Chapter 16: Acid-Base Equilibria

- In the 1st half of this chapter we will focus on the equilibria that exist in aqueous solutions containing:
  - weak acids
  - polyprotic acids
  - weak bases
  - salts

- use equilibrium tables to determine:
  - equilibrium composition of solutions
  - pH
  - % ionization
  - $K_a$ or $K_b$

- In the 2nd half of the chapter, our focus will shift to understanding solutions in which there is some combination of acidic and basic species:
  - buffer solutions
  - titration experiments

- We will need to consider that neutralization reactions can/will occur, as well as the equilibria that exist.

- use multiple steps:
  - determine the pH of solutions after neutralization reactions are complete
  - construct and interpret titration curves

Steps for solving weak acid equilibrium problems:
1. Identify all major species in solution.
2. Identify all potential $H^+$ transfer reactions that could contribute to the $[H_3O^+]_{total}$ in the sol’n.
3. By considering K values, determine the dominant source of $H_3O^+$ in the solution.
4. Set up the equilibrium calculation based on equilibrium identified in step 3.
5. Solve!
   - $x = [H_3O^+]$
   - solve for pH, % ionization, or $K_a$
Determine the pH of 0.10 M HCN (aq). For HCN, $K_a = 4.9 \times 10^{-10}$.

1. Identify all major species in solution.
   - this is an aqueous solution of a weak acid, so the major species are: HCN & H$_2$O

2. Identify all potential H$^+$ transfer reactions that could contribute to the $[\text{H}_3\text{O}^+]_{\text{total}}$ in the sol'n.
   - there are 2 possible sources of H$_3$O$^+$ in this sol'n:
     HCN (aq) + H$_2$O (aq) $\rightleftharpoons$ CN$^-$ (aq) + H$_3$O$^+$ (aq); $K_a = 4.9 \times 10^{-10}$
     2 H$_2$O (l) $\rightleftharpoons$ H$_3$O$^+$ (aq) + OH$^-$ (aq); $K_W = 1 \times 10^{-14}$

3. By considering $K$ values, determine the dominant source of H$_3$O$^+$ in the solution.
   - there are 2 possible sources of H$_3$O$^+$ in this sol'n:
     HCN (aq) + H$_2$O (aq) $\rightleftharpoons$ CN$^-$ (aq) + H$_3$O$^+$ (aq); $K_a = 4.9 \times 10^{-10}$
     2 H$_2$O (l) $\rightleftharpoons$ H$_3$O$^+$ (aq) + OH$^-$ (aq); $K_W = 1 \times 10^{-14}$

   - $K_a > K_W$, so the acid ionization of HCN will be the dominant source of H$_3$O$^+$ in his solution.

   - use a simplifying approximation
     Because $K_a$ is very small, the reaction does not proceed very far forward (toward products) before reaching equilibrium.

     We will assume that “x” in the denominator will be negligibly small relative to $[\text{HCN}]_0$.

   - $0.10 - x \approx 0.10$

4. Set up the equilibrium calculation based on equilibrium identified in step 3.

<table>
<thead>
<tr>
<th></th>
<th>HCN (aq) + H$_2$O (l) $\rightleftharpoons$ CN$^-$ (aq) + H$_3$O$^+$ (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.10 M --- 0 0</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>$-x$ --- $+x$ $+x$</td>
</tr>
<tr>
<td>equil</td>
<td>$(0.10-\text{x})\text{M}$ --- $\times\text{M}$ $\times\text{M}$</td>
</tr>
</tbody>
</table>

   $K_a = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]}$; $4.9 \times 10^{-10} = \frac{x^2}{0.10 - x}$
example:
Determine the pH of 0.10 M HCN (aq). For HCN, $K_a = 4.9 \times 10^{-10}$.

solution:

$$4.9 \times 10^{-10} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10}$$

$$x = 7.0 \times 10^{-6}$$

so at equilibrium:

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

$$[HCN] = 0.10 \text{ M}$$

$$pH = -\log (7.0 \times 10^{-6}) = 5.15$$

example:
Determine the pH and % ionization of 0.0100 M CH$_3$COOH (aq). For acetic acid, $K_a = 1.8 \times 10^{-5}$.

Percent Ionization

- What percentage of a weak acid originally present is in its ionized form at equilibrium?

$$\text{percent ionization} = \frac{[HA]_{\text{ionized}}}{[HA]_0} \times 100$$

- percent ionization is another way that we can assess the acidity of a solution and strength of an acid.

$\text{greater % ionization} \rightarrow \text{higher [ion]}$

$\text{higher [ion]} \rightarrow \text{higher [H}_3\text{O}^+]$

$\text{higher [H}_3\text{O}^+] \rightarrow \text{lower pH} \rightarrow \text{more acidic solution}$
Percent Ionization and Acid Concentration

- for a given acid, HA, % ionization will increase as [HA] decreases
- dilution effect - changing concentrations of species in solution results in Q < K
  
  reaction proceed forward to re-establish equilibrium

  new equilibrium [H₃O⁺] and [A⁻] are higher relative to new [HA]₀

∴ % ionization is greater

Some Comparisons

- compare 2 solutions of different concentration of acetic acid (HC₂H₃O₂, Kₐ = 1.8 x 10⁻⁵)
- compare 2 solutions of different concentration of hydrocyanic acid (HCN, Kₐ = 4.9 x 10⁻¹⁰)
- compare acetic acid and hydrocyanic acid solutions of the same concentration

<table>
<thead>
<tr>
<th></th>
<th>0.010 M H₂O₂</th>
<th>0.025 M H₂O₂</th>
<th>0.025 M HCN</th>
<th>0.10 M HCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>[H₃O⁺], M</td>
<td>4.2 x 10⁻⁴</td>
<td>6.7 x 10⁻⁴</td>
<td>3.5 x 10⁻⁶</td>
<td>7.0 x 10⁻⁶</td>
</tr>
<tr>
<td>pH</td>
<td>3.38</td>
<td>3.17</td>
<td>5.46</td>
<td>5.15</td>
</tr>
<tr>
<td>% ionization</td>
<td>4.2%</td>
<td>2.7%</td>
<td>0.014%</td>
<td>0.0070%</td>
</tr>
</tbody>
</table>

- Be careful when comparing solutions and making qualitative statements about them.
- You can compare 2 different acids at the same concentration: acid with larger Kₐ is the stronger acid
  ∴ acid solution with larger Kₐ will have:
    higher [H₃O⁺]
    lower pH
    higher % dissociation
- You can compare the same acid at 2 different concentrations: Kₐ is the same, so acid strength is the same
  solution with higher concentration will have:
    higher [H₃O⁺]
    lower pH
    lower % dissociation

Determination of Kₐ from Experimental Data:
Given [HA]₀ and pH

eample:
The pH of 0.250 M HF (aq) is 2.036. Determine the Kₐ for HF.
Determination of $K_a$ from Experimental Data:
Given $[HA]_0$ and % Ionization

example:
A 0.340 M solution of $\text{HNO}_2$ (aq) is 3.65% dissociated at equilibrium. Determine $K_a$ for nitrous acid, and the pH of the solution.

Polyprotic Acids
- acid with more than one acidic proton
- polyprotic acids dissociate in a step-wise manner
each step corresponds to the dissociation of one $\text{H}^+$
each step has a unique $K_a$ value

consider oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$:

1\text{st} dissociation step:
$\text{H}_2\text{C}_2\text{O}_4$ (aq) + $\text{H}_2\text{O}$ (l) $\rightleftharpoons$ $\text{HC}_2\text{O}_4^-$ (aq) + $\text{H}_3\text{O}^+$ (aq); $K_{a1} = 5.9 \times 10^{-2}$

2\text{nd} dissociation step:
$\text{HC}_2\text{O}_4^-$ (aq) + $\text{H}_2\text{O}$ (l) $\rightleftharpoons$ $\text{C}_2\text{O}_4^{2-}$ (aq) + $\text{H}_3\text{O}^+$ (aq); $K_{a2} = 6.4 \times 10^{-5}$

- $K_{a1} > K_{a2}$ this is always true for polyprotic acids
- the acids become weaker with each successive dissociation step
  $\text{H}_2\text{C}_2\text{O}_4$ is a stronger acid than $\text{HC}_2\text{O}_4^-$
  Why?

example:
Consider a 0.040 M solution of carbonic acid. Determine the pH of this solution as well as the equilibrium concentrations of: $[\text{H}_2\text{CO}_3]$, $[\text{HCO}_3^-]$, $[\text{H}_3\text{O}^+]$, $[\text{CO}_3^{2-}]$, and $[\text{OH}^-]$.

For $\text{H}_2\text{CO}_3$, $K_{a1} = 4.3 \times 10^{-7}$ and $K_{a2} = 5.6 \times 10^{-11}$.

