Chapter 10 (Acid/Base Titrations)

Strong acid with strong base

Titrate 25.00 mL of a 0.100 M HCl solution with 0.0500 M NaOH.

Calculate the pH at 0.00 mL NaOH added

$$\text{pH} = -\log(0.100) = 1.000$$

Calculate the pH at 5.00 mL NaOH added.

$$\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}, \text{ very fast and complete}$$

mmol of OH$^-$ added = (5.00mL)(0.0500) = 0.250 mmol

initial mmol H$^+$ = (25.00mL)(0.100) = 2.50 mmol

final mmol H$^+$ = 2.50 – 0.250 = 2.25 mmol

$$[\text{H}^+] = \frac{(2.25 \text{ mmol})}{(25.00 + 5.00)} = 0.0750 \text{ M}$$

$$\text{pH} = 1.125$$
Calculate the pH at 15.00 mL NaOH added.

\[
\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}, \text{ very fast and complete}
\]

\[
\text{mmol of OH}^- \text{ added} = (15.00 \text{mL})(0.0500) = 0.750 \text{ mmol}
\]

\[
\text{initial mmol H}^+ = (25.00 \text{mL})(0.100) = 2.50 \text{ mmol}
\]

\[
\text{final mmol H}^+ = 2.50 - 0.750 = 1.75 \text{ mmol}
\]

\[
[H^+] = \frac{1.75 \text{ mmol}}{25.00 + 15.00} = 0.0438 \text{ M}
\]

\[
\text{pH} = 1.359
\]
Calculate the pH at 40.00 mL NaOH added.

\[ \text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}, \text{ very fast and complete} \]

\[
\text{mmol of OH}^- \text{ added} = (40.00\text{mL})(0.0500) = 2.00 \text{ mmol}
\]

\[
\text{initial mmol H}^+ = (25.00\text{mL})(0.100) = 2.50 \text{ mmol}
\]

\[
\text{final mmol H}^+ = 2.50 - 2.00 = 0.50 \text{ mmol}
\]

\[
[\text{H}^+] = (0.50 \text{ mmol})/(25.00 + 40.00) = 0.00769 \text{ M}
\]

\[
\text{pH} = 2.11
\]
Calculate the pH at 49.50 mL NaOH added.

\[ \text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}, \text{ very fast and complete} \]

\[
\text{mmol of OH}^- \text{ added} = (49.50\text{mL})(0.0500) = 2.475 \text{ mmol}
\]

\[ \text{initial mmol H}^+ = (25.00\text{mL})(0.100) = 2.50 \text{ mmol} \]

\[ \text{final mmol H}^+ = 2.50 - 2.475 = 0.025 \text{ mmol} \]

\[ [\text{H}^+] = (0.025 \text{ mmol})(25.00 + 49.50) = 0.0003, \text{ M} \]

\[ \text{pH} = 3.5 \]
Calculate the pH at 50.00 mL NaOH added.
This is the equivalence pt, the point in the titration where you have added precisely enough base to react with the acid. The product of the reaction is water. Thus, the pH = 7

Calculate the pH at 50.50 mL NaOH added.
After the equivalence point, the excess OH\(^-\) determines the pH.

\[ \text{mmoles of excess OH}^- = \text{mole OH}^- (\text{added}) - \text{mol OH}^- (\text{equiv}) \]
\[ = 50.50(0.0500) - 50.00(0.0500) = 0.025 \text{ mmol OH}^- \]

\[ [\text{OH}^-] = \frac{0.025 \text{ mmol}}{25.00 \text{mL}+50.50 \text{mL}} \]
\[ = 3.3 \cdot 10^{-4} \text{ M} \]
\[ [\text{H}_3\text{O}^+] = 3.1 \cdot 10^{-11} \text{ M}, \text{pH} = 10.52 \]
Calculate the pH at 60.00 mL NaOH added. After the equivalence point, the excess OH\textsuperscript{-} determines the pH.

\[
\text{mmoles of excess OH}^- \quad = \text{mole OH}^-\text{(added)} - \text{mol OH}^-\text{(equiv)} \\
= 60.00(0.0500) - 50.00(0.0500) \\
= 0.500 \text{ mmol OH}^- \\
\]

\[
[\text{OH}^-] = \frac{0.500 \text{ mmol}}{25.00 \text{mL} + 60.00 \text{mL}} \\
= 5.88 \cdot 10^{-4} \text{ M} \\
[\text{H}_3\text{O}^+] = 1.72 \cdot 10^{-12} \text{ M}, \text{ pH} = 11.765
\]
Strong base with strong acid

Titrate 50.00 mL of a 0.100 M NaOH solution with 0.200 M HBr.

