15.51

HA + OH$^-$ → A$^-$ + H$_2$O; Added OH$^-$ from the strong base converts the weak acid, HA, into its conjugate base, A$^-$. Initially, before any OH$^-$ is added (point d), HA is the dominant species present. After OH$^-$ is added, both HA and A$^-$ are present and a buffer solution results (region b). At the equivalence point (points a and e), exactly enough OH$^-$ has been added to convert all of the weak acid, HA, into its conjugate base, A$^-$. Past the equivalence point (region f), excess OH$^-$ is present. For the answer to part b, we included almost the entire buffer region. The maximum buffer region (or the region which is the best buffer solution) is around the halfway point to equivalence (point c). At this point, enough OH$^-$ has been added to convert exactly one-half of the weak acid present initially into its conjugate base so [HA] = [A$^-$] and pH = pK$_a$. A best buffer has about equal concentrations of weak acid and conjugate base present.

15.53

This is a strong acid (HClO$_4$) titrated by a strong base (KOH). Added OH$^-$ from the strong base will react completely with the H$^+$ present from the strong acid to produce H$_2$O.

(a).

Only strong acid present. [H$^+$] = 0.200 M; pH = 0.699

(b).

mmol OH$^-$ added = 10.0 mL x 0.100 mmol OH$^-$ / mL = 1.00 mmol OH$^-$

mmol H$^+$ present = 40.0 mL x 0.100 mmol H$^+$ / mL = 8.0 mmol H$^+$

Note: The units mmoles are usually easier numbers to work with. The units for molarity are moles/L but are also equal to mmoles/mL.

\[
\begin{array}{c|c|c|c}
\text{H}^+ & + & \text{OH}^- & \rightarrow & \text{H}_2\text{O} \\
\hline
\text{Before} & 8.00 \text{ mmol} & 1.00 \text{ mmol} \\
\text{Change} & -1.00 \text{ mmol} & -1.00 \text{ mmol} & \text{Reacts completely} \\
\text{After} & 7.00 \text{ mmol} & 0 \\
\end{array}
\]

The excess H$^+$ determines pH. [H$^+$]$_{excess} = 7.00 \text{ mmol H}^+ / (40.0 \text{ mL} + 10.0 \text{ mL}) = 0.140 \text{ M};$

pH = 0.854

(c).

mmol OH$^-$ added = 40.0 mL x 0.100 M = 4.00 mmol OH$^-$

\[
\begin{array}{c|c|c|c}
\text{H}^+ & + & \text{OH}^- & \rightarrow & \text{H}_2\text{O} \\
\hline
\text{Before} & 8.00 \text{ mmol} & 4.00 \text{ mmol} \\
\text{After} & 4.00 \text{ mmol} \\
\end{array}
\]
$$[\text{H}^+]_{\text{excess}} = 4.00 \text{ mmol} / (40.0 + 40.0) \text{ mL} = 0.0500 \text{ M}; \ \text{pH} = 1.301$$

d. 
mmol OH\(^-\) added = 80.0 mL x 0.100 M = 8.00 mmol OH\(^-\); This is the equivalence point because we have added just enough OH\(^-\) to react with all the acid present. For a strong acid-strong base titration, pH = 7.00 at the equivalence point since only neutral species are present (K\(^+\), ClO\(_4\)\(^-\), H\(_2\)O).

e. 
mmol OH\(^-\) added = 100.0 mL x 0.100 M = 10.0 mmol OH\(^-\)

\[
\begin{align*}
\text{H}^+ & + \text{OH}^- \rightarrow \text{H}_2\text{O} \\
\text{Before} & \quad 8.00 \text{ mmol} & 10.00 \text{ mmol} \\
\text{After} & \quad 0 & 2.0 \text{ mmol}
\end{align*}
\]

Post the equivalence point, the pH is determined by the excess OH\(^-\) present.

$$[\text{OH}^-]_{\text{excess}} = 2.0 \text{ mmol} / (40.0 + 100.0) \text{ mL} = 0.014 \text{ M}; \ \text{pOH} = 1.85; \ \text{pH} = 12.15$$

