 \text{PO}_4^{3-} (aq)
\]

\[K_{sp} = \]

3) Ag_{2}S

\[
\text{Ag}_2\text{S (s)} \rightleftharpoons
\]

\[K_{sp} = \]
AND RELATIVE SOLUBILITY

- Molar solubility and $K_{sp}$ are related and each can be calculated from the other. However, the $K_{sp}$ of two different compounds cannot be generally used to compare their molar solubility.

- For example, consider the $K_{sp}$ and molar solubilities of the two compounds shown below:

<table>
<thead>
<tr>
<th>Compound</th>
<th>$K_{sp}$</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(OH)$_2$</td>
<td>$2.06 \times 10^{-13}$</td>
<td>$3.72 \times 10^{-5}$ M</td>
</tr>
<tr>
<td>FeCO$_3$</td>
<td>$3.07 \times 10^{-11}$</td>
<td>$5.54 \times 10^{-6}$ M</td>
</tr>
</tbody>
</table>

- Magnesium hydroxide has a smaller $K_{sp}$ than iron(II) carbonate, but a higher molar solubility. Why?

- The relationship between $K_{sp}$ and molar solubility depends on the stoichiometry of the dissociation reaction.

\[
\text{Mg(OH)}_2 \rightarrow \text{Mg}^{2+} + 2 \text{OH}^- \\
\text{FeCO}_3 \rightarrow \text{Fe}^{2+} + \text{CO}_3^{2-}
\]

- Consequently, any direct comparison of the $K_{sp}$ and molar solubility of compounds can only be made if their dissociation reaction has the same stoichiometry.

- For example, when considering the $K_{sp}$ and molar solubilities shown below:

<table>
<thead>
<tr>
<th>Compound</th>
<th>$K_{sp}$</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(OH)$_2$</td>
<td>$2.06 \times 10^{-13}$</td>
<td>$3.72 \times 10^{-5}$ M</td>
</tr>
<tr>
<td>CaF$_2$</td>
<td>$1.46 \times 10^{-10}$</td>
<td>$3.32 \times 10^{-4}$ M</td>
</tr>
</tbody>
</table>

- Since both compounds have the same stoichiometry in their dissociation reaction, it would be appropriate to relate the lower $K_{sp}$ of magnesium hydroxide as indication of lower solubility.
CALCULATING WITH $K_{sp}$

1. $K_{sp}$ of a slightly soluble ionic compound is expressed in terms of the molar concentrations of ions in the saturated solution.

2. It is related to the **molar solubility** of the ionic compound.

3. **Molar Solubility** = moles of compound that dissolve in 1 L of water to give a saturated solution.

**Examples:**

1. The solubility of silver chromate, $\text{Ag}_2\text{CrO}_4$, in water is 0.022 g/L. Calculate $K_{sp}$ for $\text{Ag}_2\text{CrO}_4$

   (a) First calculate the Molar Solubility:

   \[
   \text{moles} = \frac{0.022 \text{ g Ag}_2\text{CrO}_4}{1 \text{ L water}} \times \frac{1 \text{ mole Ag}_2\text{CrO}_4}{332 \text{ g Ag}_2\text{CrO}_4} = 6.62 \times 10^{-5} \text{ M}
   \]

   (b) Next, consider the Solubility Equilibrium:

<table>
<thead>
<tr>
<th></th>
<th>$\text{Ag}_2\text{CrO}_4 (s)$</th>
<th>$\text{2 Ag}^+ (aq)$</th>
<th>$\text{CrO}_4^{2-} (aq)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-----</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>-----</td>
<td>$+2x$</td>
<td>$+x$</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>-----</td>
<td>$+2x$</td>
<td>$+x$</td>
</tr>
</tbody>
</table>

   (c) Write $K_{sp}$ expression and substitute the molar concentrations of the ions in the saturated solution:

   \[
   K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}] = (2x)^2 (x) = 4x^3
   \]

   \[
   x = 6.62 \times 10^{-5} \text{ M}
   \]

   \[
   K_{sp} = [2(6.62 \times 10^{-5})]^2 [6.62 \times 10^{-5}] = 1.2 \times 10^{-12}
   \]

2. $\text{PbSO}_4$ is used as a white pigment and in car batteries. Its solubility is $4.25 \times 10^{-3}$ g/100 mL solution. What is $K_{sp}$ for $\text{PbSO}_4$?
CALCULATING WITH $K_{sp}$

Examples:

3. What is the molar solubility of $\text{MgF}_2$ in water? The $K_{sp}$ for $\text{MgF}_2$ is $7.4 \times 10^{-11}$

Let $x$ = the molar solubility of $\text{MgF}_2$

<table>
<thead>
<tr>
<th></th>
<th>$\text{MgF}_2$ (s) $\rightleftharpoons$ $\text{Mg}^{2+}$ (aq) + 2 $\text{F}^-$ (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-----</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>-----</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>-----</td>
</tr>
</tbody>
</table>

Substitute from the table into the equilibrium-constant expression:

$[\text{Mg}^{2+}] [\text{F}^-]^2 = K_{sp}$

$(x)(2x)^2 = 4x^3 = 7.4 \times 10^{-11}$

$x = \sqrt[3]{\frac{7.4 \times 10^{-11}}{4}} = 2.6 \times 10^{-4}$ M

4. The $K_{sp}$ of magnesium carbonate is $1.0 \times 10^{-5}$. Calculate the solubility of magnesium carbonate in grams per liter of water.