Calculate the pH at 0.00 mL NaOH added
\[
[H_3O^+] = \frac{K_w}{0.100} = 1.00 \cdot 10^{-13} \text{ M}
\]
\[
pH = -\log(0.100 \cdot 10^{-13}) = 13.000
\]

Calculate the pH at 5.00 mL HBr added.

\[
\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}, \text{ very fast and complete}
\]

mmol of H\(^+\) added = (5.00mL)(0.200)
= 1.00 mmol

initial mmol OH\(^-\) = (50.00mL)(0.100)
= 5.00 mmol

final mmol H\(^+\) = 5.00 - 1.00 = 4.00 mmol

\[\text{[OH}^-] = \frac{4.00 \text{ mmol}}{50.00 + 5.00} = 0.0727 \text{ M}\]

pH = 12.857
Calculate the pH at 15.00 mL HBr added.

\[ \text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}, \text{ very fast and complete} \]

mmol of \( \text{H}^+ \) added = \((15.00\text{mL})(0.200)\) = 3.00 mmol

initial mmol \( \text{OH}^- \) = \((50.00\text{ml})(0.100)\) = 5.00 mmol

final mmol \( \text{H}^+ \) = 5.00 – 3.00 = 2.00 mmol

\[ [\text{OH}^-] = (2.00 \text{ mmol})/(50.00 + 15.00) \]
\[ = 0.0308 \text{ M} \]

pH = 12.483
Calculate the pH at 24.50 mL HBr added.

\[
\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}, \text{ very fast and complete}
\]

\[
\text{mmol of } \text{H}^+ \text{ added} = (24.50 \text{mL})(0.200) = 4.90 \text{ mmol}
\]

\[
\text{initial mmol OH}^- = (50.00 \text{mL})(0.100) = 5.00 \text{ mmol}
\]

\[
\text{final mmol OH}^- = 5.00 - 4.90 = 0.10 \text{ mmol}
\]

\[
[\text{OH}^-] = (0.10 \text{ mmol})/(50.00 + 24.5) = 0.0013 \text{ M}
\]

\[
\text{pH} = 11.12
\]
Calculate the pH at 25.00 mL HBr added.

This is the equivalence pt, the point in the titration where you have added precisely enough base to react with the acid. The product of the reaction is water. Thus, the pH = 7

Calculate the pH at 25.50 mL HBr added.

After the equivalence point, the excess H\(^+\) determines the pH.

\[
\text{mmoles of excess } H^+ = \text{mole } H^+(\text{added}) - \text{mol } H^+(\text{equiv})
\]
\[
= 25.50(0.200) - 25.00(0.200) = 0.10 \text{ mmol } H^+
\]
\[
[H^+] = \frac{0.10 \text{ mmol}}{50.00 \text{mL} + 25.50 \text{mL}}
\]
\[
= 1.3 \cdot 10^{-3} \text{ M}
\]
\[
\text{pH} = 2.88
\]
Calculate the pH at 30.00 mL HBr added. After the equivalence point, the excess H\(^+\) determines the pH.

\[
\text{mmoles of } H^+_{\text{excess}} = \text{mole } H^+(\text{added}) - \text{mol } H^+_{(\text{equiv})} = 30.00(0.200) - 25.00(0.200) = 1.00 \text{ mmol } H^+ \\
[H^+] = \frac{(1.00 \text{ mmol})}{(50.00\text{mL} + 30.000\text{mL})} = 1.25 \cdot 10^{-2} \text{ M} \\
pH = 1.903
\]
Weak acid titrations