15.55
This is a weak acid (HC\(_2\)H\(_3\)O\(_2\)) titrated by a strong base (KOH).

a. 
Only a weak acid is present. Solving the weak acid problem:

\[
\begin{align*}
\text{HC}_2\text{H}_3\text{O}_2 & \rightleftharpoons \text{H}^+ & + & \text{C}_2\text{H}_3\text{O}_2^- \\
\text{Initial} & \quad 0.200 \text{ M} & 0 & 0 \\
\text{change} & \quad -x & +x & +x \\
\text{equil.} & \quad 0.200 - x & x & x \\
\end{align*}
\]

$$K_a = 1.8 \times 10^{-5} = x^2 / 0.200 - x = x^2 / 0.200, \ x = [\text{H}^+] = 1.9 \times 10^{-3} \text{ M}; \ \text{pH} = 2.72; \ \text{Assumptions good.}$$

b. 
The added OH\(^-\) will react completely with the best acid present, HC\(_2\)H\(_3\)O\(_2\). 

mmol HC\(_2\)H\(_3\)O\(_2\) present = 100.0 mL x 0.200 mmol HC\(_2\)H\(_3\)O\(_2\) / mL = 20.0 mmol HC\(_2\)H\(_3\)O\(_2\) 

mmol OH\(^-\) added = 50.0 mL x 0.100 mmol OH\(^-\) / mL = 5.00 mmol OH\(^-\)
Before reaction of all the strong base, we will have a buffered solution containing a weak acid (HC$_2$H$_3$O$_2$) and its conjugate base (C$_2$H$_3$O$_2^-$). We will use the Henderson-Hasselbalch equation to solve for the pH of this buffer.

\[
pH = pK_a = \log \left(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right) = \log \left(\frac{5.00 \text{ mmol}}{15.0 \text{ mmol}}\right) = 4.74 + \log \left(\frac{5.00}{15.0}\right) = 4.74 + (-0.477) = 4.26
\]

Note that the total volume cancels in the Henderson-Hasselbalch equation. For the [base]/[acid] terms, the mole (or mmole) ratio equals the concentration ratio because the components of the buffer are always in the same volume of solution.

c.

\[\text{mmol OH}^- \text{ added} = 100.0 \text{ mL} \times 0.100 \text{ mmol OH}^-/\text{mL} = 10.0 \text{ mmol OH}^-; \text{ The same amount (20.0 mmol) of HC}_2\text{H}_3\text{O}_2 \text{ is present as before (it never changed). As before, let the OH}^- \text{ react to completion, then see what remains in solution after the reaction.}\]

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

Before 20.0 mmol 10.0 mmol 0
Change -10.0 mmol -10.0 mmol +10.0 mmol Reacts completely
After 10.0 mmol 0 10.0 mmol

A buffered solution results after the reaction. Because \([C_2H_3O_2^-] = [HC_2H_3O_2] = 10.0 \text{ mmol/total volume, pH} = pK_a. \text{ This is always true at the halfway point to equivalence for a weak acid/strong base titration, pH} = pK_a.\]

\[\text{pH} = -\log(1.8 \times 10^{-5}) = 4.74\]

d.

\[\text{mmol OH}^- \text{ added} = 150.0 \text{ mL} \times 0.100 \text{ M} = 15.0 \text{ mmol OH}^-; \text{ Added OH}^- \text{ reacts completely with the weak acid.}\]

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

Before 20.0 mmol 15.0 mmol 0
After 5.0 mmol 0 15.0 mmol

We have a buffered solution after all the \text{OH}^- \text{ reacts to completion. Using the Henderson-Hasselbalch equation:}
pH = 4.74 + \log([C_2H_3O_2^-]/[HC_2H_3O_2]) = 4.74 + \log (15.00 \text{ mmol} / 5.0 \text{ mmol})

(Total volume cancels, so we can use mmol ratios.)

pH = 4.74 + 0.48 = 5.22

e. mmol OH\(^-\) added = 200.00 mL x 0.100 M = 20.0 mmol OH\(^-\); As before let the added OH\(^-\) react to completion with the weak acid, then see what is in solution after this reaction.