Let $x$ = molar solubility of $\text{MgCO}_3$

<table>
<thead>
<tr>
<th></th>
<th>$\text{MgCO}_3$ (s) $\rightleftharpoons$ $\text{Mg}^{2+}$ (aq) + $\text{CO}_3^{2-}$ (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-----</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>-----</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>-----</td>
</tr>
</tbody>
</table>

$K_{sp} = [\text{Mg}^{2+}] [\text{CO}_3^{2-}]$

$K_{sp} = x^2 = 1.0 \times 10^{-5}$

$x = \sqrt{(1.0 \times 10^{-5})} = 3.16 \times 10^{-3}$ M

$\frac{3.16 \times 10^{-3} \text{ moles}}{1 \text{ mol MgCO}_3} \times \frac{84.32 \text{ g}}{1 \text{ mol MgCO}_3} = 0.27 \text{ g/L}$

$\frac{? \text{ g MgCO}_3}{1 \text{ L water}} \times \frac{1 \text{ mol MgCO}_3}{84.32 \text{ g}} = 0.27 \text{ g/L}$
SOLUBILITY AND THE COMMON ION EFFECT

- Consider the solubility of one salt in the solution of another salt having the same cation or anion:
  Ex: Solubility of AB in AC  Common cation: A⁺
  Solubility of AB in DB  Common anion: B⁻
- The effect of the common ion is to **decrease the solubility** of the salt

**Example:**
Consider what happens to the solubility of calcium oxalate, CaC₂O₄ in a solution of calcium chloride, CaCl₂

In pure water:  
CaC₂O₄(s) ⇌ Ca²⁺(aq) + C₂O₄²⁻(aq)

Add CaCl₂:  
CaCl₂(aq) -> Ca²⁺(aq) + 2 Cl⁻(aq)

**Result:**
- An increase in the concentration of [Ca²⁺] ions
- This is a “stress” on the solubility equilibrium of CaC₂O₄(s)
- The solubility equilibrium will shift to the left
- Solubility of CaC₂O₄ **decreases**.

**Conclusion:**
- CaC₂O₄(s) is less soluble in a solution of CaCl₂ than in pure water

**Application:**
- Kidney stones form when the concentrations of Ca²⁺ ions are sufficiently great and calcium oxalate or phosphate slowly precipitates in the kidney.
SOLUBILITY CALCULATIONS INVOLVING COMMON ION

**Examples:**
1. The solubility of silver sulfate, in water is 8.0 g/L at 25°C. Calculate the molar solubility of silver sulfate in water and in a 0.65 M solution of sodium sulfate at 25°C? K_{sp} of silver sulfate is not available.

(a) **First calculate molar solubility of Ag_{2}SO_{4} in water**

\[
\text{moles} \quad \frac{8.0 \text{ g Ag}_{2}\text{SO}_{4}}{1 \text{ L water}} \times \frac{1 \text{ mole Ag}_{2}\text{SO}_{4}}{311.81 \text{ g}} = 0.02565 \text{ M}
\]

(b) **Calculate K_{sp} of Ag_{2}SO_{4}**

|        | Ag_{2}SO_{4} (s) &\rightleftharpoons & 2 \text{ Ag}^{+} (aq) + \text{ SO}_{4}^{2-} (aq) |
|--------|------------------|---------------------------------|
| Initial| -----            | 0                               | 0                              |
| \Delta | -----            | + 2x                            | + x                            |
| Equilibrium | ----- | + 2x | + x |

\[
K_{sp} = [\text{Ag}^{2+}]^2 [\text{SO}_{4}^{2-}] = (2x)^2 (x) = 4x^3
\]

\[
x = 0.02565 \text{ M}
\]

\[
K_{sp} = (2 \times 0.02565)^2 (0.02565) = 6.755 \times 10^{-5}
\]

(c) **Use K_{sp} to calculate the molar solubility of Ag_{2}SO_{4} in 0.65 M Na_{2}SO_{4}**

\[
K_{sp} = [\text{Ag}^{2+}]^2 [\text{SO}_{4}^{2-}] = 6.755 \times 10^{-5}
\]

\[
[\text{Ag}^{+}] = 2x \quad [\text{SO}_{4}^{2-}] = 0.65 \quad \text{(from solution of 0.65 M Na}_{2}\text{SO}_{4})
\]

\[
K_{sp} = (2x)^2 (0.65) = 6.755 \times 10^{-5}
\]

\[
2.6x^2 = 6.755 \times 10^{-5}
\]

\[
x = \sqrt{\frac{6.755 \times 10^{-5}}{2.6}} = 5.1 \times 10^{-3} \text{ M}
\]

Compare:

0.026 M = molar solubility of Ag_{2}SO_{4} in water

0.00051 M = molar solubility of Ag_{2}SO_{4} in 0.65 M Na_{2}SO_{4} (much less)
2. Which of the following compounds should most affect the solubility of PbSO₄, lead(II) sulfate, in water to which it has been added?

