

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.



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

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

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

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

$$\text{pH} = 1.125$$

Calculate the pH at 15.00 mL NaOH added.



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

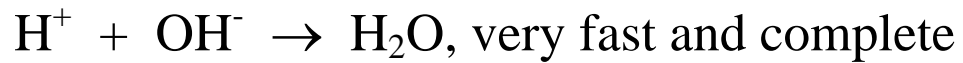
$$\text{initial mmol H}^+ = (25.00\text{mL})(0.100) = 2.50 \text{ mmol}$$

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

$$[\text{H}^+] = (1.75 \text{ mmol}) / (25.00 + 15.00) = 0.0438 \text{ M}$$

$$\text{pH} = 1.359$$

Calculate the pH at 40.00 mL NaOH added.



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

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

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

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

$$\text{pH} = 2.11$$

Calculate the pH at 49.50 mL NaOH added.



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

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

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

$$[\text{H}^+] = (0.025 \text{ mmol})(25.00 + 49.50) = 0.00033 \text{ M}$$

$$\text{pH} = 3.5$$

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.

mmoles of excess OH⁻

= mole OH⁻(added) – mol OH⁻(equiv)

= 50.50(0.0500) – 50.00(0.0500) = 0.025 mmol OH⁻

[OH⁻] = (0.025 mmol)/(25.00mL+50.50mL)

= 3.3·10⁻⁴ M

[H₃O⁺] = 3.1·10⁻¹¹ M, pH = 10.52

Calculate the pH at 60.00 mL NaOH added.

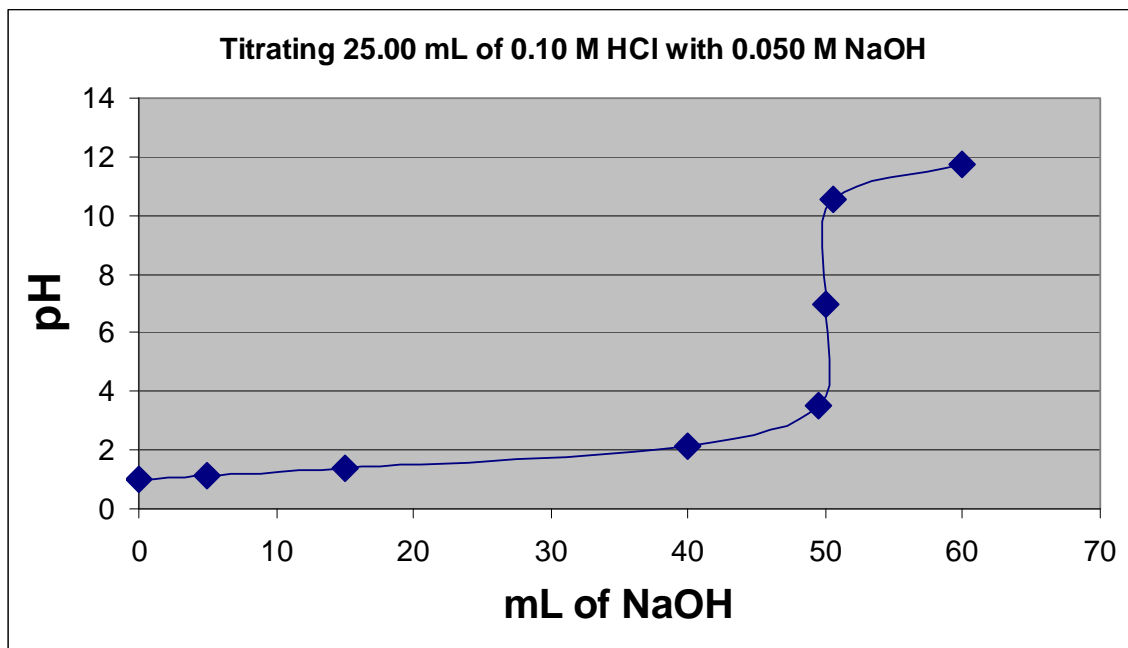
After the equivalence point, the excess OH^- determines the pH.

mmoles of excess OH^-

$$\begin{aligned} &= \text{mole } \text{OH}^- (\text{added}) - \text{mol } \text{OH}^- (\text{equiv}) \\ &= 60.00(0.0500) - 50.00(0.0500) \\ &= 0.500 \text{ mmol } \text{OH}^- \end{aligned}$$

$$\begin{aligned} [\text{OH}^-] &= (0.500 \text{ mmol}) / (25.00\text{mL} + 60.00\text{mL}) \\ &= 5.88 \cdot 10^{-4} \text{ M} \end{aligned}$$

$$[\text{H}_3\text{O}^+] = 1.72 \cdot 10^{-12} \text{ M}, \text{ pH} = 11.765$$



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

$$[\text{H}_3\text{O}^+] = K_w/0.100 = 1.00 \cdot 10^{-13} \text{ M}$$

$$\text{pH} = -\log(1.00 \cdot 10^{-13}) = 13.000$$

Calculate the pH at 5.00 mL HBr added.



$$\begin{aligned} \text{mmol of H}^+ \text{ added} &= (5.00\text{mL})(0.200) \\ &= 1.00 \text{ mmol} \end{aligned}$$

$$\begin{aligned} \text{initial mmol OH}^- &= (50.00\text{mL})(0.100) \\ &= 5.00 \text{ mmol} \end{aligned}$$

$$\text{final mmol H}^+ = 5.00 - 1.00 = 4.00 \text{ mmol}$$

$$[\text{OH}^-] = (4.00 \text{ mmol})/(50.00 + 5.00) = 0.0727 \text{ M}$$

$$\text{pH} = 12.857$$

Calculate the pH at 15.00 mL HBr added.



$$\begin{aligned} \text{mmol of H}^+ \text{ added} &= (15.00\text{mL})(0.200) \\ &= 3.00 \text{ mmol} \end{aligned}$$

$$\begin{aligned} \text{initial mmol OH}^- &= (50.00\text{ml})(0.100) \\ &= 5.00 \text{ mmol} \end{aligned}$$

$$\text{final mmol H}^+ = 5.00 - 3.00 = 2.00 \text{ mmol}$$

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

$$\text{pH} = 12.483$$

Calculate the pH at 24.50 mL HBr added.



$$\begin{aligned} \text{mmol of H}^+ \text{ added} &= (24.50\text{mL})(0.200) \\ &= 4.90 \text{ mmol} \end{aligned}$$

$$\begin{aligned} \text{initial mmol OH}^- &= (50.00\text{mL})(0.100) \\ &= 5.00 \text{ mmol} \end{aligned}$$

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

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

$$\text{pH} = 11.12$$

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.