12-6
100.0 mL of a solution of 0.100 M weak acid, HA, is titrated with 1.00 M KOH. (Ka = 1.0 \cdot 10^{-5})

@ 0 ml added
\[ Ka = \frac{[H^+]^2}{0.1} = 1.0 \cdot 10^{-5} \]
\[ [H^+] = 1.0 \cdot 10^{-3} \]
\[ pH = 3.00 \]

@ 1.00 mL added
\[ OH^- \text{ added} = (1.00 \text{ M})(1.00 \text{ mL}) = 1.00 \text{ mmol} \]
\[ HA + OH^- \rightarrow A^- + H_2O \text{ (to completion)} \]
\[ pH = pKa + \log(\frac{\text{mol A}^-}{\text{mol HA}}) \]
\[ \text{mol A}^- = 1.00 \text{ mmol} \]
\[ \text{mol HA} = (100.0 \text{ mL})(0.100 \text{ M}) - 1.00 \text{ mol} \]
\[ = 9.00 \text{ mmol} \]
\[ pH = 5.00 + \log(1/9) = 4.05 \]

@ 5.00 mL added
\[ OH^- \text{ added} = (1.00 \text{ M})(5.00 \text{ mL}) = 5.00 \text{ mmol} \]
\[ HA + OH^- \rightarrow A^- + H_2O \text{ (to completion)} \]
\[ pH = pKa + \log(\frac{\text{mol A}^-}{\text{mol HA}}) \]
\[ \text{mol A}^- = 5.00 \text{ mmol} \]
\[ \text{mol HA} = (100.0 \text{ mL})(0.500 \text{ M}) - 5.00 \text{ mol} \]
\[ = 5.00 \text{ mmol} \]
\[ \text{pH} = 5.00 + \log(5/5) = 5.00 \]

@ 9.00 mL added
\[ \text{OH}^- \text{ added} = (1.00 \text{ M})(9.00 \text{ mL}) = 9.00 \text{ mmol} \]
\[ \text{OH}^- \]
\[ \text{HA} + \text{OH}^- \rightarrow \text{A}^- + \text{H}_2\text{O} \text{ (to completion)} \]
\[ \text{pH} = \text{pKa} + \log(\text{mol A}^-/\text{mol HA}) \]
\[ \text{mol A}^- = 9.00 \text{ mmol} \]
\[ \text{mol HA} = (100.0 \text{ mL})(0.500 \text{ M}) - 9.00 \text{ mol} \]
\[ = 1.00 \text{ mmol} \]
\[ \text{pH} = 5.00 + \log(9/1) = 5.95 \]

@ 9.90 mL added
\[ \text{OH}^- \text{ added} = (1.00 \text{ M})(9.90 \text{ mL}) = 9.90 \text{ mmol} \]
\[ \text{OH}^- \]
\[ \text{HA} + \text{OH}^- \rightarrow \text{A}^- + \text{H}_2\text{O} \text{ (to completion)} \]
\[ \text{pH} = \text{pKa} + \log(\text{mol A}^-/\text{mol HA}) \]
\[ \text{mol A}^- = 9.90 \text{ mmol} \]
\[ \text{mol HA} = (100.0 \text{ mL})(0.500 \text{ M}) - 9.90 \text{ mol} \]
\[ = 0.10 \text{ mmol} \]
\[ \text{pH} = 5.00 + \log(9.9/0.1) = 7.00 \]
@ 10.00 mL added

OH⁻ added = (1.00 M)(10.00 mL) = 10.00 mmol

OH⁻

HA + OH⁻ → A⁻ + H₂O (to completion)

pH = pKa +log(mol A⁻/mol HA)

mol A⁻ = 10.00 mmol

mol HA = (100.0 mL)(0.500 M) - 10.0 mol
= 0 mmol

This is the equivalence point. The appropriate equilibrium is the Kb reaction for A⁻.