(a) Na₂SO₄  (b) PbS  (c) NaCl

\[
PbSO₄(s) \rightleftharpoons Pb^{2+}(aq) + SO₄^{2-}(aq)
\]

<table>
<thead>
<tr>
<th></th>
<th>Na₂SO₄</th>
<th>PbS</th>
<th>NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>solubility</td>
<td>soluble salt</td>
<td>practically insoluble salt</td>
<td>soluble salt</td>
</tr>
<tr>
<td>K&lt;sub&gt;sp&lt;/sub&gt;</td>
<td>K&lt;sub&gt;sp&lt;/sub&gt; not listed</td>
<td>K&lt;sub&gt;sp&lt;/sub&gt; = 2.5 x 10⁻²⁷</td>
<td>K&lt;sub&gt;sp&lt;/sub&gt; not listed</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>SO₄²⁻ is common ion</td>
<td>Pb²⁺ is common ion</td>
<td>no common ion</td>
</tr>
<tr>
<td>decreases the solubility of PbSO₄ considerably</td>
<td>decreases the solubility of PbSO₄ very little</td>
<td>no effect on the solubility of PbSO₄</td>
<td></td>
</tr>
</tbody>
</table>

**NOTE:** Some basic solubility rules must be memorized at this point

Start by memorizing simple rules:

1. All Na⁺, K⁺, and NH₄⁺ salts are **soluble** (no exceptions)
2. All nitrates (NO₃⁻) are **soluble** (no exceptions)
3. All sulfides (S²⁻) are **insoluble** (exceptions: Na⁺, K⁺, and NH₄⁺ salts)
**PRECIPITATION CALCULATIONS**

- What concentration of ions will cause a substance:

  TO PRECIPITATE OR REMAIN IN SOLUTION?

- The answer is provided by the evaluation of $Q_c$ (reaction quotient)

Recall:
- If $Q_c < K_{eq}$ Reaction goes in the forward direction
- If $Q_c > K_{eq}$ Reaction goes in the reverse direction
- If $Q_c = K_{eq}$ Reaction mixture is at equilibrium

For a solubility equilibrium:

\[
\text{AB (s)} \rightleftharpoons \text{A}^+ (aq) + \text{B}^- (aq)
\]

\[Q_{sp} = [\text{A}^+] [\text{B}^-] = \text{Ion Product}\]

<table>
<thead>
<tr>
<th>$Q_{sp} &lt; K_{sp}$</th>
<th>$Q_{sp} = K_{sp}$</th>
<th>$Q_{sp} &gt; K_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution is unsaturated</td>
<td>Solution is saturated</td>
<td>Solution is saturated</td>
</tr>
<tr>
<td>Ionic compounds remain dissolved in solution</td>
<td>Ionic compound remains dissolved in solution</td>
<td>Ionic compound precipitates</td>
</tr>
<tr>
<td></td>
<td>Reaction is at equilibrium</td>
<td></td>
</tr>
</tbody>
</table>
Examples:
1. Assume a solution containing: 0.050 M Pb$^{2+}$ and 0.10 M Cl$^{-}$
   Will PbCl$_2$ precipitate? (K$_{sp}$ = 1.6 x 10$^{-5}$)

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

\[Q_{sp} = [Pb^{2+}]_i [Cl^{-}]_i^2\]

where:  
$[Pb^{2+}]_i$ = initial concentration of Pb$^{2+}$ = 0.050 M  
$[Cl^{-}]_i$ = initial concentration of Cl$^{-}$ = 0.10 M

\[Q_{sp} = [Pb^{2+}]_i [Cl^{-}]_i^2 = (0.050 \text{ M}) (0.10)^2 = 5.0 \times 10^{-4}\]

NOTE: 5.0 x 10$^{-4}$ > 1.6 x 10$^{-5}$

$Q_{sp} > K_{sp}$  Precipitation will occur

2. One form of kidney stones is calcium phosphate, Ca$_3$(PO$_4$)$_2$, which has a $K_{sp}$ of 1 x 10$^{-26}$. A sample of urine contains 1.0 x 10$^{-3}$ M Ca$^{2+}$ and 1.0 x 10$^{-8}$ M PO$_4^{3-}$. Calculate Qc and predict whether Ca$_3$(PO$_4$)$_2$ will precipitate.

\[
Ca_3(PO_4)_2 (s) \rightleftharpoons 3 Ca^{2+}(aq) + 2 PO_4^{3-}(aq)
\]

\[Q_{sp} = [Ca^{2+}]_i^3 [PO_4^{3-}]_i^2\]

where:  
$[Ca^{2+}]_i$ = initial concentration of Ca$^{2+}$ = 1.0 x 10$^{-3}$ M  
$[PO_4^{3-}]_i$ = initial concentration of PO$_4^{3-}$ = 1.0 x 10$^{-8}$ M

\[Q_{sp} = (1.0 \times 10^{-3})^3 (1.0 \times 10^{-8})^2 = 1.0 \times 10^{-25}\]

NOTE: 1.0 x 10$^{-25}$ > 1.0 x 10$^{-26}$

$Q_{sp} > K_{sp}$  Precipitation will occur
Examples:
3. Exactly 0.400 L of 0.50 M Pb\(^{2+}\) and 1.60 L of 2.50 \times 10^{-2} M Cl\(^{-}\) are mixed together. Calculate Qc and predict whether PbCl\(_2\) will precipitate. The Ksp of PbCl\(_2\) is 1.6 \times 10^{-5}.

**First:** Calculate the molar concentrations of each ion present
(Assume that the total volume of the solution after mixing equals the sum of the volumes of the separate solutions)

Total Volume = 0.400 L + 1.60 L = 2.00 L

\[
\begin{align*}
[\text{Pb}^{2+}] &= 0.50 \text{ M} \times \frac{0.400 \text{ L}}{2.00 \text{ L}} = 0.10 \text{ M} \\
[\text{Cl}^{-}] &= 2.50 \text{ M} \times \frac{1.60 \text{ L}}{2.00 \text{ L}} = 0.0200 \text{ M} \\
\text{PbCl}_2 (s) &\rightleftharpoons \text{Pb}^{2+}\text{(aq)} + 2 \text{Cl}^{-}\text{(aq)}
\end{align*}
\]

\[Q_{sp} = [\text{Pb}^{2+}]_i [\text{Cl}^{-}]_i^2 = [0.10 \text{ M}] [0.0200]^2 = 4.0 \times 10^{-5}\]

NOTE: \(4.0 \times 10^{-5} > 1.6 \times 10^{-5}\)

\(Q_{sp} > K_{sp}\) \quad Precipitation will occur

4. A solution of Pb(NO\(_3\))\(_2\) is mixed with one containing NaBr. If the concentration of Pb(NO\(_3\))\(_2\) in the final mixture is 0.0150M, what must be the concentration of Br\(^{-}\) for a precipitation of PbBr\(_2\) to occur? (K\(_{sp}\) of PbBr\(_2\) = 4.67\times10^{-6})
FRACTIONAL PRECIPITATION

- The technique of separating two or more ions from a solution by adding a reactant that precipitates first one ion, then another, is called **fractional precipitation**.