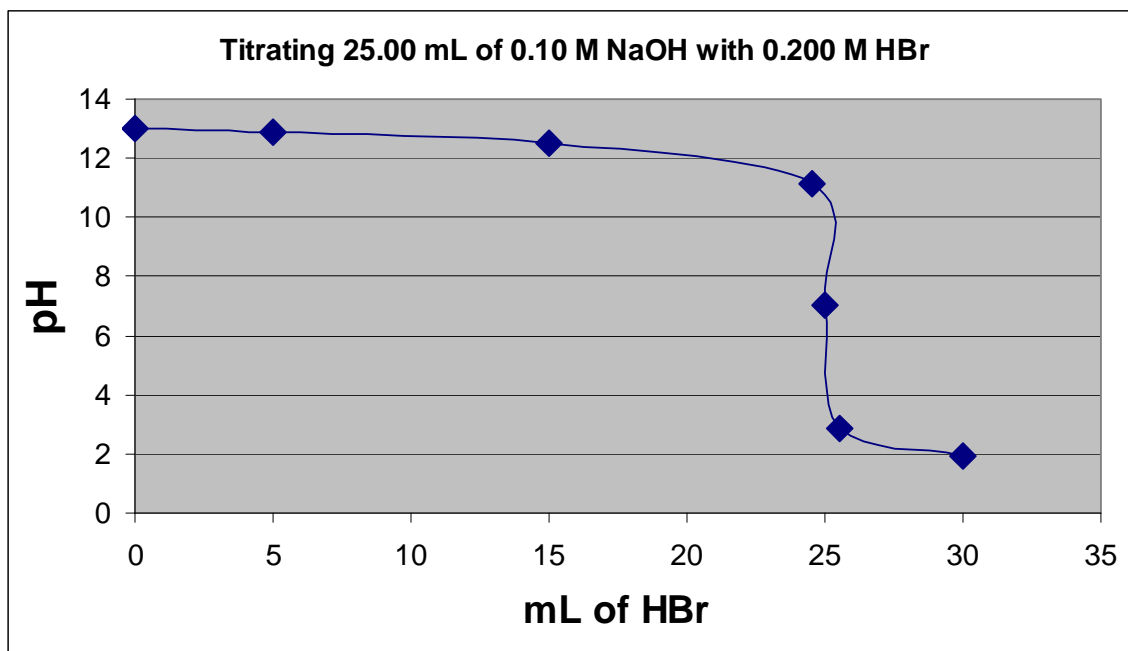
After the equivalence point, the excess H⁺ determines the pH.

$$\begin{aligned}\text{mmoles of excess H}^+ &= \text{mole H}^+(\text{added}) - \text{mol H}^+(\text{equiv}) \\ &= 25.50(0.200) - 25.00(0.200) = 0.10 \text{ mmol H}^+ \\ [\text{H}^+] &= (0.10 \text{ mmol}) / (50.00\text{mL} + 25.50\text{mL}) \\ &= 1.3 \cdot 10^{-3} \text{ M} \\ \text{pH} &= 2.88\end{aligned}$$

Calculate the pH at 30.00 mL HBr added.

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

$$\begin{aligned}\text{mmoles of H}^+_{\text{excess}} &= \text{mole H}^+(\text{added}) - \text{mol H}^+(\text{equiv}) \\ &= 30.00(0.200) - 25.00(0.200) = 1.00 \text{ mmol H}^+ \\ [\text{H}^+] &= (1.00 \text{ mmol}) / (50.00\text{mL} + 30.000\text{mL}) \\ &= 1.25 \cdot 10^{-2} \text{ M} \\ \text{pH} &= 1.903\end{aligned}$$



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. ($K_a = 1.0 \cdot 10^{-5}$)

@ 0 ml added

$$K_a = [H^+]^2/0.1 = 1.0 \cdot 10^{-5}$$

$$[H^+] = 1.0 \cdot 10^{-3}$$

$$\text{pH} = 3.00$$

@ 1.00 mL added

$$\text{OH}^- \text{ added} = (1.00 \text{ M})(1.00 \text{ mL}) = 1.00 \text{ mmol}$$

OH^-



$$\text{pH} = \text{p}K_a + \log(\text{mol A}^-/\text{mol HA})$$

$$\text{mol A}^- = 1.00 \text{ mmol}$$

$$\begin{aligned} \text{mol HA} &= (100.0 \text{ mL})(0.100 \text{ M}) - 1.00 \text{ mol} \\ &= 9.00 \text{ mmol} \end{aligned}$$

$$\text{pH} = 5.00 + \log(1/9) = 4.05$$

@ 5.00 mL added

$$\text{OH}^- \text{ added} = (1.00 \text{ M})(5.00 \text{ mL}) = 5.00 \text{ mmol}$$

OH^-



$$\text{pH} = \text{p}K_a + \log(\text{mol A}^-/\text{mol HA})$$

$$\text{mol A}^- = 5.00 \text{ mmol}$$

$$\text{mol HA} = (100.0 \text{ mL})(0.100 \text{ M}) - 5.00 \text{ mol}$$

$$= 5.00 \text{ mmol}$$
$$\text{pH} = 5.00 + \log(5/5) = 5.00$$

@ 9.00 mL added

$$\text{OH}^- \text{ added} = (1.00 \text{ M})(9.00 \text{ mL}) = 9.00 \text{ mmol}$$

OH^-



$$\text{pH} = \text{pK}_a + \log(\text{mol A}^-/\text{mol HA})$$

$$\text{mol A}^- = 9.00 \text{ mmol}$$

$$\text{mol HA} = (100.0 \text{ mL})(0.500 \text{ M}) - 9.00 \text{ mol}$$

$$= 1.00 \text{ mmol}$$

$$\text{pH} = 5.00 + \log(9/1) = 5.95$$

@ 9.90 mL added

$$\text{OH}^- \text{ added} = (1.00 \text{ M})(9.90 \text{ mL}) = 9.90 \text{ mmol}$$

OH^-



$$\text{pH} = \text{pK}_a + \log(\text{mol A}^-/\text{mol HA})$$

$$\text{mol A}^- = 9.90 \text{ mmol}$$

$$\text{mol HA} = (100.0 \text{ mL})(0.500 \text{ M}) - 9.90 \text{ mol}$$

$$= 0.10 \text{ mmol}$$

$$\text{pH} = 5.00 + \log(9.9/.1) = 7.00$$

@ 10.00 mL added

$$\text{OH}^- \text{ added} = (1.00 \text{ M})(10.00 \text{ mL}) = 10.00 \text{ mmol}$$