1\text{st} ionization equation:
$\text{H}_2\text{CO}_3$ (aq) + $\text{H}_2\text{O}$ (l) $\rightleftharpoons$ $\text{HCO}_3^-$ (aq) + $\text{H}_3\text{O}^+$ (aq)

2nd ionization equation:
$\text{HCO}_3^-$ (aq) + $\text{H}_2\text{O}$ (l) $\rightleftharpoons$ $\text{CO}_3^{2-}$ (aq) + $\text{H}_3\text{O}^+$ (aq)
solution:
- because $K_{a1} > K_{a2}$ & $K_{a1} > K_{w}$, the primary source of $H_3O^+$ in the solution will be the 1st ionization step for $H_2CO_3$:

| $H_2CO_3$ (aq) + $H_2O$ (l) $\rightleftharpoons$ HCO$_3^-$ (aq) + $H_3O^+$ (aq) |
|---|---|---|---|
| initial [ ] | 0.040 M | --- | 0 | 0 |
| $\Delta$ [ ] | $-x$ | --- | $+x$ | $+x$ |
| equil [ ] | (0.040–$x$)M | --- | $x$ M | $x$ M |

- use $K_{a1}$; solve for $x$: $x = 1.3 \times 10^{-4}$
  so: $\ [H_2CO_3] \approx 0.040$ M
  $[HCO_3^-] = [H_3O^+] = 1.3 \times 10^{-4}$ M
  $pH = 3.89$

Steps for solving weak base equilibrium problems:
1. Identify all major species in solution.
2. Identify all potential $H^+$ transfer reactions that could contribute to the $[OH^-]_{total}$ in the sol’n.
3. By considering $K$ values, determine the dominant source of $OH^-$ in the solution.
4. Set up the equilibrium calculation based on equilibrium identified in step 3.
5. Solve!
   - $x = [OH^-]$
   - solve for pH, % ionization, or $K_b$

example:
Calculate pH and % dissociation of 0.40 M NH$_3$ (aq).
For NH$_3$, $K_b = 1.8 \times 10^{-5}$.

| $NH_3$ (aq) + $H_2O$ (l) $\rightleftharpoons$ NH$_4^+$ (aq) + OH$^-$ (aq) |
|---|---|---|---|
| initial [ ] | 0.40 M | --- | 0 | 0 |
| $\Delta$ [ ] | $-x$ | --- | $+x$ | $+x$ |
| equil [ ] | (0.40–$x$)M | --- | $x$ M | $x$ M |

solution:
- to determine $[CO_3^{2-}]$ we will have to consider the 2nd ionization step:

| $HCO_3^-$ (aq) + $H_2O$ (l) $\rightleftharpoons$ CO$_3^{2-}$ (aq) + $H_3O^+$ (aq) |
|---|---|---|---|
| initial [ ] | 1.3 $\times$ 10$^{-4}$ M | --- | 0 | 1.3 $\times$ 10$^{-4}$ M |
| $\Delta$ [ ] | $-x$ | --- | $+x$ | $+x$ |
| equil [ ] | (1.3 $\times$ 10$^{-4}$–$x$)M | --- | $x$ M | (1.3 $\times$ 10$^{-4}$ + $x$)M |

- use $K_{a2}$; solve for $x$: $x = 5.6 \times 10^{-11}$
  so: $[CO_3^{2-}] = 5.6 \times 10^{-11}$ M
- $[OH^-]$? $[OH^-] = K_w/\ [H_3O^+] = 7.7 \times 10^{-11}$ M
Some Comparisons

- compare 2 solutions of different concentration of ammonia (NH₃, K_b = 1.8 x 10⁻⁵)
- compare 2 solutions of different concentration of pyridine (C₅H₅N, K_b = 1.4 x 10⁻⁹)
- compare ammonia and pyridine solutions of the same concentration

<table>
<thead>
<tr>
<th></th>
<th>0.15 M NH₃</th>
<th>0.40 M NH₃</th>
<th>0.40 M C₅H₅N</th>
<th>0.80 M C₅H₅N</th>
</tr>
</thead>
<tbody>
<tr>
<td>[OH⁻], M</td>
<td>0.0016</td>
<td>0.0027</td>
<td>2.4 x 10⁻⁵</td>
<td>3.3 x 10⁻⁵</td>
</tr>
<tr>
<td>pH</td>
<td>11.20</td>
<td>11.43</td>
<td>9.38</td>
<td>9.52</td>
</tr>
<tr>
<td>% ionization</td>
<td>1.1%</td>
<td>0.68%</td>
<td>0.0060%</td>
<td>0.0041%</td>
</tr>
</tbody>
</table>

Be careful when comparing solutions and making qualitative statements about them.

- You can compare 2 different bases at the same concentration: base with larger K_b is the stronger base.
  - base solution with larger K_b will have:
    - higher [OH⁻]
    - higher pH
    - higher % dissociation

- You can compare the same base at 2 different concentrations: K_b is the same, so base strength is the same
  - solution with higher concentration will have:
    - higher [OH⁻]
    - higher pH
    - lower % dissociation

Relationship Between K_a & K_b for Conjugate Acid/Base Pair

- consider the conjugate acid/base pair of NH₃ & NH₄⁺:
  
  NH₃ (aq) + H₂O (l) ⇌ NH₄⁺ (aq) + OH⁻ (aq)

  
  $K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$

  
  NH₄⁺ (aq) + H₂O (l) ⇌ NH₃ (aq) + H₃O⁺ (aq)

  
  $K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$

  
  so: $K_a \times K_b = \frac{[NH_3][H_3O^+]}{[NH_4^+]} \times \frac{[NH_4^+][OH^-]}{[NH_3]}$

  
  $K_a \times K_b = [H_3O^+][OH^-]$

  
  $K_a \times K_b = K_W$

example:

Codeine (C₁₈H₂₁NO₃) is a naturally occurring amine. The pH of a 0.012 M solution of codeine is determined to be 10.14.

Determine the base ionization constant for codeine, and the % ionization of the solution.
Salt Solutions and pH Considerations

- **salt** - an ionic compound
  - soluble salts dissolve in water to produce solutions that may be acidic, basic, or neutral
- consider the cation and anion separately
  - assess the potential acidic or basic nature of each
- recall the inverse nature between strengths in a conjugate acid/base pair:
  - the **stronger** an acid or base, the **weaker** its conjugate
  - the **weaker** an acid or base, the **stronger** its conjugate

Steps for solving salt solution pH problems:

1. Identify all major species in solution.
2. Identify all potential H\(^+\) transfer reactions that could contribute to the \([H_3O^+]_{\text{total}}\) OR \([OH^-]_{\text{total}}\) in the sol’n.
3. By considering K values, determine the dominant source of \(H_3O^+\) OR \(OH^-\) in the solution.
4. Set up the equilibrium calculation based on equilibrium identified in step 3.
5. Solve!
   - \(x = [H_3O^+]\) OR \([OH^-]\)
   - solve for pH

A closer look at a weak acid/conjugate base pair: \(HA & A^-\)

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

- the **stronger the acid** (HA), the **weaker its conjugate base** (A\(^-\)):
  - strong monoprotic acids produce conjugate bases that are not effective bases in solution - they are **neutral anions**

Neutral anions are: Cl\(^-\), Br\(^-\), I\(^-\), NO\(_3^-\), ClO\(_4^-\)

- the **weaker the acid** (HA), the **stronger its conjugate base** (A\(^-\)):
  - weak acids produce conjugate bases that can function as bases in solution - they are **basic anions**

Base ionization equilibrium for A\(^-\):

\[
A^- (aq) + H_2O (l) \rightleftharpoons HA (aq) + OH^- (aq); K_b
\]

Examples of basic anions include:

F\(^-\), CO\(_3^{2-}\), ClO\(_2^-\), SO\(_3^{2-}\), PO\(_4^{3-}\), NO\(_2^-\), BrO\(_4^-\)

A closer look at a weak base/conjugate acid pair: \(B & BH^+\)

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

- the **stronger the base** (B), the **weaker its cation**:
  - strong bases produce cations that are not effective acids in solution - they are **neutral cations**

Neutral cations are: Li\(^+\), Na\(^+\), K\(^+\), Rb\(^+\), Cs\(^+\), Ca\(^2+\), Sr\(^2+\), Ba\(^2+\)

- the **weaker the base** (B), the **stronger its conjugate acid** (BH\(^+\)):
  - weak bases produce conjugate acids that can function as acids in solution - they are **acidic cations**

Acid ionization equilibrium for BH\(^+\):

\[
BH^+ (aq) + H_2O (l) \rightleftharpoons B (aq) + H_3O^+ (aq); K_a
\]

Examples of acidic cations include:

NH\(_4^+\), CH\(_3\)NH\(_3^+\), C\(_2\)H\(_5\)NH\(_3^+\), C\(_5\)H\(_5\)NH\(_3^+\), C\(_6\)H\(_5\)NH\(_3^+\)
recall the relationship between $K_a$ and $K_b$ for a conjugate acid/base pair:

$$K_a \times K_b = K_w$$

OR

$$pK_a + pK_b = pK_w$$

and: at $25^\circ C$, $pK_w = -\log(1 \times 10^{-14}) = 14.00$

so: $pK_a + pK_b = 14.00$

salts that produce neutral solutions:

- pH = 7.00 at $25^\circ C$
- neutral cation with a neutral anion
  
  examples: KNO$_3$, NaCl, Ca(ClO$_4$)$_2$, SrBr$_2$, CsI

salts that produce acidic solutions:

- pH < 7.00 at $25^\circ C$
- type 1: acidic cation with neutral anion
  
  examples: NH$_4$Cl, CH$_3$NH$_3$NO$_3$, C$_5$H$_5$NHBr

  example problem: calculate the pH of 0.10 M NH$_4$Cl (aq)
  
  $\text{NH}_4^+$ (aq) + $\text{H}_2\text{O}$ (l) $\Leftrightarrow$ NH$_3$ (aq) + H$_3$O$^+$ (aq); $K_a = K_{w}/K_b$ for NH$_3$ = 5.6 x 10$^{-10}$

- type 2: neutral cation with anion from a polyprotic acid
  
  examples: KHSO$_4$, NaHCO$_3$, Ca(HC$_2$O$_4$)$_2$

  example problem: calculate the pH of .20 M Ca(HC$_2$O$_4$)$_2$ (aq)
  
  HC$_2$O$_4^-$ (aq) + $\text{H}_2\text{O}$ (l) $\Leftrightarrow$ C$_2$O$_4^{2-}$ (aq) + H$_3$O$^+$ (aq); $K_a = K_{a2}$ for H$_2$C$_2$O$_4$ = 5.1 x 10$^{-5}$

- type 3: hydrated metal cation of high positive charge-density with neutral anion
  
  recall: [Al(H$_2$O)$_6$]$^{3+}$ (aq) + $\text{H}_2\text{O}$ (l) $\Leftrightarrow$ Al[$\text{(H}_2\text{O})_5$(OH)]$^{2+}$ (aq) + H$_3$O$^+$ (aq)

  hydrated metal ion can behave as a Bronsted-Lowry acid:

  examples: MgCl$_2$, AlBr$_3$, Zn(NO$_3$)$_2$, Cr(NO$_3$)$_3$

  example problem: calculate the pH of 0.097 M AlCl$_3$ (aq); for [Al(H$_2$O)$_6$]$^{3+}$, $K_a = 1.4 \times 10^{-5}$
salts that produce basic solutions:
- pH > 7.00 at 25°C
- neutral cation with basic anion
  examples: KF, CaSO₄, Na₂CO₃, K₃PO₄, Na₂C₂O₄, NaNO₂

example problem: calculate the pH of 0.20 M NaNO₂ (aq)
NO₂⁻ (aq) + H₂O (l) ⇌ HNO₂ (aq) + OH⁻ (aq);
K_b = K_w/K_a for HNO₂ = 2.2 x 10⁻¹¹

The Common Ion Effect

What happens to the pH of a weak acid (HA) or weak base (B) solution when a salt containing its conjugate is added?
- resulting solution contains a conjugate acid base pair
- calculate and compare [H₃O⁺] or [OH⁻], pH, % ionization
- demonstration of LeChatelier’s Principle

example:
0.10 mol HC₂H₃O₂ and 0.10 mol NaC₂H₃O₂ are combined in a solution with a total volume of 1.0 L.
Determine the [H₃O⁺], pH, and % ionization in this solution. For HC₂H₃O₂, K_a = 1.8 x 10⁻⁵.

the equilibrium that controls the pH of this sol'n:

| HC₂H₃O₂(aq) + H₂O (l) ⇌ C₂H₅O₂⁻ (aq) + H₃O⁺(aq) |
|---|---|---|---|
| initial [ ] | 0.10 M | --- | 0.10 M | 0 |
| Δ [ ] | − x | --- | + x | + x |
| equil [ ] | (0.10−x)M | --- | (0.10+x)M | x M |

for comparison:

<table>
<thead>
<tr>
<th>0.10 M HC₂H₃O₂ (aq) + 0.10 M NaC₂H₃O₂ (aq)</th>
<th>0.10 M HC₂H₃O₂ (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[H₃O⁺]</td>
<td>1.3 x 10⁻³ M</td>
</tr>
<tr>
<td>pH</td>
<td>2.89</td>
</tr>
<tr>
<td>% ionization</td>
<td>1.3%</td>
</tr>
</tbody>
</table>
for comparison:

<table>
<thead>
<tr>
<th></th>
<th>0.15 M NH₃ (aq)</th>
<th>0.15 M NH₃ (aq) + 0.45 M NH₄Cl (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[OH⁻]</td>
<td>1.6 x 10⁻³ M</td>
<td>6.0 x 10⁻⁶ M</td>
</tr>
<tr>
<td>pH</td>
<td>11.20</td>
<td>8.78</td>
</tr>
<tr>
<td>% ionization</td>
<td>1.1%</td>
<td>0.0040%</td>
</tr>
</tbody>
</table>

Buffer Solutions

- common ion solutions
  sol’ns that contain a conjugate acid/base pair
  HA & A⁻ or B & BH⁺

- solution resists change in pH when small amounts of strong acid (H⁺) or strong base (OH⁻) are added

How does the pH change after the addition of 0.010 mol HCl to 1.00 L of a solution composed of 0.10 M HC₂H₃O₂ & 0.10 M NaC₂H₃O₂ (initial pH = 4.74).

1ˢᵗ: addition of strong acid (H⁺) results in a neutralization reaction (note: Cl⁻ is a spectator ion; this is the net ionic equation):

\[ \text{C₂H₃O₂}^- (aq) + \text{H}^+ (aq) \rightarrow \text{HC₂H₃O₂} (aq) \]

2ⁿᵈ: after the strong acid is consumed, equilibrium is established that determines the pH of the solution:

\[ \text{HC₂H₃O₂} (aq) \rightleftharpoons \text{C₂H₃O₂}^- (aq) + \text{H}^+ (aq) \]

resulting solution pH = 4.66; \( \Delta \text{pH} = -.08 \)

<table>
<thead>
<tr>
<th></th>
<th>C₂H₃O₂⁻ (aq)</th>
<th>H⁺ (aq)</th>
<th>HC₂H₃O₂ (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>before rxn</td>
<td>0.10 mol</td>
<td>0.010 mol</td>
<td>0.10 mol</td>
</tr>
<tr>
<td>Δ</td>
<td>-0.010 mol</td>
<td>-0.010 mol</td>
<td>+0.010 mol</td>
</tr>
<tr>
<td>after rxn</td>
<td>0.090 mol</td>
<td>0</td>
<td>0.11 mol</td>
</tr>
</tbody>
</table>
How does the pH change after the addition of 0.010 mol HCl to 1.00 L of a solution composed of 0.10 M HC₂H₃O₂ & 0.10 M NaC₂H₃O₂ (initial pH = 4.74).

2nd: after the strong acid is consumed, equilibrium is established that determines the pH of the solution:

\[
\text{HC₂H₃O₂ (aq) + H₂O (l)} \rightleftharpoons \text{C₂H₃O₂⁻ (aq) + H₃O⁺ (aq)}
\]

- initial \([\text{HC₂H₃O₂}]\) and \([\text{C₂H₃O₂⁻}]\) in equilibrium problem determined by consideration of what is in solution after the neutralization reaction is complete

<table>
<thead>
<tr>
<th></th>
<th>HC₂H₃O₂ (aq)</th>
<th>H₂O (l)</th>
<th>C₂H₃O₂⁻ (aq)</th>
<th>H₃O⁺ (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.11 M</td>
<td>---</td>
<td>0.090 M</td>
<td>0</td>
</tr>
<tr>
<td>Δ [M]</td>
<td>–x</td>
<td>---</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>equil [M]</td>
<td>(0.11–x)M</td>
<td>---</td>
<td>(0.090+x)M</td>
<td>x M</td>
</tr>
</tbody>
</table>

the result of the neutralization reaction:

\[
\text{C₂H₃O₂⁻ (aq) + H⁺ (aq)} \rightarrow \text{HC₂H₃O₂ (aq)}
\]

- \(\text{C₂H₃O₂⁻}\) is consumed
- \(\text{HC₂H₃O₂}\) is formed

[\(\text{C₂H₃O₂⁻}\)] decreases
[\(\text{HC₂H₃O₂}\)] increases

- strong acid, H⁺, is the limiting reactant
- \(\text{H⁺}\) is completely consumed
- pH of solution decreases slightly
- solution becomes slightly more acidic

Consider, again, 0.10 M HC₂H₃O₂ & 0.10 M NaC₂H₃O₂ common ion solution; pH = 4.74.