- For example, suppose a solution contains 0.10 M $\text{Ba}^{2+}$ and 0.10 M $\text{Sr}^{2+}$.
  
  ➢ The two ions can be separated by slowly adding a concentrated solution of $\text{K}_2\text{CrO}_4$.
  
  ➢ $\text{Ksp (BaCrO}_4) = 1.2 \times 10^{-10}$ and $\text{Ksp (SrCrO}_4) = 3.5 \times 10^{-5}$
  
  ➢ $\text{BaCrO}_4$ will precipitate **first**; $\text{SrCrO}_4$ will precipitate **second**. Why?

![K_2CrO_4](image)

- What is the concentration of $\text{K}_2\text{CrO}_4$ necessary to just begin the precipitation of $\text{BaCrO}_4$?

  \[
  [\text{Ba}^{2+}][\text{CrO}_4^{2-}] = \text{Ksp (for BaCrO}_4) = 1.2 \times 10^{-10}
  
  [0.10 \text{ M}][\text{CrO}_4^{2-}] = 1.2 \times 10^{-10} \quad [\text{CrO}_4^{2-}] = 1.2 \times 10^{-9} \text{ M}
  \]

- What is the concentration of $\text{K}_2\text{CrO}_4$ necessary to just begin the precipitation of $\text{SrCrO}_4$?

  \[
  [\text{Sr}^{2+}][\text{CrO}_4^{2-}] = \text{Ksp (for SrCrO}_4) = 3.5 \times 10^{-5}
  
  [0.10 \text{ M}][\text{CrO}_4^{2-}] = 3.5 \times 10^{-5} \quad [\text{CrO}_4^{2-}] = 3.5 \times 10^{-4} \text{ M}
  \]

Note: $[\text{CrO}_4^{2-}]$ to ppt $\text{Ba}^{2+} < [\text{CrO}_4^{2-}]$ to ppt $\text{Sr}^{2+}$

\[
1.2 \times 10^{-9} \text{ M} < 3.5 \times 10^{-4} \text{ M}
\]
Examples:
1. The magnesium and calcium ions present in seawater ([Mg\(^{2+}\)] = 0.059 M and [Ca\(^{2+}\)] = 0.011 M) can be separated by addition of KOH to precipitate the insoluble hydroxides.
   (a) Based on the $K_{sp}$ values given below, which ion precipitates first?

   $K_{sp}$ for Mg(OH)$_2$ = 2.06x10\(^{-13}\)  
   $K_{sp}$ for Ca(OH)$_2$ = 4.68x10\(^{-6}\)

   (b) What is the minimum [OH\(^-\)] that is required for the first ion to precipitate?
QUALITATIVE EFFECT OF pH ON SOLUBILITY

- Consider the solubility equilibrium of calcium oxalate, CaC₂O₄:

  \[
  \text{CaC}_2\text{O}_4 (s) \rightleftharpoons \text{Ca}^{2+} (aq) + \text{C}_2\text{O}_4^{2-} (aq)
  \]

- What would be effect (if any) of lowering the pH on the solubility equilibrium? **CaC₂O₄ is the salt of a weak acid (oxalic acid, H₂C₂O₄)**

- Recall: pH is lowered when [H₃O⁺] is increased (acid is added)

- C₂O₄²⁻ is the conjugate base of the weak acid HC₂O₄⁻

Therefore:

\[
\text{C}_2\text{O}_4^{2-} + \text{H}_3\text{O}^+ \rightleftharpoons \text{HC}_2\text{O}_4^- + \text{H}_2\text{O}
\]

- Equilibrium is shifted to the right (products are favored)

\[
\text{CaC}_2\text{O}_4 (s) \rightleftharpoons \text{Ca}^{2+} (aq) + \text{C}_2\text{O}_4^{2-} (aq)
\]

  **H₃O⁺ added**  **(HC₂O₄⁻ + H₂O) formed**

Result:

1. C₂O₄²⁻(aq) is removed from the solubility equilibrium

2. According to Le Chatelier’s principle, the solubility equilibrium will shift to the right

3. More CaC₂O₄(s) will dissolve

Conclusion:

- Salts of weak acids are more soluble in acidic solution (pH < 7) than in pure water (pH = 7)
**Example:**
Which salt would have its solubility more affected by lowering the pH, AgCl or AgCN?