OH^-



$$\text{pH} = \text{pK}_a + \log(\text{mol A}^- / \text{mol HA})$$

$$\text{mol A}^- = 10.00 \text{ mmol}$$

$$\begin{aligned} \text{mol HA} &= (100.0 \text{ mL})(0.500 \text{ M}) - 10.0 \text{ mol} \\ &= 0 \text{ mmol} \end{aligned}$$

This is the equivalence point. The appropriate equilibrium is the K_b reaction for A^- .



$$F_{\text{A}^-} = (10.00 \text{ mmol}) / (110.0 \text{ mL}) = 0.0909 \text{ M}$$

$$\text{K}_b = \text{K}_w / \text{K}_a = 1.00 \cdot 10^{-9}$$

$$= [\text{HA}][\text{OH}^-] / (F_{\text{A}^-} - [\text{HA}])$$

Assume $[\text{OH}^-] = [\text{HA}]$, and let $[\text{HA}] = x$

Assume $F_{\text{A}^-} \cong [\text{A}^-]$

$$1.00 \cdot 10^{-9} = x^2 / (0.0909)$$

$$x = [\text{OH}^-] = 9.53 \cdot 10^{-5} \text{ M}$$

$$[\text{H}_3\text{O}^+] = 1.05 \cdot 10^{-9}$$

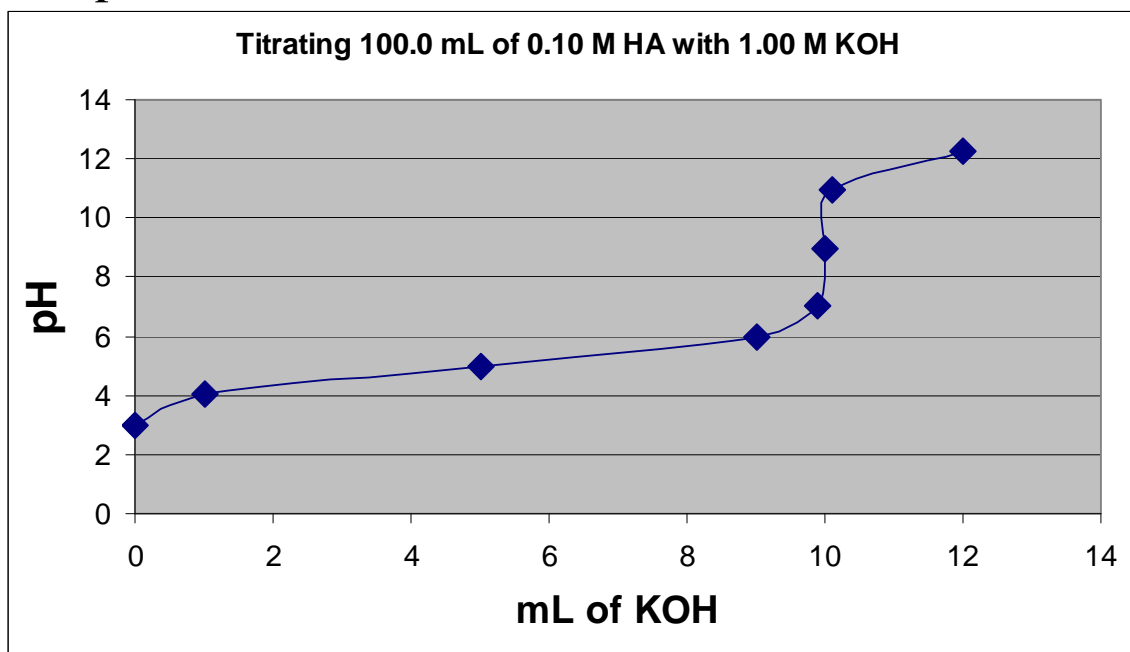
$$\text{pH} = 8.98$$

@ 10.10 mL After the equiv. point the excess OH^- is what controls the pH.

$$\begin{aligned}[\text{OH}^-] &= \\ &= [(10.10 \text{ mL KOH})(1.00 \text{ M KOH}) - (\text{mmol HA}_{\text{initial}})] / V_t \\ &= [10.10 - 10.00] / (110.10) = 9.1 \cdot 10^{-4} \text{ M} \\ \text{pH} &= 10.96\end{aligned}$$

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

$$\begin{aligned}[\text{OH}^-] &= \\ &= [(12.00 \text{ mL KOH})(1.00 \text{ M OH}^-) - (\text{mmol HA}_{\text{initial}})] / V_t \\ &= [12.00 - 10.00] / (112.00) = 1.79 \cdot 10^{-2} \text{ M} \\ \text{pH} &= 12.252\end{aligned}$$



Weak base titration

20.0 mL of a solution of 0.200 M weak base, B, is titrated with 0.0500 M HCl. ($K_a(\text{HB}^+) = 1.00 \cdot 10^{-5}$)

@ 0 ml added

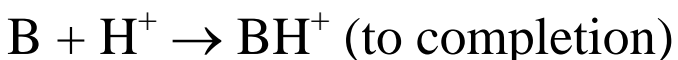
$$K_b = [\text{OH}^-]^2 / 0.200 = 1.00 \cdot 10^{-9}$$

$$[\text{OH}^-] = 4.47 \cdot 10^{-5} \text{ M}, [\text{H}^+] = 2.26 \cdot 10^{-10} \text{ M}$$

$$\text{pH} = 9.646$$

@ 5.00 mL added

$$\text{H}^+ \text{ added} = (0.0500 \text{ M})(5.00 \text{ mL}) = 0.250 \text{ mmol H}^+$$



$$\text{pH} = \text{p}K_a + \log(\text{mol B} / \text{mol BH}^+)$$

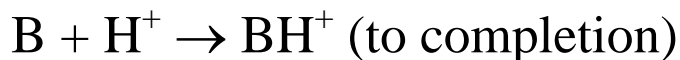
$$\text{mol BH}^+ = 0.250 \text{ mmol}$$

$$\begin{aligned} \text{mol B} &= (20.0 \text{ mL})(0.200 \text{ M}) - 0.250 \text{ mol} \\ &= 3.75 \text{ mmol} \end{aligned}$$

$$\text{pH} = 5.000 + \log(3.75 / .250) = 6.176$$

@ 20.00 mL added

$$\text{H}^+ \text{ added} = (0.0500\text{M})(20.00 \text{ mL}) = 1.00 \text{ mmol H}^+$$



