Titration-region & buffer calculations

An acid-base region is a circumstance
... not a sequence of operations

Region 1: Only weak acid (base)
Region 2: Both weak acid (base) and its conjugate base (acid)
Region 3: Only conjugate of weak acid (base)
Region 4: Strong base (acid), no matter what else

For each of these circumstances ...

It does not matter how they arise

Region 1: Strong acid only

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

<table>
<thead>
<tr>
<th></th>
<th>HA</th>
<th>H(_3)O(^+)</th>
<th>A(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>(c_a)</td>
<td>(10^{-7})</td>
<td>0</td>
</tr>
<tr>
<td>Revised initial, (K_a &gt; 1)</td>
<td>0</td>
<td>(10^{-7} + c_a = c_a)</td>
<td>(c_a)</td>
</tr>
<tr>
<td>Change</td>
<td>+ (x)</td>
<td>- (x)</td>
<td>- (x)</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>(x)</td>
<td>(c_a - x = c_a)</td>
<td>(c_a - x = c_a)</td>
</tr>
</tbody>
</table>

\(10^{-7} + c_a \approx c_a\) because \(K_a > K_w\)
\(c_a - x \approx c_a\) because \(K_a > 1\)

\[\text{(HA)} = x \approx c_a^2 / K_a\]

Region 1: Strong acid only example

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

\(K_a\) of HA is \(1 \times 10^{-6}\)

What is the pH and (HA) in 0.001 M HA?

\[
(\text{H}_3\text{O}^+)^+ = c_a = 0.001 \rightarrow \text{pH} = 3.0
\]

\[
(\text{HA}) = x = c_a^2 / K_a = (0.001)^2 / (1 \times 10^{-6}) = 1 \times 10^{-12} !!!
\]
Region 1: Weak acid only

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

<table>
<thead>
<tr>
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<th>HA</th>
<th>( \text{H}_3\text{O}^+ )</th>
<th>A⁻</th>
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<tr>
<td>Initial</td>
<td>( c_a )</td>
<td>10⁻⁻⁻</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>(-x)</td>
<td>(+x)</td>
<td>(+x)</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>( c_a - x \approx c_a )</td>
<td>10⁻⁻⁺ ( +x ) ( +x )</td>
<td></td>
</tr>
</tbody>
</table>

\( 10^{-7} + x \approx x \) because \( K_a > K_w \)
\( c_a - x \approx c_a \) because \( 1 > K_a \)
\( (\text{H}_3\text{O}^+) = x = \sqrt{K_a c_a} \)

Region 1: Weak acid only example

HA(aq) + H₂O(l) → H₃O⁺(aq) + A⁻(aq)

\( K_a \) of HA is \( 1 \times 10^{-7} \)

What is the pH of 0.001 M HA?

\( (\text{H}_3\text{O}^+) = \sqrt{K_a c_a} = \sqrt{(1 \times 10^{-10})} = 1 \times 10^{-5} \)

pH = 5.0

Region 2: Partially neutralized

HA(aq) + H₂O(l) → H₃O⁺(aq) + A⁻(aq)

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<tr>
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<th>( \text{H}_3\text{O}^+ )</th>
<th>A⁻</th>
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<tbody>
<tr>
<td>Initial</td>
<td>( c_a )</td>
<td>10⁻⁻⁻</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>(-x)</td>
<td>(+x)</td>
<td>(+x)</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>( c_a - x \approx c_a )</td>
<td>10⁻⁻⁺ ( +x ) ( +x )</td>
<td></td>
</tr>
</tbody>
</table>

\( 10^{-7} + x \approx x \) because \( K_a > K_w \)
\( c_a - x \approx c_a \) and \( c_b + x \approx c_b \) because \( 1 > K_a \)
\( (\text{H}_3\text{O}^+) = x = K_a (c_a/c_b) = K_a (\text{mol}/\text{mol}) \)

Region 2: Partially neutralized example

HA(aq) + H₂O(l) → H₃O⁺(aq) + A⁻(aq)

\( K_a \) of HA is \( 1 \times 10^{-5} \)

1.0 L each of 0.012 M HA and 0.010 M NaOH are combined. What is the pH?

\( \text{mol}_a = 0.002 \text{ mol}, \text{mol}_b = 0.010 \text{ mol} \)