1. AgCl is the salt of HCl (strong acid)

\[
\text{AgCl (s)} \rightleftharpoons \text{Ag}^+ (\text{aq}) + \text{Cl}^- (\text{aq})
\]

- H$_3$O$^+$ added
- No Rxn

- Cl$^-$ is not removed from the solubility equilibrium
- Solubility equilibrium will not shift

**The solubility of AgCl is unaffected**

2. AgCN is the salt of HCN (weak acid)

\[
\text{AgCN (s)} \rightleftharpoons \text{Ag}^+ (\text{aq}) + \text{CN}^- (\text{aq})
\]

- H$_3$O$^+$ added
- HCN + H$_2$O

- CN$^-$ is removed from the solubility equilibrium
- Solubility equilibrium will shift to the right

**The solubility of AgCN increases**

**Generalization:**
- Lowering of the pH (increased acidity) increases the solubility of salts derived from weak acids but has no effect on the solubility of salts derived from strong acids.
COMPLEX-ION EQUILIBRIA

- Complex ions are ions that form from transition metal ions attached to molecules or anions by coordinate covalent bonds

\[
\text{Ag}^+ (aq) \ + \ :\text{NH}_3 (aq) \rightleftharpoons \left[ \begin{array}{c} \text{Ag} \\ \text{NH}_3 \end{array} \right] (aq)
\]

Lewis base (electron pair donor)
coordinate covalent bond

\[
\text{H}_3\text{N}: (aq) \ + \ \left[ \begin{array}{c} \text{Ag} \\ \text{NH}_3 \end{array} \right] (aq) \rightleftharpoons \left[ \begin{array}{c} \text{H}_3\text{N} \\ \text{Ag} \\ \text{NH}_3 \end{array} \right] (aq)
\]

Lewis base (electron pair donor)
coordinate covalent bonds

Overall

\[
\text{Ag}^+ (aq) \ + \ 2 \text{NH}_3 (aq) \rightleftharpoons \text{Ag(NH}_3\text{)}^2+ (aq)
\]

- Ligand is a Lewis base (electron pair donor) that bonds to a metal ion by a coordinate covalent bond to form a complex ion (ex: NH$_3$)

Note: Different ligands usually impart different colors to the complex ions in solution:
# COMPLEX-ION FORMATION

\[ \text{Ag}^+(aq) + 2 \text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3)_2^+(aq) \]

<table>
<thead>
<tr>
<th>( K_d )</th>
<th>( K_f )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>The Dissociation Constant</strong></td>
<td><strong>The Formation Constant</strong></td>
</tr>
<tr>
<td>( K_d = \frac{[\text{Ag}^+] [\text{NH}_3]^2}{[\text{Ag(NH}_3)_2^+]} )</td>
<td>( K_f = \frac{[\text{Ag(NH}_3)_2^+]}{[\text{Ag}^+] [\text{NH}_3]^2} )</td>
</tr>
</tbody>
</table>

- The equilibrium constant for the **dissociation of the complex ion** into a metal ion and the ligands
- The dissociation constant for the **formation of the complex ion** from the aqueous metal ion and the ligands
- Also called "the stability constant"

\( K_d \) is the reciprocal of \( K_f \)

\[ K_d = \frac{1}{K_f} \]

\( K_f \) is the reciprocal of \( K_d \)

\[ K_f = \frac{1}{K_d} \]
EQUILIBRIUM CALCULATIONS WITH $K_f$

What is the concentration of Cu$^{2+}$(aq) in a solution that was originally 0.015 M Cu(NO$_3$)$_2$ and 0.100 M NH$_3$? The Cu$^{2+}$ ion forms the complex ion Cu(NH$_3$)$_4^{2+}$ ($K_f = 4.8 \times 10^{12}$).

**Step 1: Stoichiometry Calculation:**

<table>
<thead>
<tr>
<th>Amounts present in 1L:</th>
<th>Cu$^{2+}$(aq)</th>
<th>4 NH$_3$(aq)</th>
<th>Cu(NH$_3$)$_4^{2+}$(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amounts reacting:</td>
<td>0.015 mol</td>
<td>0.100 mol</td>
<td>0</td>
</tr>
<tr>
<td>Amount present at equil.</td>
<td>0</td>
<td>(0.100 – 0.060) = 0.040 mol</td>
<td>0.015 mol</td>
</tr>
</tbody>
</table>

**Step 2: Equilibrium Calculation:**

<table>
<thead>
<tr>
<th></th>
<th>Cu$^{2+}$(aq)</th>
<th>4 NH$_3$(aq)</th>
<th>Cu(NH$_3$)$_4^{2+}$(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0</td>
<td>0.040</td>
<td>0.015</td>
</tr>
<tr>
<td>Change</td>
<td>+ x</td>
<td>+4 x</td>
<td>– x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>x</td>
<td>0.040 + x</td>
<td>0.015 – x</td>
</tr>
</tbody>
</table>

$$K_f = \frac{[\text{Cu(NH}_3\text{)}_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4} = \frac{(0.015 - 4x)}{(x)(0.040 + 4x)^4}$$

$X$ is negligible compared to 0.015 and negligible compared to 0.040.

$$K_f = \frac{0.015}{(X)(0.040)^4} = 4.8 \times 10^{12} \quad x = [\text{Cu}^{2+}] = 1.2 \times 10^{-9} \text{ M}$$
AMPHOTERIC HYDROXIDES

Solubility Rule of the Day:
- **Metallic Hydroxides are insoluble.**
  - Exceptions: Hydroxides of Group IA metals (LiOH, NaOH, KOH)
  - Hydroxides of Group IIA metals: Mg(OH)₂, Ca(OH)₂, Sr(OH)₂, Ba(OH)₂

| Amphoteric Hydroxides is a metal hydroxide that reacts with both: Acids and Bases |
|---|---|
| Zn(OH)₂(s) + 2 HCl(aq) (l) → ZnCl₂(aq) + 2 H₂O | Zn(OH)₂(s) + 2 NaOH(aq) (aq) → Na₂[Zn(OH)₄] (aq) sodium zincate |
| Zn(OH)₂(s) + 2 H⁺(aq) → Zn²⁺(aq) + 2 H₂O(l) zinc cation | Zn(OH)₂(s) + 2 OH⁻(aq) → Zn(OH)₄²⁻(aq) zincate ion |
| Al(OH)₃(s) + 3 HCl(aq) (l) → AlCl₃(aq) + 3 H₂O | Al(OH)₃(s) + NaOH(aq) → Na[Al(OH)₄](aq) sodium aluminolate |
| Al(OH)₃(s) + 3 H⁺(aq) → Al³⁺(aq) + 3 H₂O(l) aluminum cation | Al(OH)₃(s) + OH⁻(aq) → Al(OH)₄⁻(aq) aluminolate ion |

Laboratory Applications of Amphoteric Hydroxides
- The identity of some metallic cations can be established by knowing that they can form amphoteric hydroxides.