$$\text{pH} = \text{pK}_a + \log(\text{mol B}/\text{mol BH}^+)$$

$$\text{mol BH}^+ = 1.00 \text{ mmol}$$

$$\begin{aligned} \text{mol B} &= (20.0 \text{ mL})(0.200 \text{ M}) - 1.00 \text{ mol} \\ &= 3.00 \text{ mmol} \end{aligned}$$

$$\text{pH} = 5.000 + \log(3.00/1.00) = 5.477$$

@ 40.00 mL added (1/2 way)

$$\begin{aligned} \text{H}^+ \text{ added} &= (0.0500\text{M})(40.00 \text{ mL}) \\ &= 2.00 \text{ mmol H}^+ \end{aligned}$$



$$\text{pH} = \text{pK}_a + \log(\text{mol B}/\text{mol BH}^+)$$

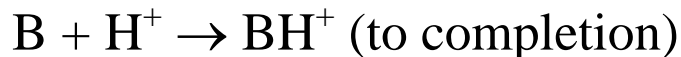
$$\text{mol BH}^+ = 2.00 \text{ mmol}$$

$$\begin{aligned} \text{mol B} &= (20.0 \text{ mL})(0.200 \text{ M}) - 2.00 \text{ mol} \\ &= 2.00 \text{ mmol} \end{aligned}$$

$$\text{pH} = 5.000 + \log(2/2) = 5.000$$

@ 60.00 mL added

$$\begin{aligned} \text{H}^+ \text{ added} &= (0.0500\text{M})(60.00 \text{ mL}) \\ &= 3.00 \text{ mmol H}^+ \end{aligned}$$



$$\text{pH} = \text{pK}_a + \log(\text{mol B}/\text{mol BH}^+)$$

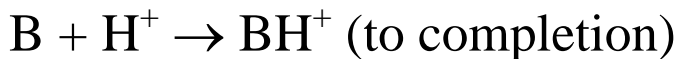
$$\text{mol BH}^+ = 3.00 \text{ mmol}$$

$$\begin{aligned} \text{mol B} &= (20.0 \text{ mL})(0.200 \text{ M}) - 3.00 \text{ mol} \\ &= 1.00 \text{ mmol} \end{aligned}$$

$$\text{pH} = 5.000 + \log(1/3) = 4.523$$

@ 70.00 mL added

$$\text{H}^+ \text{ added} = (0.0500\text{M})(70.00 \text{ mL}) = 3.50 \text{ mmol H}^+$$



$$\text{pH} = \text{pK}_a + \log(\text{mol B}/\text{mol BH}^+)$$

$$\text{mol BH}^+ = 3.50 \text{ mmol}$$

$$\text{mol B} = (20.0 \text{ mL})(0.200 \text{ M}) - 3.50 \text{ mol} = 0.50 \text{ mmol}$$

$$\text{pH} = 5.000 + \log(0.50/3.50) = 4.16$$

@ 79.50 mL added

$$\text{H}^+ \text{ added} = (0.0500\text{M})(79.50 \text{ mL}) = 3.98 \text{ mmol H}^+$$



$$\text{pH} = \text{pK}_a + \log(\text{mol B/mol BH}^+)$$

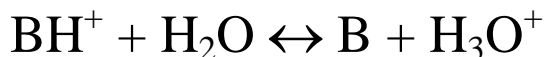
$$\text{mol BH}^+ = 3.98 \text{ mmol}$$

$$\text{mol B} = (20.0 \text{ mL})(0.200 \text{ M}) - 3.98 \text{ mol} = 0.02 \text{ mmol}$$

$$\text{pH} = 5.000 + \log(0.02/3.98) = 2.7$$

@ 80.00 mL added

This is the equivalence point. The appropriate equilibrium is the K_a reaction for BH^+ .



$$F_{\text{BH}^+} = (4.000 \text{ mmol})/(100.0 \text{ mL}) = 0.0400 \text{ M}$$

$$K_a = 1.00 \cdot 10^{-5} = [\text{B}][\text{H}_3\text{O}^+]/(F_{\text{BH}^+} - [\text{B}])$$

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

Assume $F_{\text{BH}^+} \cong [\text{BH}^+]$

$$1.00 \cdot 10^{-5} = x^2/(0.04000)$$

$$x = [\text{H}_3\text{O}^+] = 6.325 \cdot 10^{-4} \text{ M}$$

$$\text{pH} = 3.199$$

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.

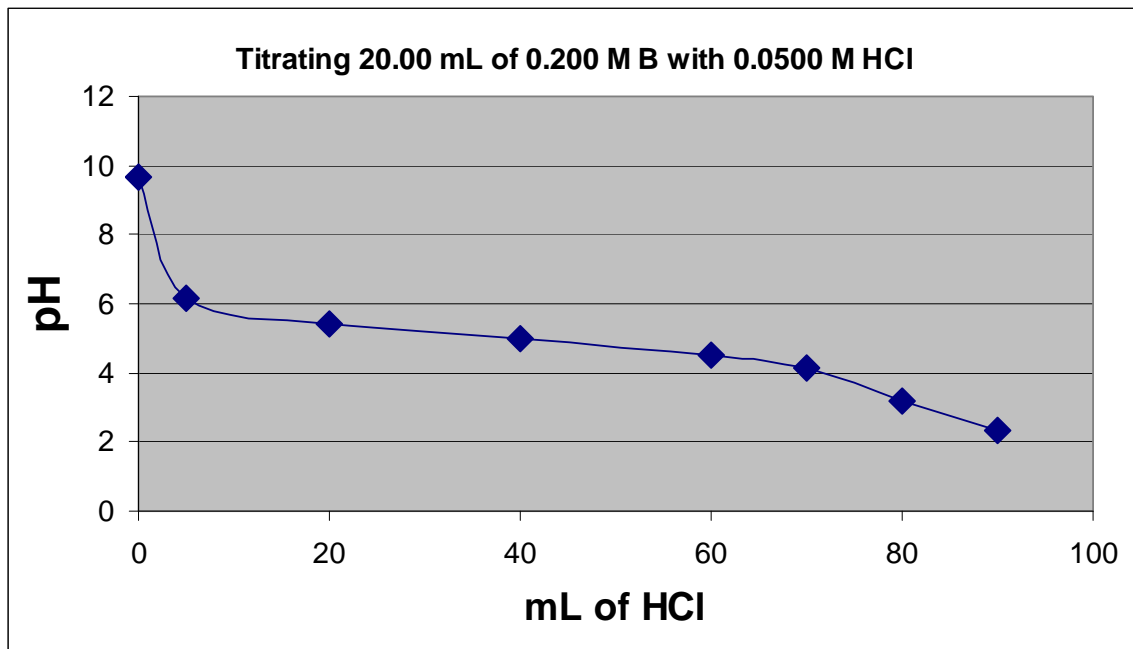
In other words the fraction of dissociation for a solution of the weak acid at this formal concentration is $6.325 \cdot 10^{-4} / 0.0400 = 1.58 \%$.