How does the pH change after the addition of 0.010 mol NaOH to 1.00 L of this solution?

1st: addition of strong base (OH⁻) results in a neutralization reaction (note: Na⁺ is a spectator ion; this is the net ionic equation):

\[
\text{HC₂H₃O₂ (aq) + OH⁻ (aq)} \rightarrow \text{C₂H₃O₂⁻ (aq) + H₂O (l)}
\]

2nd: after the strong base is consumed, equilibrium is established that determines the pH of the solution:

\[
\text{HC₂H₃O₂ (aq)} \rightleftharpoons \text{C₂H₃O₂⁻ (aq) + H⁺ (aq)}
\]

resulting solution pH = 4.82; \(\Delta\text{pH} = +.08\)

How does the pH change after the addition of 0.010 mol NaOH to 1.00 L of a solution composed of 0.10 M HC₂H₃O₂ & 0.10 M NaC₂H₃O₂ (initial pH = 4.74).

1st: addition of strong base (OH⁻) results in a neutralization reaction (note: Na⁺ is a spectator ion; this is the net ionic equation):

- the added strong base (OH⁻) will react with the acid (HC₂H₃O₂) in the buffer solution

<table>
<thead>
<tr>
<th></th>
<th>HC₂H₃O₂ (aq)</th>
<th>OH⁻ (aq)</th>
<th>C₂H₃O₂⁻ (aq)</th>
<th>H₂O (l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>before rxn</td>
<td>0.10 mol</td>
<td>0.010 mol</td>
<td>0.10 mol</td>
<td>---</td>
</tr>
<tr>
<td>Δ</td>
<td>–0.010 mol</td>
<td>–0.010 mol</td>
<td>+0.010 mol</td>
<td>---</td>
</tr>
<tr>
<td>after rxn</td>
<td>0.090 mol</td>
<td>0</td>
<td>0.11 mol</td>
<td>---</td>
</tr>
</tbody>
</table>
How does the pH change after the addition of 0.010 mol NaOH to 1.00 L of a solution composed of 0.10 M HC$_2$H$_3$O$_2$ & 0.10 M NaC$_2$H$_3$O$_2$ (initial pH = 4.74).

2nd: after the strong base is consumed, equilibrium is established that determines the pH of the solution:

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

- initial [HC$_2$H$_3$O$_2$] and [C$_2$H$_3$O$_2^-$] in equilibrium problem determined by consideration of what is in solution after the neutralization reaction is complete

<table>
<thead>
<tr>
<th></th>
<th>HC$_2$H$_3$O$_2$ (aq) + H$_2$O (l) $\rightleftharpoons$ C$_2$H$_3$O$_2^-$ (aq) + H$_3$O$^+$ (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.090 M --- 0.11 M 0</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>$-x$ --- $+x$ $+x$</td>
</tr>
<tr>
<td>equil</td>
<td>(0.090$-x$)M --- (0.11$+x$)M $x$ M</td>
</tr>
</tbody>
</table>

the result of the neutralization reaction:

HC$_2$H$_3$O$_2$ (aq) + OH$^-$ (aq) $\rightarrow$ C$_2$H$_3$O$_2^-$ (aq) + H$_2$O (l)

- HC$_2$H$_3$O$_2$ is consumed
- C$_2$H$_3$O$_2^-$ is formed
- [HC$_2$H$_3$O$_2$] decreases
- [C$_2$H$_3$O$_2^-$] increases
- strong base, OH$^-$, is the limiting reactant
- OH$^-$ is completely consumed
- pH of solution increases slightly
- solution becomes slightly more basic

How Does a Buffer Work?

- pH is controlled by [H$^+$]
- in an HA/A$^-$ buffer solution:

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

\[
K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad \text{OR} \quad [\text{H}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]}
\]

- to keep [H$^+$] (and therefore pH) relatively constant, [HA]/[A$^-$] must also remain relatively constant
in buffer solution with HA & A\textsuperscript{−}:

- addition of H\textsuperscript{+}  
  neutralization:  
  \[ H^+ + A^- \rightarrow HA \]

- addition of OH\textsuperscript{−}  
  neutralization:  
  \[ OH^- + HA \rightarrow A^- + H_2O \]

- [HA] increases slightly  
  [A\textsuperscript{−}] decreases slightly

- [HA] increases slightly  
  [A\textsuperscript{−}] decreases slightly

- [HA] decreases slightly  
  [A\textsuperscript{−}] increases slightly

- [HA] decreases slightly  
  [A\textsuperscript{−}] increases slightly

- [HA]/[A\textsuperscript{−}] increases  
  pH decreases

- [HA]/[A\textsuperscript{−}] decreases  
  pH increases

Buffer Capacity and Buffer Failure

- buffer capacity is the amount of strong acid or strong base that can be added to a buffer solution before it fails

- a buffer fails when enough strong acid or strong base is added to cause a \( \Delta pH \geq 1 \) unit

- pH of buffer solution depends on the \([HA]/[A^-]\) ratio

- capacity of a buffer solution depends on magnitude of [HA] and [A\textsuperscript{−}]

Buffer Capacity

- compare 2 HF + NaF buffer solutions:

  \[
  \begin{align*}
  0.25 \text{ M HF} & \quad 0.50 \text{ M NaF} \\
  [HF]/[F^-] & = 0.50 \\
  pH & = 3.76 \\
  \text{after add'n of 0.002 mol} & \\
  H^+ & \text{ to 100 mL solution} \\
  [HF]/[F^-] & = 0.56 \\
  pH & = 3.71 \\
  \Delta pH & = 0.05
  \end{align*}
  \]

  better buffer capacity

  \[
  \begin{align*}
  0.050 \text{ M HF} & \quad 0.10 \text{ M NaF} \\
  [HF]/[F^-] & = 0.50 \\
  pH & = 3.76 \\
  \text{after add'n of 0.002 mol} & \\
  H^+ & \text{ to 100 mL solution} \\
  [HF]/[F^-] & = 0.88 \\
  pH & = 3.51 \\
  \Delta pH & = 0.25
  \end{align*}
  \]

Henderson-Hasselbalch Equation

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

- take \(-\log\) of both sides of equation

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

- buffer solutions work best when \([\text{base}] / [\text{acid}]\) is close to 1

- when \([\text{base}] = [\text{acid}]\):  
  \[ [\text{base}] / [\text{acid}] = 1 \quad \text{pH} = pK_a \]
Consider the following acids and their $pK_a$ values:

- $H_2PO_4^-$ $pK_a = 7.21$
- $HF$ $pK_a = 3.14$
- $NH_4^+$ $pK_a = 9.25$
- $HC_7H_5O_2$ $pK_a = 4.19$

What would be the best acid/conjugate base to prepare a buffer solution with pH = 7.00?

What would be the best acid/conjugate base to prepare a buffer solution with pH = 9.00?

- Since buffer solutions work best when $[\text{base}]/[\text{acid}]$ is close to 1, the best acid to pick for a buffer is one with $pK_a$ close to the desired pH.
  
  Ideally: $pK_a$ of acid = sol'n pH + 1

Example:
What is the pH of a buffer solution prepared by mixing 100 mL of 0.104 M NaF with 200 mL of 0.275 M HF? For HF, $pK_a = 3.14$.

Example:
What concentration of $NaC_7H_5O_2$ is required to prepare a buffer solution with pH = 4.10 with 0.249 M $HC_7H_5O_2$ (aq)? For $HC_7H_5O_2$, $pK_a = 4.19$.

Acid-Base Titrations: A Quick Review

- titration is an analytical technique in which one reactant is added to another in a very controlled way

- stop when the reaction is just complete
  - at this point there is no limiting reactant, and no excess reactants
  - reactants are completely converted to products
  - stoichiometrically correct mol ratio of reactants
  - this point is called the:
    - stoichiometric point
    - equivalence point
    - end point

- usually some visible indication that you are at the stoichiometric point (use of indicators)

Acid-Base Titrations

- we will look in detail at the following titrations:
  - strong acid + strong base
  - weak acid + strong base
  - strong acid + weak base

- for each we will:
  - calculate the pH at points before, at, and beyond the stoichiometric point
  - discuss characteristics of each type of titration
  - create and interpret titration curves

- end with a discussion of acid-base indicators
**Strong Acid + Strong Base Titrations**

**basic strategy:**

1. write the *net ionic equation* for the neutralization reaction that will occur
2. using V and M, calculate mol of each reactant present
3. set up a reaction table; identify the limiting and excess reactant
4. determine [H\(^+\)] or [OH\(^-\)] after neutralization reaction is complete  
   *remember to use the total solution volume!*
5. calculate pH of solution

---

**example:**

- 40.0 mL of 0.110 M HCl (aq) is titrated with 0.095 M NaOH (aq).