\( (\text{H}_3\text{O}^+) = x = K_a (\text{mol}_a/\text{mol}_b) = 2 \times 10^{-6} \)

pH = 6 - 0.3 = 5.7
Region 3: Equivalence point

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

<table>
<thead>
<tr>
<th></th>
<th>(\text{A}^-)</th>
<th>(\text{HA})</th>
<th>(\text{OH}^-)</th>
</tr>
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<tbody>
<tr>
<td>Initial</td>
<td>(c_b)</td>
<td>0</td>
<td>(10^{-7})</td>
</tr>
<tr>
<td>Change</td>
<td>(-x)</td>
<td>(+x)</td>
<td>(+x)</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>(c_b - x = c_b)</td>
<td>(x)</td>
<td>(10^{-7} + x = x)</td>
</tr>
</tbody>
</table>

\[10^{-7} + x = x\] because \(K_b = K_w / K_a \gg K_w\)

\[c_b - x = c_b\] because \(1 \gg K_b\)

\[\text{[OH}^-\] = x = \sqrt{K_b c_b}\]

Region 3: Equivalence point example

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

\[K_a\] of HA is \(1 \times 10^{-7}\)

1.0 L each of 0.002 M HA and 0.002 M NaOH are combined. What is the pH?

\[c_b = 0.002 \text{ mol/(2 L)} = 0.001 \text{ M}\]

\[K_b = K_w / K_a = 1 \times 10^{-7}\]

\[\text{[OH}^-\] = \sqrt{K_b c_b} = \sqrt{1 \times 10^{-10}} = 1 \times 10^{-5}\]

\[\text{pOH} = 5.0 \rightarrow \text{pH} = 9.0\]

Region 4: Beyond equivalence example

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

\[K_a\] of HA is \(1 \times 10^{-7}\)

1.0 L each of 0.002 M HA and 0.003 M NaOH are combined. What is the pH?

\[\text{[OH}^-\] = 0.001 \text{ mol/(2 L)} = 0.0005 \text{ M}\]

\[\text{pOH} = 4 - 0.7 = 3.3 \rightarrow \text{pH} = 10.7\]

Buffers resist change in pH
Buffers resist change in pH
Let's see what causes these changes in pH to be so drastic in pure water, but so muted in a buffer.

Buffers resist change in pH

Added strong base (say, OH⁻) is gobbled up ...

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

\( c_a \) lowered, \( c_b \) raised, \( c_a/c_b \) lowered

Added strong acid (say, HCl) is gobbled up ...

\[ \text{HCl(aq)} + \text{A}^- (aq) \rightarrow \text{HA(aq)} + \text{Cl}^- (aq) \]

\( c_a \) lowered, \( c_b \) raised, \( c_a/c_b \) raised

Add strong base to buffer

1 L buffer, \( c_a = c_b = 1.00 \text{ M} \), \( K_a = 1 \times 10^{-5} \), pH = ...

Add 100. mL of 0.100 M NaOH

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

HA \( \rightarrow \) 1.00 mol - 0.010 mol = 0.99 mol

A⁻ \( \rightarrow \) 1.00 mol + 0.010 mol = 1.01 mol

\( c_a = 0.99 \text{ mol/1.10 L}, c_b = 1.01 \text{ mol/1.10 L} \)

\( c_a/c_b = 1.00 \rightarrow 0.99/1.01, \text{ pH} \rightarrow 5.01 \) (tiny change!)

Add strong acid to buffer

1 L buffer, \( c_a = c_b = 1.00 \text{ M} \), \( K_a = 1 \times 10^{-5} \), pH = 5.00

Add 100. mL of 0.100 M HCl

\[ \text{HCl(aq)} + \text{A}^- (aq) \rightarrow \text{HA(aq)} + \text{Cl}^- (aq) \]

HA \( \rightarrow \) 1.00 mol + 0.010 mol = 1.01 mol

A⁻ \( \rightarrow \) 1.00 mol - 0.010 mol = 0.99 mol

\( c_a = 1.01 \text{ mol/1.10 L}, c_b = 0.99 \text{ mol/1.10 L} \)

\( c_a/c_b = 1.00 \rightarrow 1.01/0.99, \text{ pH} \rightarrow 4.99 \) (tiny change!)
Add strong acid/base to water

1 L of water, $K_a = 1 \times 10^{-14}$, pH = 7.00

Add 100. mL of 0.100 M HCl

$(\text{H}_3\text{O}^+)$ = 0.010 mol / 1.10 L = 0.0091

pH = 2.04 (huge change!)

Add 100. mL of 0.100 M NaOH

$(\text{OH}^-)$ = 0.010 mol / 1.10 L = 0.0091

pOH = 2.04, pH = 11.96 (huge change!)