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

Less. This implies that the reaction $B + H^+ \rightarrow BH^+$ does not go to completion.

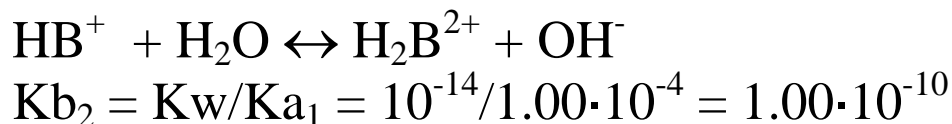
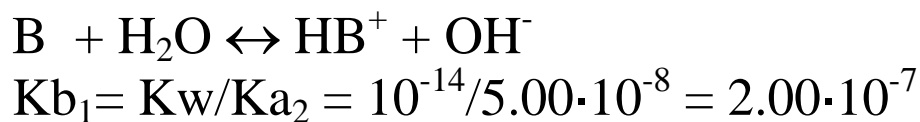
@ 90.00 mL After the equiv. point the excess H^+ is what controls the pH.

$$\begin{aligned} [\text{H}^+] &= [(10.0 \text{ mL HOCl})(0.0500 \text{ M HOCl}) / V_t \\ &= [(0.500) / (110.00)] = 4.556 \cdot 10^{-3} \text{ M} \\ \text{pH} &= 2.34 \end{aligned}$$

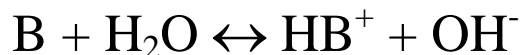


Polyprotics titrations

Titrate 40.0 mL of a 0.100 M diprotic base (B) solution with 0.100 M HCl ($K_{a1} = 1.00 \cdot 10^{-4}$ and $K_{a2} = 5.00 \cdot 10^{-8}$)



@ 0 mL added



$$F_B = 0.100 \text{ M}$$

Assume $[OH^-] = [HB^+]$, and let $[HB^+] = x$

$$\text{Assume } F_{A^-} \cong [B] = 0.100 \text{ M}$$

$$2.00 \cdot 10^{-7} = x^2/(0.100)$$

$$x = [OH^-] = 1.41 \cdot 10^{-4} \text{ M}, \alpha_{BH^+} = 0.0014$$

(apprx. valid)

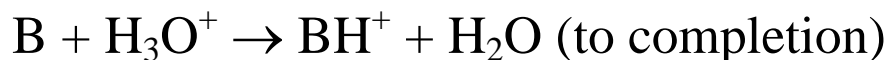
$$[H_3O]^+ = 7.16 \cdot 10^{-11} \text{ M}$$

$$\text{pH} = 10.15$$

@ 10.00 mL added

$$\text{pK}_{\text{a}2} = 7.301$$

$$\begin{aligned}\text{H}^+ \text{ added} &= (0.100\text{M})(10.00 \text{ mL}) \\ &= 1.00 \text{ mmol H}^+\end{aligned}$$



$$\text{pH} = \text{pK}_{\text{a}} + \log(\text{mol P/mol HP}^+)$$

$$\text{mol BH}^+ = 1.00 \text{ mmol}$$

$$\begin{aligned}\text{mol B} &= (40.0 \text{ mL})(0.100 \text{ M}) - 1.00 \text{ mol} \\ &= 3.00 \text{ mmol}\end{aligned}$$

$$\text{pH} = 7.301 + \log(3/1) = 7.778$$

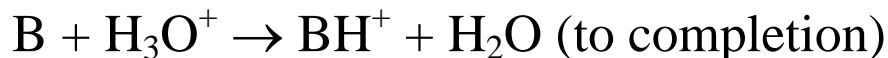
@ 20 mL we are half way to the first equivalence point

$$\text{pH} = \text{pK}_{\text{a}2} = 7.301$$

@ 30 mL added

$$\text{pK}_{\text{a}2} = 7.301$$

$$\begin{aligned}\text{H}^+ \text{ added} &= (0.100\text{M})(30.00 \text{ mL}) \\ &= 3.00 \text{ mmol H}^+\end{aligned}$$



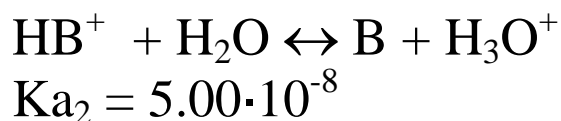
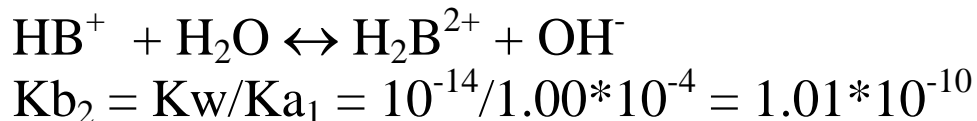
$$\text{pH} = \text{pK}_{\text{a}} + \log(\text{mol B/mol HB}^+)$$

$$\text{mol BH}^+ = 3.00 \text{ mmol}$$

$$\begin{aligned}\text{mol B} &= (40.0 \text{ mL})(0.100 \text{ M}) - 3.00 \text{ mol} \\ &= 1.00 \text{ mmol}\end{aligned}$$

$$\text{pH} = 7.301 + \log(1/3) = 6.824$$

@ 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.



$$[\text{H}^+] = [(K_1 K_2 F + K_1 K_w)/(K_1 + F)]^{0.5}$$

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

$$K_1 = 1.00 \cdot 10^{-4}$$

$$K_2 = 5.00 \cdot 10^{-8}$$

$$K_w = 1.01 \cdot 10^{-14}$$

After simplifying

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

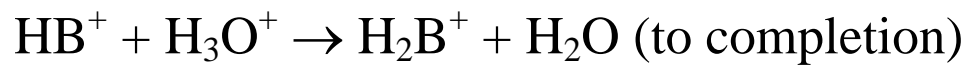
$$\text{(strictly } \rightarrow 2.23 \cdot 10^{-6} \text{ M)}$$

$$\text{pH} = 5.651$$

@ 50.00 mL added

$$\text{pK}_{\text{a}_1} = 4.000$$

$$\begin{aligned}\text{H}^+ \text{ added (after eq pt)} &= (0.100\text{M})(10.00 \text{ mL}) \\ &= 1.00 \text{ mmol}\end{aligned}$$



$$\text{pH} = \text{pK}_{\text{a}_1} + \log(\text{mol HB}^+ / \text{mol H}_2\text{B}^{2+})$$