  - **neutralization reaction (Na\(^+\) and Cl\(^-\) spectator ions):**  
    \[ \text{H}^+ (aq) + \text{OH}^- (aq) \rightarrow \text{H}_2\text{O} (l) \]
  
  - calculate mol H\(^+\) (aq):
    \[
    \text{mol H}^+ = (0.0400 \text{ L})(0.110 \text{ mol/L}) \\
    = 0.00440 \text{ mol H}^+ 
    \]
  
  - calculate volume NaOH (aq) required to reach the stoichiometric point:
    \[
    0.00440 \text{ mol H}^+ \times \frac{1 \text{ mol OH}^-}{1 \text{ mol H}^+} \times \frac{1 \text{ L soln}}{0.095 \text{ mol OH}^-} = 0.0463 \text{ L or 46.3 mL}
    \]
  
---

**Strong Acid + Strong Base Titrations**

**example:**

40.0 mL of 0.110 M HCl (aq) is titrated with 0.095 M NaOH (aq).

**Determine the following:**

- initial pH of the solution
- pH after the addition of 30.0 mL of NaOH
- pH at the stoichiometric point
- pH after the addition of 60.0 mL NaOH

---

- Determine the initial pH; *pH of the solution before adding any NaOH (aq).*

  another way to say this . . .

  What is the pH of 0.110 M HCl (aq)?

  \[
  [\text{H}^+] = 0.110 \text{ M} \\
  \text{pH} = – \log (0.110) = 0.96
  \]
Determine the pH after the addition of 30.0 mL NaOH (aq).

\[ \text{mol OH}^- \text{added} = (0.0300 \text{ L})(0.095 \text{ mol/L}) = 0.0029 \text{ mol OH}^- \]

- set up a reaction table to identify limiting and excess reactant:

<table>
<thead>
<tr>
<th>H(^+) (aq)</th>
<th>OH(^-) (aq)</th>
<th>(\rightarrow) H(_2)O (l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>before rxn:</td>
<td>0.00440 mol</td>
<td>0.0029 mol</td>
</tr>
<tr>
<td>change:</td>
<td>-0.0029 mol</td>
<td>-0.0029 mol</td>
</tr>
<tr>
<td>after rxn:</td>
<td>0.0015 mol</td>
<td>0</td>
</tr>
</tbody>
</table>

Example:
40.0 mL of 0.110 M HCl (aq) is titrated with 0.095 M NaOH (aq).

- Determine [excess reactant] after neutralization reaction is complete:

\[ [H^+] = \frac{\text{mol H}^+ \text{after rxn}}{\text{total sol'n volume}} \]

\[ [H^+] = \frac{0.0015 \text{ mol H}^+}{(0.0400 + 0.0300) \text{ L}} \]

\[ [H^+] = 0.021 \text{ M} \]

\[ \text{pH} = 1.68 \]

Example:
40.0 mL of 0.110 M HCl (aq) is titrated with 0.095 M NaOH (aq).

- Determine the pH at the stoichiometric point.

46.3 mL NaOH (aq) added to reach stoichiometric pt at stoichiometric point:

\[ \text{mol OH}^- \text{added} = \text{mol H}^+ \text{present} = 0.00440 \text{ mol} \]

- set up reaction table:

<table>
<thead>
<tr>
<th>H(^+) (aq)</th>
<th>OH(^-) (aq)</th>
<th>(\rightarrow) H(_2)O (l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>before rxn:</td>
<td>0.00440 mol</td>
<td>0.0044 mol</td>
</tr>
<tr>
<td>change:</td>
<td>-0.0044 mol</td>
<td>-0.0044 mol</td>
</tr>
<tr>
<td>after rxn:</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

- after reaction the solution is neutral; pH = 7.00

Example:
40.0 mL of 0.110 M HCl (aq) is titrated with 0.095 M NaOH (aq).

- Determine the pH after the addition of 60.0 mL NaOH (aq).

\[ \text{mol OH}^- \text{added} = (0.0600 \text{ L})(0.095 \text{ mol/L}) = 0.0057 \text{ mol OH}^- \]

- set up reaction table to identify limiting and excess reactant:

<table>
<thead>
<tr>
<th>H(^+) (aq)</th>
<th>OH(^-) (aq)</th>
<th>(\rightarrow) H(_2)O (l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>before rxn:</td>
<td>0.00440 mol</td>
<td>0.0057 mol</td>
</tr>
<tr>
<td>change:</td>
<td>-0.0044 mol</td>
<td>-0.0044 mol</td>
</tr>
<tr>
<td>after rxn:</td>
<td>0</td>
<td>0.0013 mol</td>
</tr>
</tbody>
</table>
example:
40.0 mL of 0.110 M HCl (aq) is titrated with 0.095 M NaOH (aq).

- Determine [excess reactant] after neutralization reaction is complete:

\[ [\text{OH}^-] = \frac{\text{mol OH}^-}{\text{total sol'n volume}} \]

\[ [\text{OH}^-] = \frac{0.0013 \text{ mol}}{(0.0400 + 0.0600) \text{ L}} \]

\[ [\text{OH}^-] = 0.013 \text{ M} \]

pOH = 1.89; pH = 12.11

Strong Acid/Strong Base Titrations:
- Consider the titration of 40.0 mL of 0.110 M HCl (aq) with 0.095 M NaOH (aq).

<table>
<thead>
<tr>
<th>mL NaOH added</th>
<th>total sol'n vol.</th>
<th>[H3O+] after rxn</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>before stoichiometric point:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>40</td>
<td>0.110 M</td>
<td>0.96</td>
</tr>
<tr>
<td>5</td>
<td>45</td>
<td>0.087 M</td>
<td>1.07</td>
</tr>
<tr>
<td>10</td>
<td>50</td>
<td>0.070 M</td>
<td>1.13</td>
</tr>
<tr>
<td>30</td>
<td>70</td>
<td>0.021 M</td>
<td>1.68</td>
</tr>
<tr>
<td>45</td>
<td>85</td>
<td>0.012 M</td>
<td>1.92</td>
</tr>
<tr>
<td>46</td>
<td>86</td>
<td>3.5 x 10^-7 M</td>
<td>3.46</td>
</tr>
<tr>
<td>at stoichiometric point:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>46.3</td>
<td>86.3</td>
<td>1.0 x 10^-7 M</td>
<td>7.00</td>
</tr>
<tr>
<td>beyond stoichiometric point:</td>
<td></td>
<td>[OH^-] after rxn</td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>87</td>
<td>0.00115 M</td>
<td>11.06</td>
</tr>
<tr>
<td>50</td>
<td>90</td>
<td>0.0044 M</td>
<td>11.64</td>
</tr>
<tr>
<td>60</td>
<td>100</td>
<td>0.0013 M</td>
<td>12.11</td>
</tr>
<tr>
<td>70</td>
<td>110</td>
<td>0.020 M</td>
<td>12.31</td>
</tr>
<tr>
<td>80</td>
<td>120</td>
<td>0.027 M</td>
<td>12.43</td>
</tr>
</tbody>
</table>

Weak Acid + Strong Base Titrations

strategy:
1. write the net ionic equation for the neutralization reaction that will occur
   - strong base is completely ionized
   - weak acid is only partially ionized
2. using V and M, calculate mol of each reactant present
3. set up a reaction table; identify the limiting and excess reactant

notes:
- start at low (acidic) pH
- pH < 7 before stoichiometric point (OH^- limiting reactant)
- pH = 7 at stoichiometric point (neutral solution)
- pH > 7 beyond stoichiometric point (H^+ limiting reactant)
- end at high (basic) pH
4. Identify the species present when the neutralization reaction is complete, and determine which of them are key to determining the pH of the solution.
   - Before the stoichiometric point, the neutralization reaction results in a HA/A⁻ buffer solution.
   - At the stoichiometric point, the base ionization of A⁻ will determine the pH.
   - Beyond the stoichiometric point, excess OH⁻ determines the pH.

5. Using post-neutralization concentrations of species, set up the appropriate calculation and determine pH of solution.

Example:
30.0 mL of 0.125 M HC₃H₄O₂ (aq) is titrated with 0.100 M NaOH (aq).

Determine the following:
- Initial pH of the solution.
- pH after the addition of 20.0 mL of NaOH.
- pH at the stoichiometric point.
- pH after the addition of 50.0 mL NaOH.

