Polyprotic Acid Titrations – Problems

1. When 100.0 mL of 0.10 M malonic acid is titrated with 0.10 M NaOH the following titration curve is observed:

\[
\text{Malonic acid} = \text{HOOC–CH\textsubscript{2}–COOH} \\
\text{abbreviated H\textsubscript{2}A}
\]

Given that \( K_{a1} = 1.5 \times 10^{-3} \) and \( K_{a2} = 2.0 \times 10^{-6} \) for malonic acid, answer the following questions:

A. Write out the reactions and the equilibrium expressions associated with \( K_{a1} \) and \( K_{a2} \).

B. Calculate the pH at:
   1) point A (pH = 1.94)
   2) point B
   3) point C
   4) point D
   5) point E

Note: To calculate the pH at point A, the quadratic equation (or the method of successive approximations) must be used. The correct calculated pH is listed above. Understand how to calculate the pH at point A, but ignore the actual calculation for tonight's homework assignment.
2. Phosphoric acid, $\text{H}_3\text{PO}_4$, is a triprotic acid with $K_{a1} = 7.5 \times 10^{-3}$, $K_{a2} = 6.2 \times 10^{-8}$ and $K_{a3} = 4.8 \times 10^{-13}$. Consider the titration of 50.0 mL of 1.0 $M$ $\text{H}_3\text{PO}_4$ by 1.0 $M$ NaOH and answer the following questions.

A. Write out the reactions associated with $K_{a1}$, $K_{a2}$, $K_{a3}$.

B. Calculate the pH after the following total volumes of NaOH have been added:

1) 0.0 mL of NaOH (pH = 1.08)
2) 25.0 mL of NaOH
3) 50.0 mL of NaOH
4) 75.0 mL of NaOH
5) 100.0 mL of NaOH
6) 125.0 mL of NaOH
7) 150.0 mL of NaOH (pH = 12.80)

Note: To solve for the pH at points 1 and 7, the quadratic equation (or the method of successive approximations) must be used. The correct calculated pHs at points 1 and 7 are listed above. Understand how to calculate the pH at points 1 and 7, but ignore the actual calculation for tonight’s homework assignment.

C. Sketch the titration curve for this titration.

D. What weak acid and what conjugate base makes the best phosphate buffer at pH ~7.0?

Note:
For an amphoteric species, $p\text{H} = \frac{pK_{a1} + pK_{a2}}{2}$, regardless of the concentration.

An amphoteric species can act as either an acid or as a base. Examples of amphoteric species are: $\text{HCO}_3^-$, $\text{H}_2\text{PO}_4^-$, $\text{HPO}_4^{2-}$. 
SOLUTIONS TO POLYPROTONIC ACID ASSIGNMENT, pp.114-115

1. A. \[\text{HOOC-CH}_2\text{-COOH} \rightleftharpoons \text{H}^+ + \text{HOOC-CH}_2\text{-COO}^-\]

\[K_{a1} = \frac{[\text{H}^+][\text{HOOCCH}_2\text{COO}^-]}{[\text{HOOCCH}_2\text{COOH}]} = 1.5 \times 10^{-3}\]

\[\text{HOOCCH}_2\text{COO}^- \rightleftharpoons \text{H}^+ + \text{OOCCH}_2\text{COO}^2^-\]

\[K_{a2} = \frac{[\text{H}^+][\text{OOCCH}_2\text{COO}^2^-]}{[\text{HOOCCH}_2\text{COO}^-]} = 2.0 \times 10^{-6}\]

B. Point A: 100 mL of 0.10 M H\textsubscript{2}A

\[
\begin{array}{ccc}
\text{H}_2\text{A} & \rightleftharpoons & \text{H}^+ + \text{HA}^- \\
\text{I} & 0.10 \text{ M} & 0 & 0 \\
\text{C} & -x & +x & +x \\
\text{E} & 0.10 - x & x & x \\
\end{array}
\]

\[K_{a1} = 1.5 \times 10^{-3} = \frac{x^2}{0.10 - x}\]

The 5% rule fails. \(x = 1.15 \times 10^{-2}\) M by successive approximations.

Ignore the amount of [H\textsuperscript{+}] released by 2\textsuperscript{nd} dissociation (it will be negligible).

\[\text{pH} = -\log(1.15 \times 10^{-2}) = 1.94\]

Point B: halfway to first equivalence point where \([\text{H}_2\text{A}] = [\text{HA}^-]\)

\[\text{pH} = pK_{a1} = -\log (1.5 \times 10^{-3}) = 2.82\]

Point C: first equivalence point

Major species is HA\textsuperscript{-} which is both an acid and a base (amphoteric species).

\[\text{pH} = \frac{pK_{a1} + pK_{a2}}{2} = \frac{2.82 + 5.70}{2} = 4.26\]

Note: \(pK_{a2} = -\log (2.0 \times 10^{-6}) = 5.70\)
Point D: halfway to second equivalence point where \([HA^-] = [A^{2-}]\).