$$\text{mol H}_2\text{B}^{2+} = 1.00 \text{ mmol}$$

$$\begin{aligned}\text{mol HB}^+ &= (40.0 \text{ mL})(0.100 \text{ M}) - 1.00 \text{ mol} \\ &= 3.00 \text{ mmol}\end{aligned}$$

$$\text{pH} = 4.000 + \log(3/1) = 4.477$$

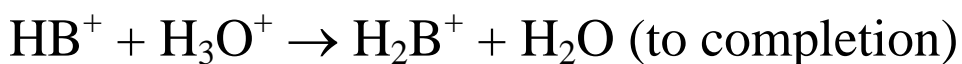
@ 60 mL we are half way to the second equivalence point

$$\text{pH} = \text{pK}_{\text{a}_1} = 4.000 @ 60.00 \text{ mL added}$$

@ 70 mL added

$$\text{pK}_{\text{a}_1} = 4.000$$

$$\begin{aligned} \text{H}^+ \text{ added (after eq pt)} &= (0.100\text{M})(30.00 \text{ mL}) \\ &= 3.00 \text{ mmol} \end{aligned}$$



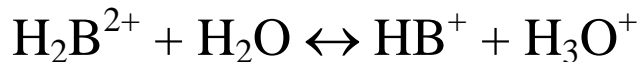
$$\text{pH} = \text{pK}_{\text{a}_1} + \log(\text{mol HB}^+ / \text{mol H}_2\text{B}^{2+})$$

$$\text{mol H}_2\text{B}^{2+} = 3.00 \text{ mmol}$$

$$\begin{aligned} \text{mol HB}^+ &= (40.0 \text{ mL})(0.100 \text{ M}) - 3.00 \text{ mol} \\ &= 1.00 \text{ mmol} \end{aligned}$$

$$\text{pH} = 4.000 + \log(1/3) = 3.523$$

@ 80 ml we hit the second equivalence point. The dominant species is H_2B^{2+} . We can find the pH by examining the hydrolysis of this species.



$$\begin{aligned} F_{\text{H}_2\text{B}^{2+}} &= (40.0 \text{ mL})(0.100 \text{ M})/(120.0 \text{ mL}) \\ &= 0.0333 \text{ M} \end{aligned}$$

$$\begin{aligned} K_a &= 1.00 \cdot 10^{-4} = [\text{HB}^+][\text{H}^+]/(F_{\text{H}_2\text{B}^{2+}} - [\text{HB}^+]) \\ &\text{Assume } [\text{H}_3\text{O}^+] = [\text{HB}^+], \text{ and let } [\text{HB}^+] = x \\ &\text{Assume } F_{\text{B}^+} \cong [\text{H}_2\text{B}^{2+}] \end{aligned}$$

$$\begin{aligned} 1.00 \cdot 10^{-4} &= x^2/(0.0333) \\ x = [\text{H}_3\text{O}^+] &= 1.82 \cdot 10^{-3} \text{ M (approx. failed!!!)} \\ \text{pH} &= 2.739 \end{aligned}$$

$$\begin{aligned} 1.00 \cdot 10^{-4} &= x^2/(0.0333-x) \\ x = [\text{H}_3\text{O}^+] &= 1.776 \cdot 10^{-3} \text{ M} \\ \text{pH} &= 2.751 \end{aligned}$$

@ 90.0 mL

Excess H^+ from strong acid

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

$$\text{pH} = 2.114$$

@ 100.0 mL added

$$[\text{H}^+] = (20.0 \text{ mL})(0.100) / (90 \text{ mL} + 50 \text{ mL}) \\ = 1.43 \cdot 10^{-2} \text{ M}$$

$$\text{pH} = 1.845$$

Primary Standards

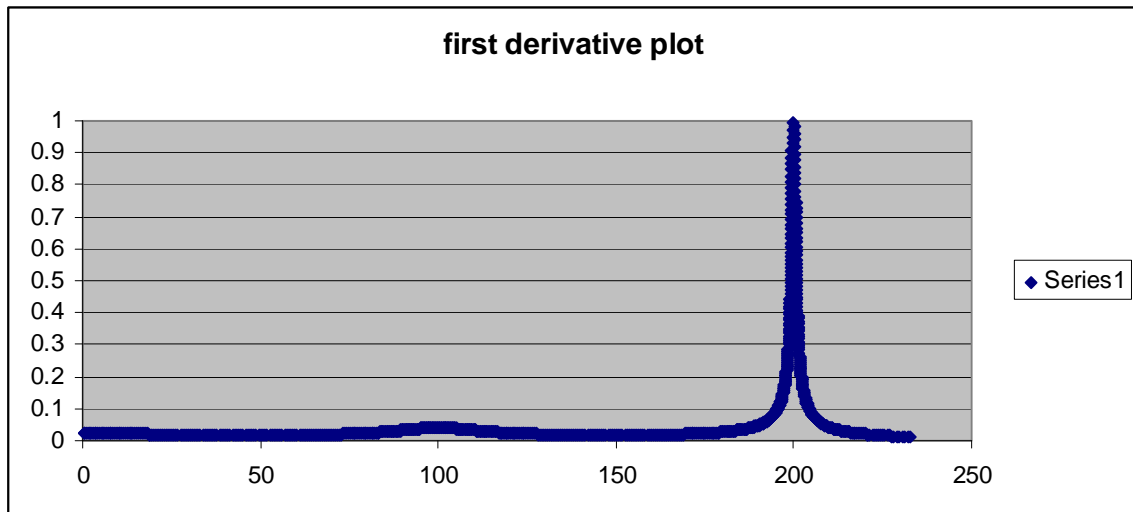
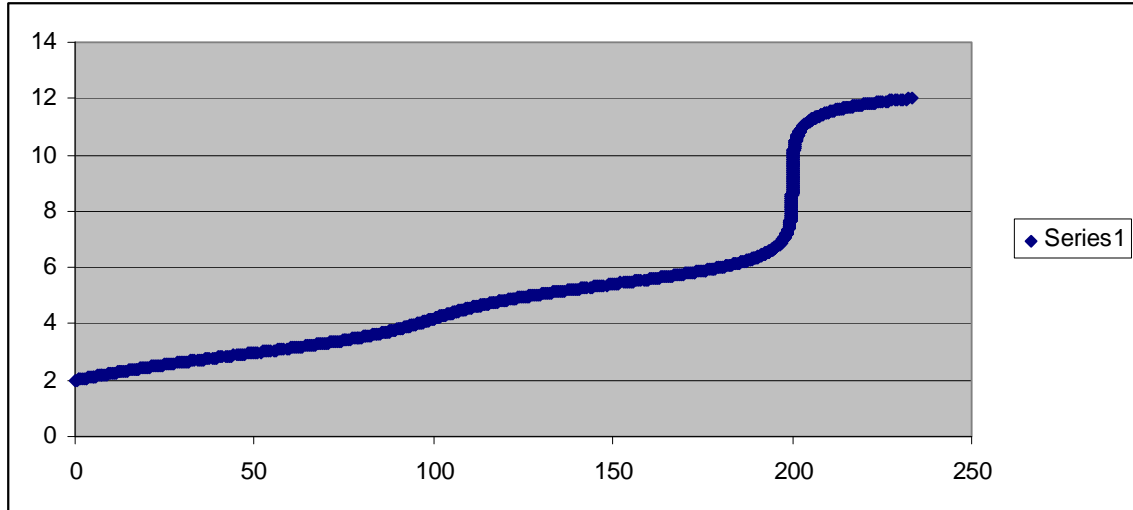
KHP