\[
\begin{align*}
\text{HC}_2\text{H}_3\text{O}_2^- & \quad + \quad \text{OH}^- & \quad \rightarrow & \quad \text{C}_2\text{H}_3\text{O}_2^- & \quad + \quad \text{H}_2\text{O} \\
\text{Before} & \quad 20.0 \text{ mmol} & \quad 20.0 \text{ mmol} & \quad 0 \\
\text{After} & \quad 0 & \quad 0 & \quad 20.0 \text{ mmol}
\end{align*}
\]

This is the equivalence point. Enough OH\(^-\) has been added to exactly neutralize all the weak acid present initially. All that remains that affects the pH at the equivalence point is the conjugate base of the weak acid, C_2H_3O_2^-\(\). This is a weak base equilibrium problem because the conjugate bases of all weak acids are weak bases themselves.

\[
\begin{align*}
\text{C}_2\text{H}_3\text{O}_2^- & \quad + \quad \text{H}_2\text{O} & \quad \rightleftharpoons & \quad \text{HC}_2\text{H}_3\text{O}_2^- & \quad + \quad \text{OH}^- \quad K_b = K_w/K_a = 1.0 \times 10^{-14}/1.8 \times 10^{-5} \\
\text{Initial} & \quad 20.0 \text{ mmol}/300.0 \text{ mL} & \quad 0 & \quad 0 & \quad K_b = 5.6 \times 10^{-10} \\
\text{x mol/L C}_2\text{H}_3\text{O}_2^- & \text{reacts with H}_2\text{O} \text{ to reach equilibrium} \\
\text{Ch.} & \quad -x & \quad +x & \quad +x \\
\text{Equil.} & \quad 0.0667 - x & \quad x & \quad x
\end{align*}
\]

\[
K_b = 5.6 \times 10^{-10} = x^2 / 0.0667 - x \approx x^2 / 0.0667, \quad x = [\text{OH}^-] = 6.1 \times 10^{-6} \text{ M}
\]

pOH = 5.21; pH = 8.79; Assumptions good.

f. mmol OH\(^-\) added = 250.0 mL x 0.100 M = 25.0 mmol OH\(^-\)

\[
\begin{align*}
\text{HC}_2\text{H}_3\text{O}_2^- & \quad + \quad \text{OH}^- & \quad \rightarrow & \quad \text{C}_2\text{H}_3\text{O}_2^- & \quad + \quad \text{H}_2\text{O} \\
\text{Before} & \quad 20.0 \text{ mmol} & \quad 25.0 \text{ mmol} & \quad 0 \\
\text{After} & \quad 0 & \quad 5.0 \text{ mmol} & \quad 20.0 \text{ mmol}
\end{align*}
\]

After the titration reaction, we will have a solution containing excess OH\(^-\) and a weak base, C_2H_3O_2^-\(\). When a strong base and a weak base are both present, assume the amount of OH\(^-\) added from the weak base will be minimal, i.e., the pH past the equivalence point will be determined by the amount of excess strong base.

\[
[\text{OH}^-]_{\text{excess}} = 5.0 \text{ mmol} / (100.0 \text{ mL} + 250.0 \text{ mL}) = 0.014 \text{ M}; \quad \text{pOH} = 1.85; \quad \text{pH} = 12.15
\]
15.57
We will do sample calculations for the various parts of the titration. All results are summarized in Table 15.1 at the end of Exercise 15.60.

At the beginning of the titration, only the weak acid $\text{HC}_3\text{H}_5\text{O}_3$ is present.

$$\text{HLac} \rightleftharpoons \text{H}^+ + \text{Lac}^-$$

$K_a = 10^{-3.86} = 1.4 \times 10^{-4}$

<table>
<thead>
<tr>
<th>Initial</th>
<th>0.100 M</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
</table>

$x$ mol/L HLac dissociates to reach equilibrium

<table>
<thead>
<tr>
<th>Change</th>
<th>-x</th>
<th>+x</th>
<th>+x</th>
</tr>
</thead>
</table>

| Equil. | 0.100 – x | x | x |

$1.4 \times 10^{-4} = x^2 / 0.100 – x \approx x^2 / 0.100, x = [\text{H}^+] = 3.7 \times 10^{-3}$ M; pH = 2.43  Assumptions good.