Example: Consider an aqueous solution of ZnCl₂(aq)

1. If a strong base is added to this solution a precipitate forms:
   \[
   \text{ZnCl}_2(\text{aq}) + 2 \text{NaOH(\text{aq})} \rightarrow \text{Zn(OH)}_2(\text{s}) + 2 \text{NaCl(\text{aq})}
   \]
   \[
   \text{Zn}^{2+}(\text{aq}) + 2 \text{OH}^-(\text{aq}) \rightarrow \text{Zn(OH)}_2(\text{s}) \quad \text{insoluble}
   \]

2. If more of the strong base is added, the precipitate dissolves:
   \[
   \text{Zn(OH)}_2(\text{s}) + 2 \text{NaOH(\text{aq})} \rightarrow \text{Na}_2[\text{Zn(OH)}_4](\text{aq}) \quad \text{soluble}
   \]
   \[
   \text{Zn(OH)}_2(\text{s}) + 2 \text{OH}^-(\text{aq}) \rightarrow \text{Zn(OH)}_4^{2-}(\text{aq}) \quad \text{complex anion}
   \]

- Other metallic cations that form insoluble hydroxides that dissolve in excess of strong base added: Al³⁺, Cr³⁺, Pb²⁺, Sn²⁺, and Sn⁴⁺
AN INDUSTRIAL APPLICATION OF AN AMPHOTERIC HYDROXIDE

- The amphoterism of Al(OH)$_3$ is used in the industrial process by which Aluminum metal is obtained.
- **Aluminum ore**: Bauxite (hydrated Al$_2$O$_3$ + SiO$_2$ + Fe$_2$O$_3$ + impurities)
- **Goal**: to obtain pure Al(OH)$_3$ from which Al is extracted by electrolysis.

![Diagram of the process]

- **Bauxite suspended in water**
- **NaOH**
- **Filtration**
- **Solution**: dissolved Na[Al(OH)$_4$]  
  Na$^+$ (aq) + Al(OH)$_4$ (aq)
- **Undissolved material**: SiO$_2$(s) + Fe$_2$O$_3$(s) + impurities
- **Waste**
- **Al(OH)$_3$(s)** + H$_2$O(l) **pure**
COMPLEX IONS AND SOLUBILITY

- The formation of a complex ion reduces the concentration of the metallic ion in solution.
- Consider a 0.010 M AgNO₃ solution.
  - In pure water: \([\text{Ag}^+](\text{aq}) = 0.010 \text{ M}\)
  - In 1.00 M NH₃: \([\text{Ag}^+](\text{aq}) = 6.1 \times 10^{-10} \text{ M}\)

**Consequences:**
1. The ion product for a slightly soluble salt could be decreased by complexation below the Ksp value.
2. A slightly soluble salt that:
   - would precipitate in an aqueous solution
   - might not precipitate in a solution that provides ligands for complexation

**Examples:**
1. Predict whether nickel(II) hydroxide, \(\text{Ni(OH)}_2\), will precipitate from a solution that is 0.0020 M NiSO₄, 0.010 M NaOH, and 0.100 M NH₃. Note that the nickel(II) ion forms the \(\text{Ni(NH}_3\)_6}^{2+}\) complex ion with a \(K_f = 5.6 \times 10^8\).
   The Ksp for \(\text{Ni(OH)}_2\) is \(2.0 \times 10^{-15}\)

Net Ionic: \[\text{Ni}^{2+} (\text{aq}) + 2\text{OH}^- (\text{aq}) \xrightarrow{\text{NH}_3} \frac{\text{Ni(OH)}_2(s)}{?}\]

- Will a precipitate of \(\text{Ni(OH)}_2\) form or not?

**Step 1: Stoichiometry & Equilibrium Calculation:**

<table>
<thead>
<tr>
<th></th>
<th>Ni²⁺(aq)</th>
<th>6 NH₃(aq)</th>
<th>(\text{Ni(NH}_3)_6}^{2+}(\text{aq}))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initial</strong></td>
<td>0.0020</td>
<td>0.100</td>
<td>0</td>
</tr>
<tr>
<td><strong>Change</strong></td>
<td>−0.0020</td>
<td>−0.012</td>
<td>+0.0020</td>
</tr>
<tr>
<td><strong>End</strong></td>
<td>0</td>
<td><strong>0.088</strong></td>
<td><strong>0.0020</strong></td>
</tr>
<tr>
<td><strong>Change</strong></td>
<td>+x</td>
<td>+6x</td>
<td>−x</td>
</tr>
<tr>
<td><strong>Equilibrium</strong></td>
<td>x</td>
<td>0.088+6x</td>
<td>0.0020−x</td>
</tr>
</tbody>
</table>
Step 2: Calculation of Ion Product for Ni(OH)$_2$

\[
\text{Ni}^{2+} \text{(aq)} + 2 \text{OH}^- \text{(aq)} \rightleftharpoons \text{Ni(OH)}_2 \text{(s)}
\]

K$_{sp}$ = 2.0 x 10$^{-15}$

Actual Conc's:
- Ni$^{2+}$: 7.69 x 10$^{-6}$ M
- OH$^-$: 0.010 M

Q$_c$ = [Ni$^{2+}$][OH$^-$]$^2$ = (7.69 x 10$^{-6}$)(0.010)$^2$ = 7.69 x 10$^{-10}$

Note: 7.69 x 10$^{-10}$ > 2.0 x 10$^{-15}$

- The solution is supersaturated before equilibrium.
- At equilibrium a precipitate of Ni(OH)$_2$(s) will form and the solution will become saturated.