Neutralization reaction (Na⁺ spectator ion):

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

Calculate mol HC₃H₄O₂ (aq):
\[
\text{mol HC}_2\text{H}_3\text{O}_2 = (0.0300 \text{ L})(0.125 \text{ mol/L}) = 0.00375 \text{ mol HC}_2\text{H}_3\text{O}_2
\]

Calculate volume NaOH (aq) required to reach the stoichiometric point:
\[
0.00375 \text{ mol HC}_2\text{H}_3\text{O}_2 \times \frac{\text{1 mol OH}^-}{\text{1 mol HC}_2\text{H}_3\text{O}_2} \times \frac{\text{1 L soln}}{\text{0.100 mol OH}^-} = 0.0375 \text{ L or 37.5 mL}
\]

Another way to say this . . .

What is the pH of 0.125 M HC₂H₃O₂ (aq)?

Weak acid calculation; \( K_a \) for HC₂H₃O₂ = 1.8 \times 10^{-5}

\[ x = [\text{H}^+] = 0.0015 \text{ M} \]
\[ \text{pH} = -\log (0.0015) = 2.82 \]
example:
30.0 mL of 0.125 M HC$_2$H$_3$O$_2$ (aq) is titrated with 0.100 M NaOH.

- Determine the pH after the addition of 20.0 mL NaOH (aq).

\[
\text{mol OH}^- \text{ added} = (0.0200 \text{ L})(0.100 \text{ mol/L}) = 0.00200 \text{ mol OH}^- 
\]

- Set up a reaction table to identify limiting and excess reactant:

<table>
<thead>
<tr>
<th>before rxn:</th>
<th>HC$_2$H$_3$O$_2$</th>
<th>OH$^-$</th>
<th>$\rightarrow$</th>
<th>C$_2$H$_3$O$_2^-$</th>
<th>+</th>
<th>H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>mol HC$_2$H$_3$O$_2$</td>
<td>.00375 mol</td>
<td>.00200 mol</td>
<td>0</td>
<td>---</td>
<td></td>
<td></td>
</tr>
<tr>
<td>mol OH$^-$</td>
<td>-.00200 mol</td>
<td>-.00200 mol</td>
<td>+.00200 mol</td>
<td>---</td>
<td></td>
<td></td>
</tr>
<tr>
<td>after rxn:</td>
<td>.00175 mol</td>
<td>0</td>
<td>.00200 mol</td>
<td>---</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- This is a buffer solution
determine [H$^+$] and pH by using an equilibrium table 
   OR
   the Henderson-Hasselbalch equation

\[
\text{pH} = 4.74 + \log \frac{.0400}{.0350} \\
pH = 4.80
\]
example:
30.0 mL of 0.125 M HC₂H₃O₂ (aq) is titrated with 0.100 M NaOH.

- after the neutralization reaction, HC₂H₃O₂ and OH⁻ are completely consumed
- base ionization of C₂H₃O₂⁻ controls the pH of sol’n:
  \[ \text{C}_2\text{H}_3\text{O}_2^- \text{(aq)} + \text{H}_2\text{O} (l) \rightleftharpoons \text{HC}_2\text{H}_3\text{O}_2 \text{(aq)} + \text{OH}^- \text{(aq)} \]
  \[ K_b = K_w/(K_a \text{ for HC}_2\text{H}_3\text{O}_2) = 5.6 \times 10^{-10} \]
- determine [C₂H₃O₂⁻] after neutralization reaction:
  \[ [\text{C}_2\text{H}_3\text{O}_2^-] = \frac{0.00375 \text{ mol}}{0.0675 \text{ L}} = 0.0556 \text{ M} \]

example:
30.0 mL of 0.125 M HC₂H₃O₂ (aq) is titrated with 0.100 M NaOH.
- the equilibrium table and calculation:

<table>
<thead>
<tr>
<th></th>
<th>C₂H₃O₂⁻</th>
<th>H₂O</th>
<th>⇌</th>
<th>HC₂H₃O₂</th>
<th>OH⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.0556 M</td>
<td>---</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Δ</td>
<td>–x</td>
<td>---</td>
<td>+x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>equil</td>
<td>(0.0556 –x) M</td>
<td>---</td>
<td>x M</td>
<td>x M</td>
<td></td>
</tr>
</tbody>
</table>
  \[ K_b = 5.6 \times 10^{-10} = \frac{x^2}{0.0556 - x} \]
- solve for x: \[ x = [\text{OH}^-] = 5.6 \times 10^{-6} \text{ M} \]
  \[ \text{pOH} = 5.25 \]
  \[ \text{pH} = 8.75 \]
- for a weak acid titrated with a strong base, the pH > 7 at the stoichiometric point

example:
30.0 mL of 0.125 M HC₂H₃O₂ (aq) is titrated with 0.100 M NaOH.
- Determine the pH after the addition of 50.0 mL NaOH (aq).
  \[ \text{mol OH}^- \text{ added} = (0.0500 \text{ L})(0.100 \text{ mol/L}) \]
  \[ = 0.00500 \text{ mol OH}^- \]
- set up a reaction table to identify limiting and excess reactant:

<table>
<thead>
<tr>
<th></th>
<th>HC₂H₃O₂</th>
<th>OH⁻</th>
<th>→</th>
<th>C₂H₃O₂⁻</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>before rxn:</td>
<td>0.00375 mol</td>
<td>0.00500 mol</td>
<td>0</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>change:</td>
<td>–0.00375 mol</td>
<td>–0.00375 mol</td>
<td>+0.00375 mol</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>after rxn:</td>
<td>0</td>
<td>0.00125 mol</td>
<td>0.00375 mol</td>
<td>---</td>
<td></td>
</tr>
</tbody>
</table>

\[ [\text{OH}^-] = \frac{0.00125 \text{ mol}}{(0.0300 + 0.0500) \text{ L}} \]
\[ [\text{OH}^-] = 0.0156 \text{ M} \]
\[ \text{pOH} = 1.81; \quad \text{pH} = 12.19 \]
Weak Acid/Strong Base Titrations:
- Consider the titration of 30.0 mL of 0.125 M HC$_2$H$_3$O$_2$ (aq) with 0.100 M NaOH (aq).

<table>
<thead>
<tr>
<th>mL NaOH added</th>
<th>total sol'n vol.</th>
<th>[H$_3$O$^+$] after rxn</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>30</td>
<td>1.5 x 10$^{-3}$ M</td>
<td>2.82</td>
</tr>
<tr>
<td>5</td>
<td>35</td>
<td>1.2 x 10$^{-3}$ M</td>
<td>3.83</td>
</tr>
<tr>
<td>10</td>
<td>40</td>
<td>5.0 x 10$^{-4}$ M</td>
<td>4.30</td>
</tr>
<tr>
<td>20</td>
<td>50</td>
<td>1.6 x 10$^{-4}$ M</td>
<td>4.80</td>
</tr>
<tr>
<td>30</td>
<td>60</td>
<td>4.6 x 10$^{-5}$ M</td>
<td>5.14</td>
</tr>
<tr>
<td>35</td>
<td>65</td>
<td>1.3 x 10$^{-5}$ M</td>
<td>5.89</td>
</tr>
<tr>
<td>37</td>
<td>67</td>
<td>2.5 x 10$^{-5}$ M</td>
<td>6.11</td>
</tr>
</tbody>
</table>

- at stoichiometric point:

<table>
<thead>
<tr>
<th>before stoichiometric point:</th>
<th>after stoichiometric point:</th>
</tr>
</thead>
<tbody>
<tr>
<td>before stoichiometric point:</td>
<td>at stoichiometric point:</td>
</tr>
<tr>
<td>37.5 mL</td>
<td>67.5 mL</td>
</tr>
<tr>
<td>0.00375 mol</td>
<td>0.001875 mol</td>
</tr>
<tr>
<td>0.001875 mol</td>
<td>0.001875 mol</td>
</tr>
<tr>
<td>0.001875 mol</td>
<td>0.00357 mol</td>
</tr>
</tbody>
</table>

- beyond stoichiometric point:

<table>
<thead>
<tr>
<th>beyond stoichiometric point:</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>11.56</td>
</tr>
<tr>
<td>50</td>
<td>12.19</td>
</tr>
<tr>
<td>60</td>
<td>12.40</td>
</tr>
<tr>
<td>75</td>
<td>12.55</td>
</tr>
</tbody>
</table>

**Titration Curve for Weak Acid + Strong Base**

- start at low (acidic) pH
- pH < 7 before stoichiometric point (OH$^-$ limiting reactant)
- pH > 7 at stoichiometric point (basic solution)
- pH > 7 beyond stoichiometric point (H$^+$ limiting reactant)
- end at high (basic) pH

**Example:**

30.0 mL of 0.125 M HC$_2$H$_3$O$_2$ (aq) is titrated with 0.100 M NaOH.
- an important point in a weak acid + strong base titration is the **half-way point**
  - half-way to the stoichiometric point
  - vol required = $\frac{1}{2}$ (vol to reach stoich.pt.)
- for this titration:
  - vol required = $\frac{1}{2}$ (37.5 mL)
  - $\therefore$ half-way to the stoichiometric point is after the addition of 18.75 mL NaOH