A⁻ + H₂O ⇌ HA + OH⁻

F_A⁻ = (10.00 mmol)/(110.0 mL) = 0.0909 M

Kb = Kw/Ka = 1.00·10⁻⁹

= [HA][OH⁻]/ (F_A⁻ - [HA])

Assume [OH⁻] = [HA], and let [HA] = x

Assume F_A⁻ ≅ [A⁻]

1.00·10⁻⁹ = x²/(0.0909)

x = [OH⁻] = 9.53·10⁻⁵ M

[H₃O⁺]⁺ = 1.05·10⁻⁹

pH = 8.98
@ 10.10 mL After the equiv. point the excess OH\(^-\) is what controls the pH.

\[
[\text{OH}^-] = \\
\frac{(10.10 \text{ mL KOH})(1.00 \text{ M KOH})-(\text{mmol HA}\text{initial})}{V_t} \\
= \frac{[10.10 - 10.00]}{(110.10)} = 9.1 \cdot 10^{-4} \text{ M} \\
pH = 10.96
\]

@ 12.00 mL After the equiv. point the excess OH\(^-\) is what controls the pH.

\[
[\text{OH}^-] = \\
\frac{(12.00 \text{ mL KOH})(1.00 \text{ M OH}^-)-(\text{mmol HA}\text{initial})}{V_t} \\
= \frac{[12.00 - 10.00]}{(112.00)} = 1.79 \cdot 10^{-2} \text{ M} \\
pH = 12.252
\]
Weak base titration
20.0 mL of a solution of 0.200 M weak base, B, is titrated with 0.0500 M HCl. (Ka(HB\(^+\)) = 1.00 \cdot 10^{-5})

@ 0 ml added
Kb = [OH\(^-\)]^2/0.200 = 1.00 \cdot 10^{-9}
[OH\(^-\)] = 4.47 \cdot 10^{-5} M, [H\(^+\)] = 2.26 \cdot 10^{-10} M
pH = 9.646

@ 5.00 mL added
H\(^+\) added = (0.0500M)(5.00 mL) = 0.250 mmol H\(^+\)
B + H\(^+\) → BH\(^+\) (to completion)
pH = pKa + log(mol B/mol BH\(^+\))

mol BH\(^+\) = 0.250 mmol
mol B = (20.0 mL)(0.200 M) - 0.250 mol
= 3.75 mmol

pH = 5.000 + log(3.75/.250) = 6.176
@ 20.00 mL added
H\(^+\) added = (0.0500M)(20.00 mL) = 1.00 mmol H\(^+\)

B + H\(^+\) → BH\(^+\) (to completion)

pH = pKa + log(mol B/mol BH\(^+\))

mol BH\(^+\) = 1.00 mmol
mol  B  = (20.0 mL)(0.200 M)- 1.00 mol
       = 3.00 mmol

pH = 5.000 + log(3.00/1.00) = 5.477

@ 40.00 mL added (1/2 way)

H\(^+\) added  = (0.0500M)(40.00 mL)
              = 2.00 mmol H\(^+\)

B + H\(^+\) → BH\(^+\) (to completion/or near to)

pH = pKa + log(mol B/mol BH\(^+\))

mol BH\(^+\)  = 2.00 mmol
mol  B = (20.0 mL)(0.200 M)- 2.00 mol
       = 2.00 mmol

pH = 5.000 + log(2/2) = 5.000
@ 60.00 mL added
H^+ added = (0.0500M)(60.00 mL)
= 3.00 mmol H^+

B + H^+ → BH^+ (to completion)
pH = pKa +log(mol B/mol BH^+)

mol BH^+ = 3.00 mmol
mol B = (20.0 mL)(0.200 M)- 3.00 mol
= 1.00 mmol

pH = 5.000 + log(1/3) = 4.523

@ 70.00 mL added
H^+ added = (0.0500M)(70.00 mL) = 3.50 mmol H^+

B + H^+ → BH^+ (to completion)
pH = pKa +log(mol B/mol BH^+)

mol BH^+ = 3.50 mmol
mol B = (20.0 mL)(0.200 M)- 3.50 mol = 0.50 mmol

pH = 5.000 + log(0.50/3.50) = 4.16
@ 79.50 mL added
H⁺ added = (0.0500 M)(79.50 mL) = 3.98 mmol H⁺

B + H⁺ → BH⁺ (to completion (or does it?))

pH = pKa + log(mol B/mol BH⁺)

mol BH⁺ = 3.98 mmol
mol B = (20.0 mL)(0.200 M) - 3.98 mol = 0.02 mmol
pH = 5.000 + log(0.02/3.98) = 2.7

@ 80.00 mL added
This is the equivalence point. The appropriate equilibrium is the Ka reaction for BH⁺.