\[
pH = pK_{a2} = -\log K_{a2} = -\log (2.0 \times 10^{-6}) = 5.70
\]

Point E: second equivalence point; only \(A^{2-}\) present (a weak base).

\[
A^{2-} + H_2O \rightleftharpoons HA^- + OH^- \quad K_b = K_w/K_{a2} = 5.0 \times 10^{-9}
\]

\[
\begin{array}{c|ccc}
 & I & C & E \\
I & 10 \text{ mmol/300 mL} & 0 & 0 \\
C & -x & +x & +x \\
E & 0.033 \text{ M} & -x & x \\
\end{array}
\]

\[
5.0 \times 10^{-9} = \frac{x^2}{0.033 - x} \approx \frac{x^2}{0.033}
\]

\(x = 1.3 \times 10^{-5} \text{ M} = [OH^-]\)

Check assumption: \(\frac{1.3 \times 10^{-5}}{0.033} \times 100\% = 0.04\% < 5\%\) so assumption good

\[
pOH = -\log [OH^-] = 4.89
\]

\[
pH = 14.00 - pOH = 9.11
\]

2. A. \(H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-\) \(K_{a1} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = 7.5 \times 10^{-3}\)

\(H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}\) \(K_{a2} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 6.2 \times 10^{-8}\)

\(HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}\) \(K_{a3} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 4.8 \times 10^{-13}\)
B. 50.0 mL of 1.0 M H₃PO₄ titrated by 1.0 M NaOH

1) 0 mL NaOH added, H₃PO₄ major species present

Ignore H⁺ contributed by 2nd and 3rd dissociation since $K_{a3} \ll K_{a2} \ll K_{a1}$.

\[ H₃PO₄ \rightleftharpoons H⁺ + H₂PO₄⁻ \quad K_{a1} = 7.5 \times 10^{-3} \]

\[
\text{Eq} \quad 1.0 \quad -x \quad x \quad x
\]

\[ K_{a1} = 7.5 \times 10^{-3} = \frac{x}{1.0 - x} \]

The 5% rule fails. Using successive approximations:

\[ x = [H⁺] = 8.3 \times 10^{-2} \; M \; ; \; pH = 1.08 \]

2) Add 25.0 mL NaOH. This is halfway to the first equivalence point where $[H₃PO₄] = [H₂PO₄⁻]$.

\[ pH = pK_{a1} = -\log (7.5 \times 10^{-3}) = 2.12 \]

3) Add 50.0 mL NaOH. This is the first equivalence point.

H₂PO₄⁻ is the major species present. H₂PO₄⁻ is amphoteric.

\[ pH = \frac{pK_{a1} + pK_{a2}}{2} = \frac{(2.12 + 7.21)}{2} = 4.67 \]

4) Add 75.0 mL NaOH. This is halfway to the second equivalence point where $[H₂PO₄⁻] = [HPO₄^{2-}]$.

\[ pH = pK_{a2} = -\log (6.2 \times 10^{-8}) = 7.21 \]
5) Add 100 mL NaOH. This is the second equivalence point. 
HPO$_4^{2-}$ is the major species present. HPO$_4^{2-}$ is also amphoteric.

\[
\text{pH} = \frac{pK_{a2} + pK_{a3}}{2} = \frac{7.21 + 12.32}{2} = 9.76
\]

6) 125 mL of NaOH added. This is halfway to the third equivalence point where [HPO$_4^{2-}$] = [PO$_4^{3-}$].

\[
\text{pH} = pK_{a3} = -\log (4.8 \times 10^{-13}) = 12.32
\]

7) 150 mL of NaOH added. This is at the third equivalence point. 
PO$_4^{3-}$ is the major species present.

PO$_4^{3-}$ is a weak base; 
\[
K_b = \frac{K_w}{K_{a3}} = \frac{1.0 \times 10^{-14}}{4.8 \times 10^{-13}} = 2.1 \times 10^{-2}
\]

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

<table>
<thead>
<tr>
<th>I</th>
<th>50 mmol/200 mL</th>
<th>0</th>
<th>0</th>
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</thead>
<tbody>
<tr>
<td>C</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>E</td>
<td>0.25 M - x</td>
<td>x</td>
<td>x</td>
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</tbody>
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\[
K_b = \frac{x^2}{0.25 - x} = 2.1 \times 10^{-2}
\]

The 5% rule fails. Using successive approximations,

\[
x = [\text{OH}^-] = 6.3 \times 10^{-2} \text{ M}
\]

\[
\text{pOH} = -\log (6.3 \times 10^{-2}) = 1.20; \quad \text{pH} = 14.00 - 1.20 = 12.80
\]
Note: in this plot, the pH break at the third equivalence point is overexaggerated for this titration.

D. A best buffer has equal concentrations of weak acid and conjugate base. When this occurs, pH = pK_a. The best phosphate buffer for pH = 7.0 will be the weak acid/conjugate base pair with a pK_a value closest to 7.0. Since pK_a2 = 7.21 is closest to 7.0, H_2PO_4^-/HPO_4^{2-} will be the best phosphate buffer for pH = 7.0.