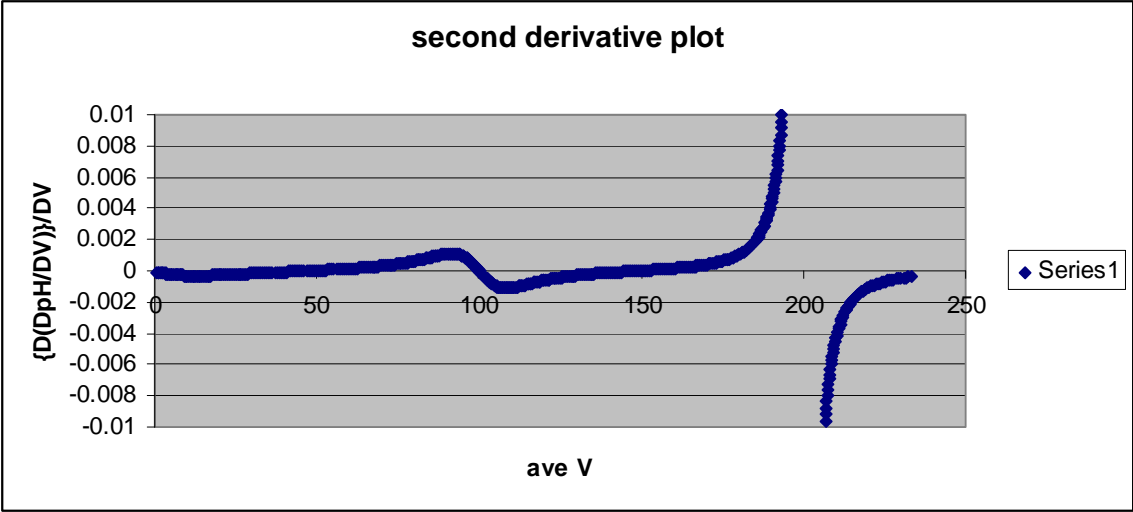
- Gives four or five significant figures on the number of moles of weak acid.
- Useful for standardizing NaOH.
- NaOH is hygroscopic. Therefore it is impossible to prepare a precise concentration of NaOH.
- Standardization against a primary standard is the accepted strategy.

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 ($\Delta\text{pH}/\Delta V$ vs. V_{ave}) and second derivative plots ($\Delta(\Delta\text{pH}/\Delta V)$) vs V_{ave}





Leveling effect

HClO₄ and HCl (in water) are both strong acids

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

$$K(\text{HClO}_4) = 1.3 \cdot 10^{-5}$$

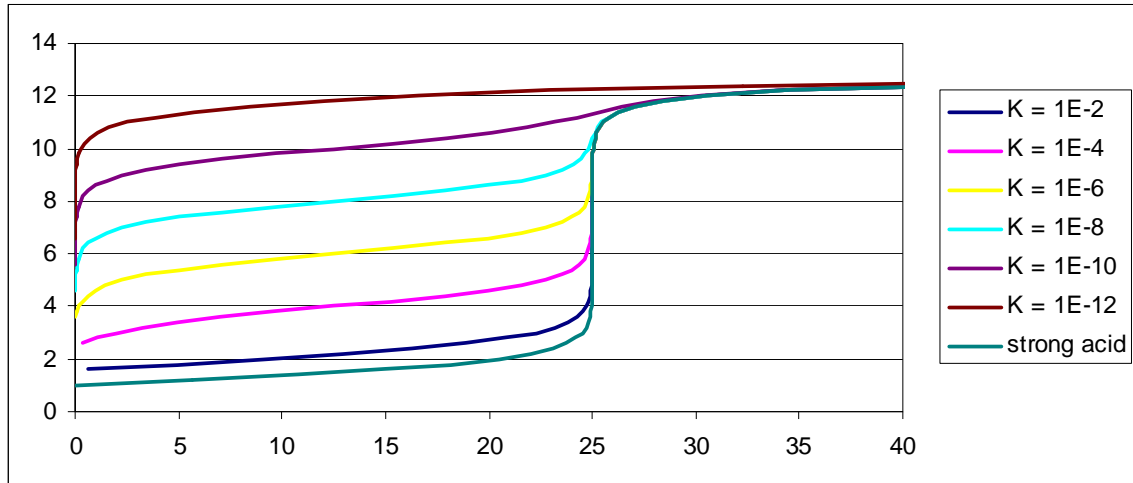
$$K(\text{HCl}) = 2.8 \cdot 10^{-9}$$

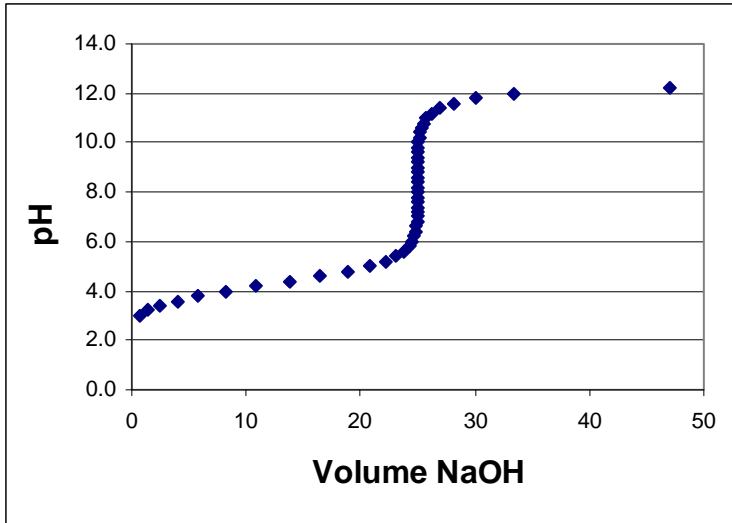
This is because acetic acid is less basic than water