BH⁺ + H₂O ⇌ B + H₃O⁺

F_BH⁺ = (4.000 mmol)/(100.0 mL) = 0.0400 M

Ka = 1.00 · 10⁻⁵ = [B][H₃O⁺]/(F_BH⁺ - [B])

Assume [H₃O⁺] = [B], and let [B] = x
Assume F_BH⁺ ≈ [BH⁺]

1.00 · 10⁻⁵ = x²/(0.04000)
x = [H₃O⁺] = 6.325 · 10⁻⁴ M
pH = 3.199
Why is the pH higher than what we calculated at 79.50 mL added?

The weak acid dissociates to produce weak base at these ratios to find an equilibrium.

In other words the fraction of dissociation for a solution of the weak acid at this formal concentration is $6.325 \times 10^{-4}/0.0400 = 1.58 \%$.

And the alpha fraction for $A^-$ at 79.50 mL from our calculations is $0.02/4.0 \times 100 = 0.50 \%$

Less. This implies that the reaction $B + H^+ \rightarrow BH^+$ does not go to completion.
@ 90.00 mL After the equiv. point the excess H\(^+\) is what controls the pH.

\[
[H^+] = \frac{(10.0 \text{ mL} \text{ HOCl})(0.0500 \text{ M HOCl})}{V_t} = \frac{(0.500)}{(110.00)} = 4.556 \cdot 10^{-3} \text{ M}
\]

\[
pH = 2.34
\]
Polyprotics titrations

Titrer 40.0 mL of a 0.100 M diprotic base (B) solution with 0.100 M HCl (Ka1 = 1.00 \times 10^{-4} \text{ and } K_{a2} = 5.00 \times 10^{-8})

\[ \text{B} + \text{H}_2\text{O} \leftrightarrow \text{HB}^+ + \text{OH}^- \]

\[ K_{b1} = \frac{K_w}{K_{a2}} = \frac{10^{-14}}{5.00 \times 10^{-8}} = 2.00 \times 10^{-7} \]

\[ \text{HB}^+ + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{B}^{2+} + \text{OH}^- \]

\[ K_{b2} = \frac{K_w}{K_{a1}} = \frac{10^{-14}}{1.00 \times 10^{-4}} = 1.00 \times 10^{-10} \]

@ 0 mL added

\[ \text{B} + \text{H}_2\text{O} \leftrightarrow \text{HB}^+ + \text{OH}^- \]

F_B = 0.100 M
Assume [OH^-] = [HB^+], and let [HB^+] = x
Assume \( F_{A^-} \approx [B] = 0.100 \) M

\[ 2.00 \times 10^{-7} = \frac{x^2}{0.100} \]

\[ x = [\text{OH}^-] = 1.41 \times 10^{-4} \text{ M, } \alpha_{\text{BH}^+} = 0.0014 \]
(approx. valid)

\[ [\text{H}_3\text{O}]^+ = 7.16 \times 10^{-11} \text{ M} \]

pH = 10.15
@ 10.00 mL added
   pKa₂ = 7.301
   H⁺ added = (0.100M)(10.00 mL)
            = 1.00 mmol H⁺
   B + H₃O⁺ → BH⁺ + H₂O (to completion)

   pH = pKa +log(mol P/mol HP⁺)
   mol BH⁺ = 1.00 mmol
   mol B = (40.0 mL)(0.100 M) - 1.00 mol
         = 3.00 mmol
   pH = 7.301 + log(3/1) = 7.778

@ 20 mL we are half way to the first equivalence point
pH = pKa₂ = 7.301

@ 30 mL added
   pKa₂ = 7.301
   H⁺ added = (0.100M)(30.00 mL)
            = 3.00 mmol H⁺
   B + H₃O⁺ → BH⁺ + H₂O (to completion)

   pH = pKa +log(mol B/mol HB⁺)
   mol BH⁺ = 3.00 mmol
   mol B = (40.0 mL)(0.100 M) - 3.00 mol
         = 1.00 mmol
   pH = 7.301 + log(1/3) = 6.824
@ 40 mL added we have reached the first equivalence point, and the dominant species is therefore BH⁺. This is an intermediate species that can act as both an acid and a base.