**Example:**

30.0 mL of 0.125 M HC$_2$H$_3$O$_2$ (aq) is titrated with 0.100 M NaOH.
- Determine the pH after the addition of 18.75 mL NaOH (aq).
  - $\text{mol OH}^-\text{added} = (0.01875 \text{ L})(0.100 \text{ mol/L})$
  - $= 0.001875 \text{ mol OH}^-$
- set up a reaction table to identify limiting and excess reactant:

<table>
<thead>
<tr>
<th>before rxn:</th>
<th>change:</th>
<th>after rxn:</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC$_2$H$_3$O$_2$</td>
<td>OH$^-$</td>
<td>C$_2$H$_3$O$_2^-$</td>
</tr>
<tr>
<td>.00375 mol</td>
<td>-.001875 mol</td>
<td>.001875 mol</td>
</tr>
<tr>
<td>.001875 mol</td>
<td>.001875 mol</td>
<td>.001875 mol</td>
</tr>
</tbody>
</table>
### Strong Acid + Weak Base Titrations

**30.0 mL of 0.125 M HC₂H₃O₂ (aq) is titrated with 0.100 M NaOH.**

- determine [HC₂H₃O₂] and [C₂H₃O₂⁻] after neutralization reaction is complete:

  \[
  [\text{HC}_2\text{H}_3\text{O}_2] = \frac{0.01875 \text{ mol}}{0.04875 \text{ L}} \quad [\text{C}_2\text{H}_3\text{O}_2^-] = \frac{0.01875 \text{ mol}}{0.04875 \text{ L}}
  \]

  \[
  [\text{HC}_2\text{H}_3\text{O}_2] = 0.0385 \text{ M} \quad [\text{C}_2\text{H}_3\text{O}_2^-] = 0.0385 \text{ M}
  \]

- this is a buffer solution with [acid] = [base]

- using Henderson-Hasselbalch (pKₐ = 4.74):

  \[
  \text{pH} = 4.74 + \log \frac{0.0385}{0.0385}
  \]

  \[
  \text{pH} = \text{pK}_a = 4.74
  \]

- at the half-way point in a weak + strong titration, the pH of the solution equals the pKₐ of the acid

### Strong Acid + Weak Base Titrations

**example:**

30.0 mL of 0.125 M HC₂H₃O₂ (aq) is titrated with 0.100 M NaOH.

- determine [HC₂H₃O₂] and [C₂H₃O₂⁻] after neutralization reaction is complete:

  \[
  [\text{HC}_2\text{H}_3\text{O}_2] = \frac{0.01875 \text{ mol}}{0.04875 \text{ L}} \quad [\text{C}_2\text{H}_3\text{O}_2^-] = \frac{0.01875 \text{ mol}}{0.04875 \text{ L}}
  \]

  \[
  [\text{HC}_2\text{H}_3\text{O}_2] = 0.0385 \text{ M} \quad [\text{C}_2\text{H}_3\text{O}_2^-] = 0.0385 \text{ M}
  \]

- this is a buffer solution with [acid] = [base]

- using Henderson-Hasselbalch (pKₐ = 4.74):

  \[
  \text{pH} = 4.74 + \log \frac{0.0385}{0.0385}
  \]

  \[
  \text{pH} = \text{pK}_a = 4.74
  \]

- at the half-way point in a weak + strong titration, the pH of the solution equals the pKₐ of the acid

### Strong Acid + Weak Base Titrations

4. identify the species present when the neutralization reaction is complete, and determine which of them are key to determining the pH of the solution

- before the stoichiometric point, the neutralization reaction results in a B/BH⁺ buffer solution

- at the stoichiometric point, the acid ionization of BH⁺ will determine the pH

- beyond the stoichiometric point excess H⁺ determines the pH

5. using post-neutralization concentrations of species, set up the appropriate calculation and determine pH of solution

### Strong Acid + Weak Base Titrations

**strategy:**

1. write the *net ionic equation* for the neutralization reaction that will occur

   - strong acid is completely ionized
   - weak base is only partially ionized

2. using V and M, calculate mol of each reactant present

3. set up a reaction table; identify the limiting and excess reactant

**example:**

20.0 mL of 1.20 M CH₃NH₂ (aq) is titrated with 0.750 M HNO₃ (aq).

Determine the following:

- initial pH of the solution
- pH after the addition of 10.0 mL of HNO₃
- pH at the stoichiometric point
- pH after the addition of 50.0 mL HNO₃
example:
20.0 mL of 1.20 M CH₃NH₂ (aq) is titrated with 0.750 M HNO₃.

- neutralization reaction (NO₃⁻ spectator ion):
  \[ \text{CH₃NH₂ (aq)} + \text{H}^+ (aq) \rightarrow \text{CH₃NH₃}^+ (aq) \]

- calculate mol CH₃NH₂ (aq):
  \[ \text{mol CH₃NH₂} = (0.0200 \text{ L})(1.20 \text{ mol/L}) = 0.0240 \text{ mol CH₃NH₂} \]

- calculate volume HNO₃ (aq) required to reach the stoichiometric point:
  \[ 0.0240 \text{ mol CH₃NH₂} \times \frac{1 \text{ mol H}^+}{1 \text{ mol CH₃NH₂}} \times \frac{1 \text{ L sol'n}}{0.750 \text{ mol H}^+} = 0.0320 \text{ L or 32.0 mL} \]

example:
20.0 mL of 1.20 M CH₃NH₂ (aq) is titrated with 0.750 M HNO₃.

- Determine the initial pH; \textit{pH of the solution before adding any CH₃NH₂ (aq)}.
  another way to say this . . .
  \textit{What is the pH of 1.20 M CH₃NH₂ (aq)}?
  weak base calculation; \(K_b\) for CH₃NH₂ = \(3.7 \times 10^{-4}\)
  \[ x = [\text{OH}^-] = 0.021 \text{ M} \]
  \[ \text{pOH} = - \log (0.021) = 1.68 \]
  \[ \text{pH} = 12.32 \]

example:
20.0 mL of 1.20 M CH₃NH₂ (aq) is titrated with 0.750 M HNO₃.

- determine [CH₃NH₂] and [CH₃NH₃⁺] after neutralization reaction is complete:
  \[ [\text{CH₃NH₂}] = \frac{0.0165 \text{ mol}}{(0.200 + 0.0100) \text{ L}} \]
  \[ [\text{CH₃NH₃}^+] = \frac{0.00750 \text{ mol}}{(0.200 + 0.0100) \text{ L}} \]
  \[ [\text{CH₃NH₂}] = 0.550 \text{ M} \]
  \[ [\text{CH₃NH₃}^+] = 0.250 \text{ M} \]

- this is a buffer solution
  determine [OH⁻] and pH by using an equilibrium table

  \[ \text{OR} \]

  the Henderson-Hasselbalch equation
example:
20.0 mL of 1.20 M CH₃NH₂ (aq) is titrated with 0.750 M HNO₃.

- using an equilibrium table ($K_b = 3.7 \times 10^{-4}$):

<table>
<thead>
<tr>
<th>CH₃NH₂</th>
<th>+</th>
<th>H₂O</th>
<th>⇌</th>
<th>CH₃NH₃⁺</th>
<th>+</th>
<th>OH⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial []:</td>
<td>.550 M</td>
<td>---</td>
<td>.250 M</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Δ []:</td>
<td>− x</td>
<td>---</td>
<td>+ x</td>
<td>+ x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>equil []:</td>
<td>(.550 −x)M</td>
<td>---</td>
<td>(.250+x) M</td>
<td>x M</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- using Henderson-Hasselbalch ($pK_a$ of CH₃NH₃⁺ = 10.57):

$$pH = 10.57 + \log \frac{.550}{.250}$$

$$pH = 10.91$$

example:
20.0 mL of 1.20 M CH₃NH₂ (aq) is titrated with 0.750 M HNO₃.

- determine the pH at the stoichiometric point.

32.0 mL HNO₃ (aq) added to reach stoichiometric pt at stoichiometric point:

$$\text{mol } H^+ \text{ added} = \text{mol CH₃NH₂ present} = 0.0240 \text{ mol}$$

- set up reaction table:

<table>
<thead>
<tr>
<th>before rxn:</th>
<th>CH₃NH₂</th>
<th>+</th>
<th>H⁺</th>
<th>→</th>
<th>CH₃NH₃⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>mol</td>
<td>.0240 mol</td>
<td>.0240 mol</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>change:</td>
<td>−.0240 mol</td>
<td>−.0240 mol</td>
<td>+.0240 mol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>after rxn:</td>
<td>0</td>
<td>0</td>
<td>.0240 mol</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

example:
20.0 mL of 1.20 M CH₃NH₂ (aq) is titrated with 0.750 M HNO₃.

