Worksheet 24 – Polyprotic Acid Titration Curves

1. **Initial pH**
   This is determined by the most acidic of the $K_a$ values and the initial concentration of the acid. (Same as a monoprotic acid)

2. **Half-way points**
   At each half-way point, the pH = $pK_a$ of the group you are titrating. At this point in the titration curve, we are in a buffering region, and the curve will be relatively flat.

3. **Equivalence points**
   At each equivalence point, the pH is the average of the $pK_a$ values above and below. At the last equivalence point (the end point), the pH is determined by the $K_b$ of the conjugate base of the weakest acid.

The example below should illustrate these points. We will plot the titration of 100 mL of 0.10 M phosphoric acid with 1.0 M NaOH.

\[
\begin{align*}
\text{H}_3\text{PO}_4 + \text{H}_2\text{O} & \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{H}_3\text{O}^+ & K_{a1} = 7.5 \times 10^{-3} \\
\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} & \rightleftharpoons \text{HPO}_4^{2-} + \text{H}_3\text{O}^+ & K_{a2} = 6.2 \times 10^{-8} \\
\text{HPO}_4^{2-} + \text{H}_2\text{O} & \rightleftharpoons \text{PO}_4^{3-} + \text{H}_3\text{O}^+ & K_{a3} = 4.2 \times 10^{-13}
\end{align*}
\]

1. The initial pH is determined by $K_{a1}$. In this case, the 5% approximation doesn't work and the value of $x$ must be determined using the quadratic equation.

\[
\begin{align*}
\text{H}_3\text{PO}_4 & \quad \text{H}_2\text{PO}_4^- & \quad \text{H}_3\text{O}^+ \\
\text{Initial} & 0.10 & 0 & 0 \\
\text{Change} & -x & +x & +x \\
\text{Equil.} & 0.10-x & x & x
\end{align*}
\]

\[
K_a = 7.5 \times 10^{-3} = \frac{[\text{H}_2\text{PO}_4^-][\text{H}_3\text{O}^+]}{[\text{H}_3\text{PO}_4]} = \frac{x^2}{0.10-x}
\]

\[
x^2 + 7.5 \times 10^{-3}x - 7.5 \times 10^{-4} = 0
\]

\[
x = \frac{-7.5 \times 10^{-3} \pm \sqrt{(7.5 \times 10^{-3})^2 - 4(1)(-7.5 \times 10^{-4})}}{2}
\]

\[
x = 0.02389, \ -0.03139
\]

\[
x = \boxed{0.0239} = [\text{H}_3\text{O}^+]
\]

\[
\text{pH} = -\log(0.0239) = 1.62
\]
2. The half-way points will occur after the addition of how many mL of base? What are the pH values at each half-way point?

\[ \text{mol } H_3PO_4 = 0.100 \text{ L} \times \frac{0.1 \text{ mol } H_3PO_4}{1 \text{ L}} = 0.01 \text{ mol } H_3PO_4 \]

The first half-way point occurs when 0.005 mol of OH\(^-\) have been added (half the value of the initial moles of H\(_3\)PO\(_4\)):

\[ 0.005 \text{ mol OH}^- \times \frac{1 \text{ mol NaOH}}{1 \text{ mol OH}^-} \times \frac{1 \text{ L mol NaOH solution}}{1.0 \text{ mol NaOH}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 5 \text{ mL solution} \]

first half-way point = 5 mL of base \( \text{pH} = \text{pK}_{a1} = -\log(7.5 \times 10^{-3}) = 2.12 \)

The second half-way point occurs when 0.015 mol of OH\(^-\) have been added (use all initial moles of H\(_3\)PO\(_4\) and half of the H\(_2\)PO\(_4\)-):

\[ 0.015 \text{ mol OH}^- \times \frac{1 \text{ mol NaOH}}{1 \text{ mol OH}^-} \times \frac{1 \text{ L mol NaOH solution}}{1.0 \text{ mol NaOH}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 15 \text{ mL solution} \]

second half-way point = 15 mL of base \( \text{pH} = \text{pK}_{a2} = -\log(6.2 \times 10^{-8}) = 7.21 \)