\[
\begin{align*}
HB^+ + H_2O & \leftrightarrow H_2B^{2+} + OH^- \\
K_{b2} &= Kw/K_{a1} = 10^{-14}/1.00 \times 10^{-4} = 1.01 \times 10^{-10} \\
HB^+ + H_2O & \leftrightarrow B + H_3O^+ \\
K_{a2} &= 5.00 \cdot 10^{-8}
\end{align*}
\]

\[
[H^+] = \left[ \frac{K_1 K_2 F + K_1 K_{w}}{K_1 + F} \right]^{0.5}
\]

\[
F = (40 \text{ mL})(0.100)/(80 \text{ mL}) = 0.05 \text{ M}
\]

\[
K_1 = 1.00 \cdot 10^{-4}
\]

\[
K_2 = 5.00 \cdot 10^{-8}
\]

\[
K_{w} = 1.01 \cdot 10^{-14}
\]

After simplifying
\[
[H^+] = (K_1 K_2)^{0.5} = 2.24 \cdot 10^{-6}
\]

(strictly → 2.23 \cdot 10^{-6} \text{ M})

pH = 5.651
@ 50.00 mL added

pKa₁ = 4.000

H⁺ added (after eq pt) = (0.100 M)(10.00 mL)

= 1.00 mmol

HB⁺ + H₃O⁺ → H₂B⁺ + H₂O (to completion)

\[
\text{pH} = \text{pKa}_1 + \log(\text{mol HB}^+/\text{mol H}_2\text{B}^+) \\
m\text{mol H}_2\text{B}^{2+} = 1.00 \text{ mmol} \\
m\text{mol HB}^+ = (40.0 \text{ mL})(0.100 \text{ M})- 1.00 \text{ mol} \\
= 3.00 \text{ mmol}
\]

\[
\text{pH} = 4.000 + \log(3/1) = 4.477
\]
@ 60 mL we are half way to the second equivalence point
pH = pKa₁ = 4.000

@ 60.00 mL added

@ 70 mL added
pKa₁ = 4.000
H⁺ added (after eq pt) = (0.100M)(30.00 mL) = 3.00 mmol

HB⁺ + H₃O⁺ → H₂B⁺ + H₂O (to completion)

pH = pKa₁ + \log(\text{mol HB}⁺/\text{mol H}_2\text{B}^{2⁺})

\text{mol H}_2\text{B}^{2⁺} = 3.00 \text{ mmol}
\text{mol } \text{HB}⁺ = (40.0 \text{ mL})(0.100 \text{ M}) - 3.00 \text{ mol}
= 1.00 \text{ mmol}

\text{pH} = 4.000 + \log(1/3) = 3.523
@ 80 ml we hit the second equivalence point. The dominant species is $\text{H}_2\text{B}^{2+}$. We can find the pH by examining the hydrolysis of this species.

$$\text{H}_2\text{B}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{HB}^+ + \text{H}_3\text{O}^+$$

$$F_{\text{H}_2\text{B}^{2+}} = \frac{(40.0 \text{ mL})(0.100 \text{ M})}{(120.0 \text{ mL})} = 0.0333 \text{ M}$$

$$K_a = 1.00 \cdot 10^{-4} = \frac{[\text{HB}^+][\text{H}^+]}{F_{\text{H}_2\text{B}^{2+}} - [\text{HB}^+]}$$