Ni$^{2+}$ (aq) + 2 OH$^-$ (aq) $\xrightarrow{\text{precipitation}}$ Ni(OH)$_2$ (s)
Examples:
2. What is the molar solubility of NiS in 0.10 M NH₃?
   (Ksp for NiS = 3.0 x 10⁻¹⁹ and Kf for Ni(NH₃)₆²⁺ = 5.6 x 10⁻⁸)

Step 1: Write the solubility equilibrium and the complex-ion equilibrium:

\[
\begin{align*}
\text{NiS (s)} & \rightleftharpoons \text{Ni}^{2+}(aq) + \text{S}^{2-}(aq) & \text{Ksp} = 3.0 \times 10^{-19} \\
\text{Ni}^{2+}(aq) + 6 \text{NH}_3(aq) & \rightleftharpoons \text{Ni(NH}_3)_6^{2+}(aq) & \text{Kf} = 5.6 \times 10^{-8}
\end{align*}
\]

If you add the two equilibria the overall equilibrium for dissolving the NiS in NH₃ is obtained:

\[
\text{NiS (s)} + 6 \text{NH}_3(aq) \rightleftharpoons \text{Ni(NH}_3)_6^{2+}(aq) + \text{S}^{2-}(aq) \quad \text{Kc} = ?
\]

- Recall: Kc for the overall equilibrium is the product of the two equilibrium constants:
  \[
  \text{Kc} = \text{Ksp} \times \text{Kf} = (3.0 \times 10^{-19}) (5.6 \times 10^{-8}) = 1.7 \times 10^{-10}
  \]

Step 2: Equilibrium Calculation:

\[
\begin{array}{|c|c|c|c|c|}
\hline
\text{NiS (s)} + 6 \text{NH}_3(aq) & \leftrightarrow & \text{Ni(NH}_3)_6^{2+}(aq) + \text{S}^{2-}(aq) \\
\hline
\text{Initial}  & ----- & 0.10 & 0 & 0 \\
\text{Change}   & ----- & -6x & +x & +x \\
\text{Equilibrium} & ----- & 0.10 - 6x & x & x \\
\hline
\end{array}
\]

\[
\text{Kc} = \frac{[\text{Ni(NH}_3)_6^{2+}] [\text{S}^{2-}]}{[\text{NH}_3]^6} = \frac{x^2}{(0.10 - 6x)^6} = 1.7 \times 10^{-10}
\]

Taking the square root of both sides:

\[
\frac{x}{(0.10)^3} = 1.3 \times 10^{-5}
\]

\[
x = \text{Molar Solubility of NiS in 0.10 M NH}_3
\]

\[
x = 1.3 \times 10^{-8} \text{ M}
\]
Qualitative analysis is the determination of the presence of a metallic ion in the mixture by which a cation is detected by the presence of a characteristic precipitate.

**The Sulfide Scheme**

Divides metallic ions into 5 analytical groups:

- **Analytical Group I ions**: $\text{Ag}^{+}$, $\text{Hg}^{2+}$ [mercurous, or mercury (I)], and $\text{Pb}^{2+}$
  - These ions are separated from a solution of other ions by adding dilute hydrochloric acid

  $$\begin{align*}
  \text{Ag}^{+}, \\
  \text{Hg}^{2+}, \\
  \text{Pb}^{2+} \\
  + \quad \text{HCl(aq)}
  \end{align*}$$

  $\text{AgCl(s)}$, $\text{Hg}_2\text{Cl}_2(s)$, $\text{PbCl}_2(s)$

- **Analytical Group II ions**: $\text{As}^{3+}$, $\text{Bi}^{3+}$, $\text{Cd}^{2+}$, $\text{Cu}^{2+}$, $\text{Hg}^{2+}$, $\text{Pb}^{2+}$, $\text{Sb}^{3+}$, and $\text{Sn}^{4+}$
  - These ions are separated from a solution by precipitation with an acidic solution of $\text{H}_2\text{S}$

  $$\begin{align*}
  \text{As}^{3+}, \text{Bi}^{3+}, \text{Cd}^{2+}, \\
  \text{Cu}^{2+}, \text{Hg}^{2+}, \text{Pb}^{2+} \\
  + \quad \text{H}_2\text{S} \\
  \text{Sb}^{3+}, \text{and} \quad \text{Sn}^{4+}
  \end{align*}$$

  0.3 M $\text{H}_3\text{O}^+$

  As$_2$S$_3$  Bi$_2$S$_3$  CdS  CuS  HgS  PbS  Sb$_2$S$_3$  SnS$_2$

- **Analytical Group III ions**: $\text{Co}^{2+}$, $\text{Fe}^{2+}$, $\text{Mn}^{2+}$, $\text{Ni}^{2+}$, $\text{Zn}^{2+}$, $\text{Al}^{3+}$, $\text{Cr}^{3+}$
  - These ions are separated from a solution by precipitation with a weakly basic solution of $\text{H}_2\text{S}$

  $$\begin{align*}
  \text{Co}^{2+}, \text{Fe}^{2+}, \text{Mn}^{2+} \\
  \text{Ni}^{2+}, \text{Zn}^{2+} \\
  \text{Al}^{3+}, \text{Cr}^{3+} \\
  + \quad \text{H}_2\text{S}
  \end{align*}$$