- after the neutralization reaction, CH₃NH₂ and H⁺ are completely consumed
- acid ionization of CH₃NH₃⁺ controls the pH of sol'n:

$$\text{CH₃NH₃⁺ (aq)} \rightleftharpoons \text{CH₃NH₂ (aq)} + \text{H⁺ (aq)}$$

$$K_a = K_w/K_b \text{ for CH₃NH₂} = 2.7 \times 10^{-11}$$

- determine $[\text{CH₃NH₃⁺}]$ after neutralization reaction:

$$[\text{CH₃NH₃⁺}] = \frac{.0240 \text{ mol}}{.0520 \text{ L}} = 0.462 \text{ M}$$

- solve for $x$:

$$x = [H^+] = 3.5 \times 10^{-6} \text{ M}$$

$$pH = 5.46$$

- for a weak base titrated with a strong acid, the pH < 7 at the stoichiometric point
Determine the pH after the addition of 50.0 mL HNO₃ (aq).

\[ \text{mol H}^+ \text{ added} = (0.0500 \text{ L})(0.750 \text{ mol/L}) = 0.0375 \text{ mol H}^+ \]

- set up a reaction table to identify limiting and excess reactant:

<table>
<thead>
<tr>
<th>before rxn</th>
<th>CH₃NH₂</th>
<th>+</th>
<th>H⁺</th>
<th>→</th>
<th>CH₃NH₃⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>before rxn</td>
<td>.0240 mol</td>
<td>.0375 mol</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>change</td>
<td>-.0240 mol</td>
<td>-.0240 mol</td>
<td>+.0240 mol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>after rxn</td>
<td>0</td>
<td>.0135 mol</td>
<td>.0240 mol</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- determine [excess reactant] after neutralization

reaction is complete:

\[ [\text{H}^+] = \frac{\text{mol H}^+}{\text{total sol'n volume}} \]

\[ [\text{H}^+] = \frac{0.0135 \text{ mol}}{(0.0200 + 0.0500) \text{ L}} \]

\[ [\text{H}^+] = 0.193 \text{ M} \]

\[ \text{pH} = 0.741 \]

20.0 mL of 1.20 M CH₃NH₂ (aq) is titrated with 0.750 M HNO₃.

- determine [CH₃NH₂] & [CH₃NH₃⁺] after neutralization

reaction is complete:

\[ [\text{CH₃NH₂}] = \frac{0.0120 \text{ mol}}{0.0360 \text{ L}} \quad [\text{C₂H₃O₂⁻}] = \frac{0.0120 \text{ mol}}{0.0360 \text{ L}} \]

\[ [\text{HC₂H₃O₂}] = 0.330 \text{ M} \quad [\text{C₂H₃O₂⁻}] = 0.330 \text{ M} \]

- this is a buffer solution with [acid] = [base]

- using Henderson-Hasselbalch (pKₐ = 10.57):

\[ \text{pH} = 10.57 + \log \frac{0.330}{0.330} \]

\[ \text{pH} = \text{pK}_a = 10.57 \]

- at the half-way point in a weak + strong titration, the pH of the solution equals the pKₐ of the acid
Weak Base/Strong Acid Titrations:
- Consider the titration of 20.0 mL of 1.20 M CH\(_3\)NH\(_2\) (aq) with 0.75 M HNO\(_3\) (aq).

<table>
<thead>
<tr>
<th>mL HNO(_3) added</th>
<th>total sol’n vol.</th>
<th>[OH(^-)] after rxn</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>20</td>
<td>0.021 M</td>
<td>12.32</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>0.0020 M</td>
<td>11.30</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>8.1 x 10(^{-4}) M</td>
<td>10.91</td>
</tr>
<tr>
<td>20</td>
<td>40</td>
<td>3.7 x 10(^{-4}) M</td>
<td>10.35</td>
</tr>
<tr>
<td>25</td>
<td>45</td>
<td>2.2 x 10(^{-4}) M</td>
<td>10.01</td>
</tr>
<tr>
<td>30</td>
<td>50</td>
<td>2.5 x 10(^{-4}) M</td>
<td>9.40</td>
</tr>
<tr>
<td>32</td>
<td>52</td>
<td>3.5 x 10(^{-6}) M</td>
<td>5.46</td>
</tr>
<tr>
<td>35</td>
<td>55</td>
<td>0.042 M</td>
<td>1.38</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>0.100 M</td>
<td>1.00</td>
</tr>
<tr>
<td>45</td>
<td>65</td>
<td>0.151 M</td>
<td>0.821</td>
</tr>
<tr>
<td>50</td>
<td>70</td>
<td>0.193 M</td>
<td>0.714</td>
</tr>
<tr>
<td>60</td>
<td>80</td>
<td>0.263 M</td>
<td>0.580</td>
</tr>
</tbody>
</table>

\[\text{HIn} (aq) + H_2O (l) \rightleftharpoons In^- (aq) + H_3O^+ (aq)\]

Acid-Base Indicators
- An indicator is used to **indicate** the stoichiometric point in a titration - typically by change in color.
- You want to choose an indicator that will change color very close to the stoichiometric point in your titration.
- Results in minimal experimental error.
- pH of indicator color change should be close (±1) to pH at stoichiometric point.
- Acid-base indicators tend to be large organic molecules that are weak acids.

**Titration Curve for Strong Acid + Weak Base**

- Start at high (basic) pH.
- pH > 7 before stoichiometric point (H\(^+\) limiting reactant).
- pH < 7 at stoichiometric point (acidic solution).
- pH < 7 beyond stoichiometric point (OH\(^-\) limiting reactant).
- End at low (acidic) pH.

Acid-Base Indicators
- A few examples of indicators:

  - **phenolphthalein**
    - Acid form: colorless
    - Base form: pink
    - pH range of color change: 8 – 10
  - **bromocresol green**
    - Acid form: yellow
    - Base form: blue
    - pH range of color change: 3.8 – 5.3
  - **methyl red**
    - Acid form: orange
    - Base form: yellow
    - pH range of color change: 4.2 – 6.2
Acid-Base Indicators

- The color of an indicator solution depends on the pH (and $[H_3O^+]$) and the relative amounts of $HIn$ and $In^-$ present.

$$HIn (aq) + \text{H}_2\text{O} (l) \rightleftharpoons In^- (aq) + H_3O^+ (aq)$$

\[ K_{In} = \frac{[In^-][H_3O^+]}{[HIn]} \quad ; \quad [H_3O^+] = K_{In} \frac{[HIn]}{[In^-]} \]

- pH affects the equilibrium position, and therefore the ratio of acid form : base form of indicator in sol’n.

2 extremes:

- In acidic solution:
  - Low pH
  - High $[H_3O^+]$
  - Equilibrium position far to the left
  - $[HIn]$ high, $[In^-]$ low
  - Indicator is in its acid form and color

- In basic solution:
  - High pH
  - Low $[H_3O^+]$
  - Equilibrium position far to the right
  - $[HIn]$ low, $[In^-]$ high
  - Indicator is in its base form and color

<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>
Choosing an Indicator for a Titration

- In general, an indicator will change color at a solution pH = \( pK_{In} + 1 \).

- You should choose an indicator with \( pK_{In} \) value that is close to the pH of the solution at the stoichiometric point of your titration.
Final Thoughts on Acid-Base Titrations

- neutralization reactions happen 1st fast
go to completion
- set up reaction table (with mol of species) for the neutralization reaction
- assess what is in solution when the neutralization reaction is complete
- calculate post-neutralization [ ] of important species
  \[ [ ] = \text{mol} \div \text{total sol'n volume} \]

- if \( H_3O^+ \) or \( OH^- \) is present after the neutralization reaction, go straight to pH calculation
  - at any point in a strong acid + strong base titration
  - beyond the stoichiometric point in weak + strong titration
- if HA & A\(^-\) or B & BH\(^+\) are present after the neutralization reaction:
  - buffer solution – use equilibrium calculation or Henderson-Hasselbalch equation
  - before the stoichiometric point in weak + strong titration
- if A\(^-\) or BH\(^+\) are present after the neutralization reaction:
  - equilibrium calculation based on ionization:
    \[ A^- (aq) + H_2O (l) \rightleftharpoons \text{HA (aq)} + \text{OH}^- (aq) \]
    \[ \text{BH}^+ (aq) \rightleftharpoons \text{B (aq)} + \text{H}^+ (aq) \]
  - at the stoichiometric point in weak + strong titration

Final Thoughts on Acid-Base Titrations

- pH titration curves:
  - know the characteristic profiles for the 3 categories of titrations
  - know the important points on the curve:
    - stoichiometric point
    - half-way point
    - buffer zone
- calculations for titrations:
  - volume of acid or base req'd to reach stoichiometric pt
  - initial pH of solution
  - pH before, at, beyond & half-way to the stoichiometric pt