Up to the stoichiometric point, we calculate the pH using the Henderson-Hasselbalch equation because we have buffer solutions that result after the OH$^-$ from the strong base reacts completely with the best acid present, HLac. This is the buffer region. For example, at 4.0 mL of NaOH added:

initial mmol HLac present = 25.0 mL x 0.100 mmol / mL = 2.50 mmol HLac

mmol OH$^-$ added = 4.0 mL x 0.100 mmol / mL = 0.40 mmol OH$^-$

Note: The units mmol are usually easier numbers to work with. The units for molarity are moles/L but are also equal to mmoles/mL.

The 0.40 mmol added OH$^-$ convert 0.40 mmoles HLac to 0.40 mmoles Lac$^-$ according to the equation:

$$\text{HLac} + \text{OH}^- \rightarrow \text{Lac}^- + \text{H}_2\text{O}$$

Reacts completely

mmol HLac remaining = 2.50 – 0.40 = 2.10 mmol; mmol Lac$^-$ produced = 0.40 mmol

We have a buffer solution. Using the Henderson-Hasselbalch equation where $pK_a = 3.86$:

$$\text{pH} = pK_a + \log([\text{Lac}^-] / [\text{HLac}]) = 3.86 + \log (0.40 / 2.10)$$

(Total volume cancels, so we can use the mole or mmole ratio.)

$$\text{pH} = 3.86 – 0.72 = 3.14$$

Other points in the buffer region are calculated in a similar fashion. Perform a stoichiometry problem first, followed by a buffer problem. The buffer region includes all points up to 24.9 mL OH$^-$ added.
At the stoichiometric (equivalence) point (25.0 mL OH\(^-\) added), we have added enough OH\(^-\) to convert all of the HLac (2.50 mmol) into its conjugate base, Lac\(^-\). All that is present is a weak base. To determine the pH, we perform a weak base calculation.

\[
\text{[Lac}^-\text{]}_0 = 2.50 \text{ mmol / (25.0 mL + 25.0 mL)} = 0.0500 \text{ M}
\]

\[
\text{Lac}^- + \text{H}_2\text{O} \rightleftharpoons \text{HLac} + \text{OH}^- \\
K_b = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-4}} = 7.1 \times 10^{-11}
\]

Initial 0.0500 M 0 0

\[
x \text{ mol/L Lac}^- \text{ reacts with H}_2\text{O to reach equilibrium}
\]

Change -x +x +x

Equil. 0.0500 – x x x

\[
K_b = x^2 / 0.0500 - x \approx x^2 / 0.0500 = 7.1 \times 10^{-11}
\]

\[
x = [\text{OH}^-] = 1.9 \times 10^{-6} \text{ M; pOH} = 5.72; \text{pH} = 8.28 \quad \text{Assumptions good.}
\]

Past the stoichiometric point, we have added more than 2.50 mmol of NaOH. The pH will be determined by the excess OH\(^-\) ion present. An example of this calculation follows.

At 25.1 mL: OH\(^-\) added = 25.1 mL \times 0.100 mmol/mL = 2.51 mmol OH\(^-\)

2.50 mmol OH\(^-\) neutralizes all the weak acid present. The remainder is excess OH\(^-\).

\[
[\text{OH}^-]_{\text{excess}} = 2.51 - 2.50 = 0.01 \text{ mmol}
\]

\[
[\text{OH}^-]_{\text{excess}} = 0.01 \text{ mmol / (25.0 mL + 25.1 mL)} = 2 \times 10^{-4} \text{ M; pOH} = 3.7; \text{pH} = 10.3
\]

All results are listed in Table 15.1 at the end of solution to Exercise 15.60.