Assume $[\text{H}_3\text{O}^+] = [\text{HB}^+]$, and let $[\text{HB}^+] = x$

Assume $F_{\text{B}^+} \approx [\text{H}_2\text{B}^{2+}]$

$$1.00 \cdot 10^{-4} = \frac{x^2}{0.0333}$$

$$x = [\text{H}_3\text{O}^+] = 1.82 \cdot 10^{-3} \text{ M} \quad \text{(approx. failed!!)}$$

$$\text{pH} = 2.739$$

$$1.00 \cdot 10^{-4} = \frac{x^2}{(0.0333-x)}$$

$$x = [\text{H}_3\text{O}^+] = 1.776 \cdot 10^{-3} \text{ M}$$

$$\text{pH} = 2.751$$

@ 90.0 mL

Excess $\text{H}^+$ from strong acid

$$[\text{H}^+] = \frac{(10.0 \text{ mL})(0.100)/(90 \text{ mL} + 40 \text{ mL})}{(90 \text{ mL} + 40 \text{ mL})} = 7.69 \cdot 10^{-3} \text{ M}$$

$$\text{pH} = 2.114$$
@ 100.0 mL added

\[ [H^+] = \frac{(20.0 \text{ mL})(0.100)}{(90 \text{ mL} + 50 \text{ mL})} \]

\[ = 1.43 \cdot 10^{-2} \text{ M} \]

pH = 1.845
Primary Standards

KHP

-Gives four or five significant figures on the number of moles of weak acid.
-Useful for standardizing NaOH.
-NaOH is hygroscopic. Therefore it is impossible to prepare a precise concentration of NaOH.
-Standardization against a primary standard is the accepted strategy.

Indicators

Instead of following the titration with a pH meter in real time, we select an appropriate indicator that changes color near the equivalence point. An indicator is a dye that has acid base properties. Its color changes dramatically near its pKa. You select an indicator that has a pKa near the equivalence point of your weak acid or weak base titration.
First derivative plots ($\Delta pH/\Delta V$ vs. $V_{ave}$) and second derivative plots ($\Delta (\Delta pH/\Delta V)$) vs $V_{ave}$
second derivative plot

\[ \frac{D(DpH/DV)}{DV} \]

Series 1
Leveling effect

HClO₄ and HCl (in water) are both strong acids

HClO₄ and HCl (in acetic acid) are weak acids of different strengths.

K(HClO₄) = 1.3 \cdot 10^{-5}

K(HCl) = 2.8 \cdot 10^{-9}

This is because acetic acid is less basic than water

Titration Spreadsheet (Do Problem 12-66)
INTERPRETING TITRATION CURVES

Weak Acid Titrations
(0.1 M HA with 0.1 M NaOH at various Kas)
pKa 4.31
K1 4.90E-05
Ca 0.05
Cb 0.1
Va 50
Vb 25

pKa 9.69
K1 2.06E-10
Ca 0.05
Cb 0.1
Va 50
Vb 25
pKa 2.40
   4.00E-
K1 0.05
Ca 0.05
Cb 0.1
Va 50
Vb 25
Weak Base Titrations
(0.1 M B with 0.1 M HCl at various Kbs)
Polyprotic titrations

**Titrating H₃A**

\[
pK_a^1 = 2.0 \quad pK_a^2 = 5.0 \quad pK_a^3 = 9.0
\]

**H₃PO₄**

**Titrating H₃PO₄**

\[
pK_a^1 = 2.2 \quad pK_a^2 = 7.2 \quad pK_a^3 = 12.4
\]
Matching

Leucine-HCl 2.32, 9.58
malonic acid 2.847, 5.696
8-hydroxyquinoline-HCl 4.94, 9.82
malic acid 3.459, 5.097
alpha fraction plot

pH

alpha fraction

Volume base

pH

0 2 4 6 8 10 12 14 16

0 0.2 0.4 0.6 0.8 1 1.2

0 2 4 6 8 10 12 14 16

0 2 4 6 8 10 12 14 16

0 2 4 6 8 10 12 14 16

H2A
HA-
A2-

0 2 4 6 8 10 12 14 16

0 2 4 6 8 10 12 14 16

0 2 4 6 8 10 12 14 16

Volume base

pH

0 2 4 6 8 10 12 14 16

0 2 4 6 8 10 12 14 16

0 2 4 6 8 10 12 14 16

Volume base

pH

0 2 4 6 8 10 12 14 16

0 2 4 6 8 10 12 14 16

0 2 4 6 8 10 12 14 16

Volume base
alpha fraction plot

![Alpha fraction plot](image)

Volume base

![Volume base](image)