The third half-way point occurs when 0.025 mol of OH\(^-\) have been added (use all initial moles of H\(_3\)PO\(_4\) and H\(_2\)PO\(_4\)- and half of the HPO\(_4\)\(^{-2}\)):

\[ 0.025 \text{ mol OH}^- \times \frac{1 \text{ mol NaOH}}{1 \text{ mol OH}^-} \times \frac{1 \text{ L mol NaOH solution}}{1.0 \text{ mol NaOH}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 25 \text{ mL solution} \]

third half-way point = 25 mL of base \( \text{pH} = \text{pK}_{a3} = -\log(4.2 \times 10^{-13}) = 12.38 \)

3. The equivalence points:

The first equivalence point occurs when 0.010 mol of OH\(^-\) have been added (the value of the initial moles of H\(_3\)PO\(_4\)):

\[ 0.010 \text{ mol OH}^- \times \frac{1 \text{ mol NaOH}}{1 \text{ mol OH}^-} \times \frac{1 \text{ L mol NaOH solution}}{1.0 \text{ mol NaOH}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 10 \text{ mL solution} \]

The pH is the average of \( \text{pK}_{a1} \) and \( \text{pK}_{a2} \): \( \text{pH} = (2.12+7.21)/2 = 4.67 \)

The second equivalence point occurs when 0.020 mol of OH\(^-\) have been added (twice the value of the initial moles of H\(_3\)PO\(_4\)):

\[ 0.020 \text{ mol OH}^- \times \frac{1 \text{ mol NaOH}}{1 \text{ mol OH}^-} \times \frac{1 \text{ L mol NaOH solution}}{1.0 \text{ mol NaOH}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 20 \text{ mL solution} \]

The pH is the average of \( \text{pK}_{a2} \) and \( \text{pK}_{a3} \): \( \text{pH} = (7.21+12.38)/2 = 9.79 \)
4. The end point. Again, the 5% approximation will not work. First calculate the moles of $\text{PO}_4^{3-}$ formed in the complete titration. The moles of $\text{PO}_4^{3-}$ at the end point are equal to the moles of $\text{H}_3\text{PO}_4$ at the start of the titration (see the ICE tables in the Lecture 24 notes)

$$\text{mol } \text{PO}_4^{3-} = 0.10$$

Next, calculate the total volume after the complete titration. The end point occurs when 0.030 mol of $\text{OH}^-$ have been added (three times the value of the initial moles of $\text{H}_3\text{PO}_4$):

$$\text{vol} = 0.130 \text{ L}$$

$$[\text{PO}_4^{3-}] = \frac{0.10 \text{ mol}}{0.130 \text{ L}} = 0.0769 \text{ M}$$

Complete the reaction of $\text{PO}_4^{3-}$ with water:

$$\text{PO}_4^{3-} + \text{H}_2\text{O} \rightleftharpoons \text{HPO}_4^{2-} + \text{OH}^-$$

For $\text{PO}_4^{3-}$, $K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.2 \times 10^{-13}} = 2.38 \times 10^{-2}$

<table>
<thead>
<tr>
<th></th>
<th>$\text{PO}_4^{3-}$</th>
<th>$\text{HPO}_4^{2-}$</th>
<th>$\text{OH}^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.0769</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Equil.</td>
<td>0.0769-x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

$$K_b = 2.38 \times 10^{-2} = \frac{[\text{HPO}_4^{2-}][\text{OH}^-]}{[\text{PO}_4^{3-}]} = \frac{x^2}{0.0769 - x}$$

$$x^2 + 2.38 \times 10^{-2} x - 1.83 \times 10^{-3} = 0$$

$$x = \frac{-2.38 \times 10^{-2} \pm \sqrt{(2.38 \times 10^{-2})^2 - 4(1)(-1.83 \times 10^{-3})}}{2}$$

$$x = 0.0325, -0.0563$$

$$[\text{OH}^-] = 0.0325 \text{ M}$$

$$\text{pOH} = -\log(0.0325) = 1.49$$

$$\text{pH} \text{ at the end point of the titration} = 14 - \text{pOH} = 12.51$$
5. Plot these points and connect them to determine the titration curve of phosphoric acid. The curve should be relatively flat around each of the half-way points when we are in a buffering region.

The titration curve should have flat regions centered around each of the three halfway point (buffer zones) and sharp increases in pH around the equivalence points.