  $\text{OH}^-$

  CoS  FeS  MnS  NiS  ZnS  Al(OH)$_3$  Cr(OH)$_3$

  sulfide or hydroxide precipitates

  that can be filtered off
Analytical Group IV ions: Alkaline earth metals (Group IIA): Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$,

- These ions are separated from a solution by precipitation with a solution of (NH$_4$)$_2$CO$_3$ or (NH$_4$)$_3$PO$_4$.

\[
\begin{array}{c}
\text{Mg}^{2+}, \text{Ca}^{2+} \\
\text{Sr}^{2+}, \text{Ba}^{2+}
\end{array} \xrightarrow{\text{(NH}_4\text{)}_2\text{CO}_3 \text{ or } (\text{NH}_4\text{)}_3\text{PO}_4} \begin{array}{c}
\text{MgCO}_3 \quad \text{CaCO}_3 \quad \text{SrCO}_3 \quad \text{BaCO}_3 \\
\text{or} \\
\text{Mg}_3(\text{PO}_4)_2 \quad \text{Ca}_3(\text{PO}_4)_2 \quad \text{Sr}_3(\text{PO}_4)_2 \quad \text{Ba}_3(\text{PO}_4)_2
\end{array}
\]

Carbonate or phosphate precipitates that can be filtered off.

Analytical Group V ions: Alkaline metals (Group IIA): Na$^+$ and K$^+$,

- These ions remain in the filtrate after filtering off all of the precipitates.

- These ions do not form any precipitates since all their compounds are soluble.
SEPARATION FLOW CHART

Mixture of metal ions

Analytical Group I
(Ag⁺, Hg₂²⁺, Pb²⁺)
Precipitated as chlorides

Filtrate of soluble metal chlorides

Add H₂S in 0.3M H₃O⁺

Analytical Group II
(As³⁺, Bi³⁺, Cd²⁺, Cu²⁺, Hg²⁺, Pb²⁺, Sb³⁺, Sn⁴⁺)
Precipitated as sulfides

Filtrate of metal sulfides soluble in 0.3M H₃O⁺

Add H₂S in dilute NH₃

Analytical Group III
(Co²⁺, Fe²⁺, Mn²⁺, Ni²⁺, Zn²⁺, Al³⁺, Cr³⁺)
Precipitated as sulfides except for Al(OH)₃ and Cr(OH)₃

Filtrate of metal ions not precipitated by H₂S or HCl

Add (NH₄)₂CO₃ or (NH₄)₃PO₄

Analytical Group IV
(Mg²⁺, Ca⁺, Sr²⁺, Ba²⁺)
Precipitated as carbonates or phosphates

Analytical Group V
(Na⁺, K⁺)
Filterate
EXAMPLE OF SEPARATION OF A MIXTURE OF FIVE METALLIC CATIONS

**Mixture of Ag⁺, Cu²⁺, Zn²⁺, Ca²⁺ and Na⁺**

1. **Analytical Group I**
   - Ag⁺ precipitated as AgCl (can be filtered off)

2. **Filtrate of soluble chlorides**
   - (Cu⁺, Zn²⁺, Ca²⁺, Na⁺)

3. **Analytical Group II**
   - Cu²⁺ precipitated as CuS (can be filtered off)

4. **Filtrate of metal sulfides**
   - soluble in 0.3M H₃O⁺ (Zn²⁺, Ca²⁺, and Na⁺)

5. **Analytical Group III**
   - Zn²⁺ precipitated as ZnS (can be filtered off)

6. **Filtrate of metal ions not precipitated by H₂S or HCl**
   - (Ca²⁺ and Na⁺)

7. **Analytical Group IV**
   - Ca⁺ precipitated as CaCO₃ (can be filtered off)

8. **Filtrate of metal ions not precipitated by H₂S or HCl**

9. **Analytical Group V**
   - Na⁺
**SEPARATION OF A MIXTURE OF GROUP I METALLIC CATIONS**

**Mixture of Ag\(^+\), Hg\(^{2+}\), Pb\(^{2+}\)**

- **Add dilute HCl (aq)**
  - Ag\(^+\), Hg\(^{2+}\) and Pb\(^{2+}\) precipitate as AgCl, Hg\(_2\)Cl\(_2\) and PbCl\(_2\)

- **Add hot water**
  - Mixture of precipitates of AgCl and Hg\(_2\)Cl\(_2\)
    - (insoluble in hot water; can be filtered off)
  - Filtrate containing Pb\(^{2+}\)
    - (can be identified by adding K\(_2\)CrO\(_4\))
    - Pb\(^{2+}\) (aq) + CrO\(_4^{2-}\) (aq) → PbCrO\(_4\) (s)

- **Add NH\(_3\) solution**
  - Hg\(^{2+}\) forms a black ppt
    - HgNH\(_2\)Cl (s) + Hg (l)
  - Ag\(^+\) dissolves and forms a stable soluble complex ion
    - Ag(NH\(_3\))\(^2+\) (aq) + Cl\(^-\) (aq)

- **Add HCl (aq)**
  - If Ag\(^+\) is present, a white ppt of AgCl forms
    - Ag(NH\(_3\))\(^+\) (aq) + 2 HCl (aq) → AgCl (s) + 2 NH\(_4^+\) (aq)