**15.59**

At beginning of the titration, only the weak base NH\(_3\) is present. As always, solve for the pH using the \(K_b\) reaction for NH\(_3\).

\[
\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \\
K_b = 1.8 \times 10^{-5}
\]

Initial 0.100 M 0 0

Equil. 0.100 – x x x

\[
K_b = x^2 / 0.100 - x \approx x^2 / 0.100 = 1.8 \times 10^{-5}
\]

\[
x = [\text{OH}^-] = 1.3 \times 10^{-3} \text{ M; pOH} = 2.89; \text{pH} = 11.11 \quad \text{Assumptions good.}
\]

In the buffer region (4.0 – 24.9 mL), we can use the Henderson-Hasselbalch equation:
\[ K_a = 1.0 \times 10^{-14} / 1.8 \times 10^{-5} = 5.6 \times 10^{-10}; \] 
\[ pK_a = 9.25; \] 
\[ \text{pH} = 9.25 + \log([\text{NH}_3]/[\text{NH}_4^+]) \]

We must determine the amounts of \( \text{NH}_3 \) and \( \text{NH}_4^+ \) present after the added \( \text{H}^+ \) reacts completely with the \( \text{NH}_3 \). For example, after 8.0 mL HCl are added:

\[
\text{initial mmol NH}_3 \text{ present} = 25.0 \text{ mL} \times 0.100 \text{ mmol/mL} = 2.50 \text{ mmol NH}_3
\]
\[
\text{mmol H}^+ \text{ added} = 8.0 \text{ mL} \times 0.100 \text{ mmol/mL} = 0.80 \text{ mmol H}^+
\]

Added \( \text{H}^+ \) reacts with \( \text{NH}_3 \) to completion: \( \text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+ \)

\[
\text{mmol NH}_3 \text{ remaining} = 2.50 - 0.80 = 1.70 \text{ mmol}; \text{mmol NH}_4^+ \text{ produced} = 0.80 \text{ mmol}
\]

\[
\text{pH} = 9.25 + \log (1.70 / 0.80) = 9.58 \quad \text{(Mole or mmole ratios can be used since the total volume cancels.)}
\]

Other points in the buffer region are calculated in similar fashion. Results are summarized in Table 15.1 at the end of Exercise 15.60.

At the stoichiometric point (25.0 mL \( \text{H}^+ \) added), just enough HCl has been added to convert all of the weak base (\( \text{NH}_3 \)) into its conjugate acid (\( \text{NH}_4^+ \)). Because all conjugate acids of weak bases are weak acids themselves, perform a weak acid calculation to determine the pH.

\[
[\text{NH}_4^+]_0 = 2.50 \text{ mmol/50.0 mL} = 0.0500 \text{ M}
\]

\[
\begin{array}{ccc}
\text{NH}_4^+ & = & \text{H}^+ + \text{NH}_3 \\
\text{Initial} & = & 0.0500 \text{ M} \quad 0 \quad 0 \\
\text{Equil.} & = & 0.0500 - x \quad x \quad x
\end{array}
\]

\[
5.6 \times 10^{-10} = x^2 / 0.0500 - x \approx x^2 / 0.0500, \quad x = [\text{H}^+] = 5.3 \times 10^{-6} \text{ M}; \quad \text{pH} = 5.28 \quad \text{Assumptions good.}
\]

Beyond the stoichiometric point, the \( \text{pH} \) is determined by the excess \( \text{H}^+ \). For example, at 28.0 mL of \( \text{H}^+ \) added:

\[
\text{mmol H}^+ \text{ added} = 28.0 \text{ mL} \times 0.100 \text{ mol/mL} = 2.80 \text{ mmol H}^+
\]

\[
\text{Excess mmol H}^+ = 2.80 \text{ mmol} - 2.50 \text{ mmol} = 0.30 \text{ mmol excess H}^+
\]

\[
[\text{H}^+]_{\text{excess}} = 0.30 \text{ mmol}/(25.0 + 28.0) \text{ mL} = 5.7 \times 10^{-3} \text{ M}; \quad \text{pH} = 2.24
\]

All results are summarized in Table 15.1.

15.61
a.
This is a weak acid/strong base titration. At the halfway point to equivalence, \([\text{weak acid}] = [\text{conjugate base}], \text{ so pH} = pK_a \) (always true for a weak acid/strong base titration).
pH = -log(6.4 x 10^{-5}) = 4.19

mmol HC_7H_5O_2 present = 100. mL x 0.10 M = 10. mmol HC_7H_5O_2. For the equivalence point, 10. mmol of OH^{-} must be added. The volume of OH^{-} added to reach the equivalence point is:

10. mmol OH^{-} x 1 mL/0.10 mmol OH^{-} = 1.0 x 10^{2} mL OH^{-}

At the equivalence point, 10. mmol of HC_7H_5O_2 is neutralized by 10. mmol of OH^{-} to produce 10. mmol of C_7H_5O_2^{-}. This is a weak base. The total volume of the solution is 100.0 mL + 1.0 x 10^{2} mL = 2.0 x 10^{2} mL = 2.0 x 10^{2} mL. Solving the weak base equilibrium problem:

C_7H_5O_2^{-} + H_2O ⇄ HC_7H_5O_2 + OH^{-} \quad K_b = K_w/K_a = 1.0 x 10^{-14}/6.4 x 10^{-5}

Initial 10. mmol/2.0x10^{2} mL 0 0
Equil. 0.050 – x 0 0

K_b = 1.6 x 10^{-10} = x^2/0.050-x \approx x^2/0.050, x = [OH^{-}] = 2.8 x 10^{-6} M

pOH = 5.55; pH = 8.45 Assumptions good.

b. At the halfway point to equivalence for a weak base/strong acid titration, pH = pK_a since [weak base] = [conjugate acid].

K_a = K_w/K_b = 1.0 x 10^{-14} / 5.6 x 10^{-4} = 1.8 x 10^{-11}; pH = pK_a = -log(1.8 x 10^{-11}) = 10.74

For the equivalence point (mmol acid added = mmol base present):

mmol C_2H_5NH_2 present = 100.0 mL x 0.10 M = 10. mmol C_2H_5NH_2

mL HNO_3 added = 10. mmol H^{+} x 1 mL / 0.20 mmol = 50. mL H^{+}

The strong acid added completely converts the weak base into its conjugate acid. Therefore, at the equivalence point, [C_2H_5NH_3^{+}]_0 = 10. mmol/(100.0 + 50.) mL = 0.067 M. Solving the weak acid equilibrium problem:

C_2H_5NH_3^{+} ⇄ H^{+} + C_2H_5NH_2

Initial 0.067 M 0 0
Equil. 0.067 – x 0 0

K_a = 1.8 x 10^{-11} = x^2 / 0.067 – x \approx x^2 / 0.067, x = [H^{+}] = 1.1 x 10^{-6} M

pH = 5.96; Assumption good.
c. In a strong acid/strong base titration, the halfway point has no special significance other than exactly one-half of the original amount of acid present has been neutralized.

\[ \text{mmol } H^+ \text{ present} = 100.0 \text{ mL} \times 0.50 \text{ M} = 50. \text{ mmol } H^+ \]

\[ \text{mL OH}^- \text{ added} = 25 \text{ mmol OH}^- \times 1 \text{ mL} / 0.25 \text{ mmol} = 1.0 \times 10^2 \text{ mL OH}^- \]

\[ H^+ + OH^- \rightarrow H_2O \]

Before 50 mmol  25 mmol
After  25 mmol  0

\[ [H^+]_{\text{excess}} = \frac{25 \text{ mmol}}{(100.0 + 1.0 \times 10^2) \text{ mL}} = 0.13 \text{ M}; \text{ pH} = 0.89 \]

At the equivalence point of a strong acid/strong base titration, only neutral species are present (Na\(^+\), Cl\(^-\), H\(_2\)O), so the pH = 7.00.

15.63
75.0 mL x 0.10 mmol/mL = 7.5 mmol HA; 30.0 mL x 0.10 mmol/mL = 3.0 mmol OH\(^-\) added

The added strong base reacts to completion with the weak acid to form the conjugate base of the weak acid and H\(_2\)O.

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

Before  7.5 mmol  3.0 mmol  0
After  4.5 mmol  0  3.0 mmol

A buffer results after the OH\(^-\) reacts to completion. Using the Henderson-Hasselbalch equation:

\[ \text{pH} = \text{pK}_a + \log ([\text{A}^-] / [\text{HA}]), \quad 5.50 = \text{pK}_a + \log [(3.0 \text{ mmol} / 105.0 \text{ mmol}) / (4.5 \text{ mmol} / 105.0 \text{ mmol})] \]

\[ \text{pK}_a = 5.50 - \log(3.0/4.5) = 5.50 - (-0.18) = 5.68; \quad K_a = 10^{-5.68} = 2.1 \times 10^{-6} \]