Titration Spreadsheet (Do Problem 12-66)

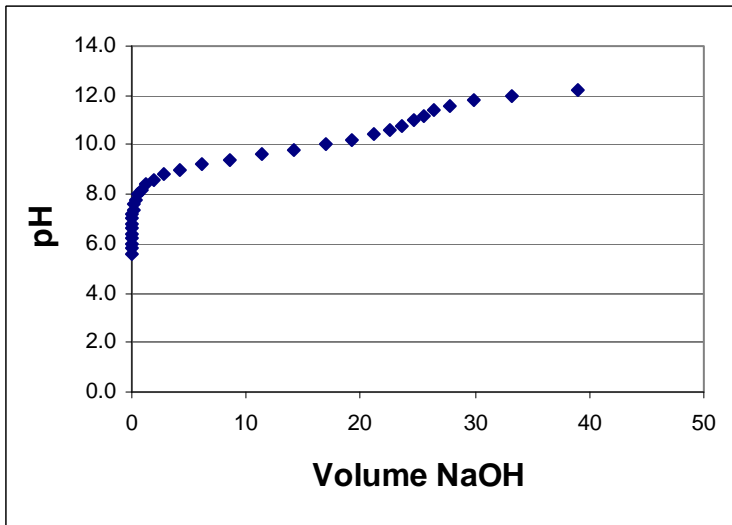
INTERPRETING TITRATION CURVES

Weak Acid Titrations
(0.1 M HA with 0.1 M NaOH at various K_a s)

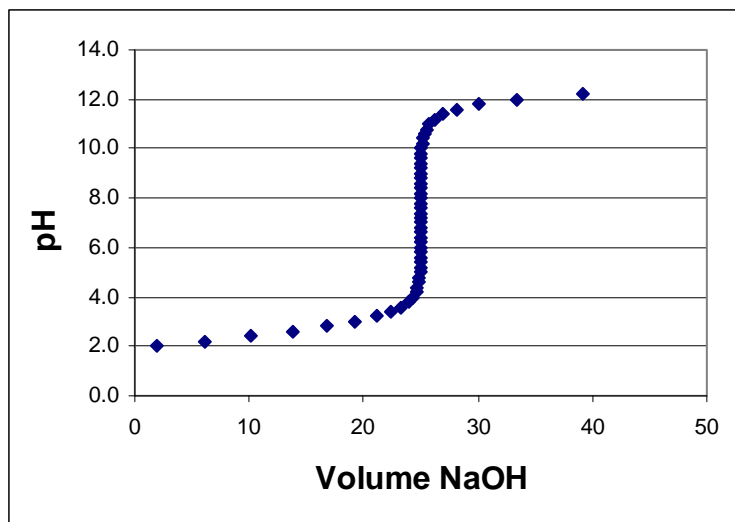




pKa	4.31
K1	4.90E-05
Ca	0.05
Cb	0.1
Va	50
Vb	25

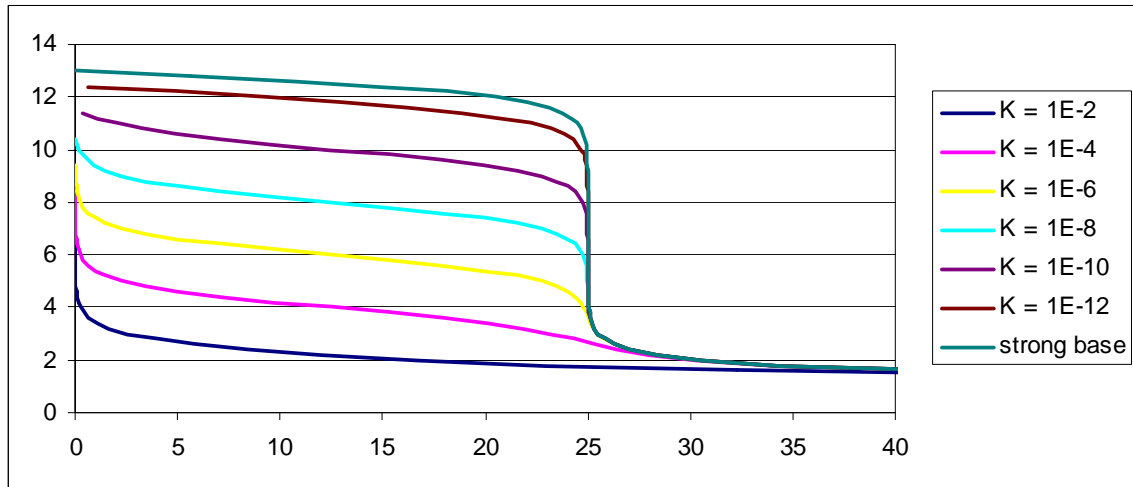


pKa	9.69
K1	2.06E-10
Ca	0.05
Cb	0.1
Va	50
Vb	25

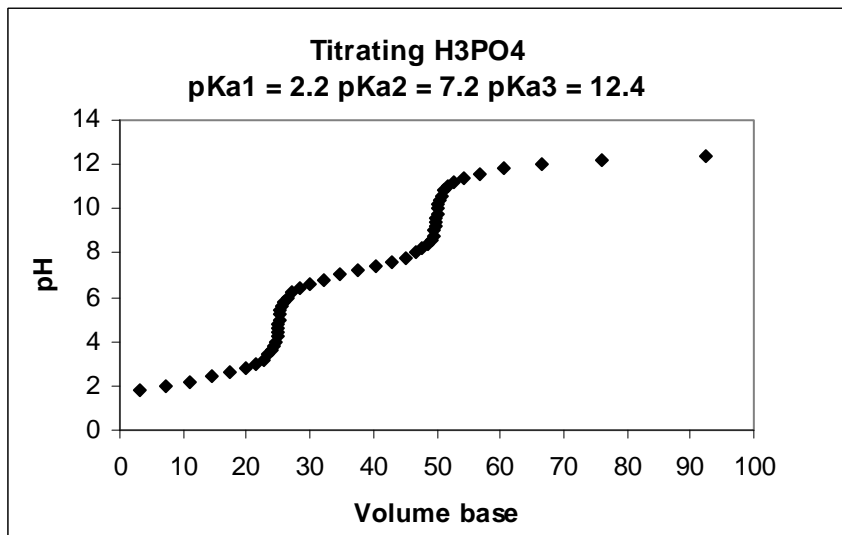
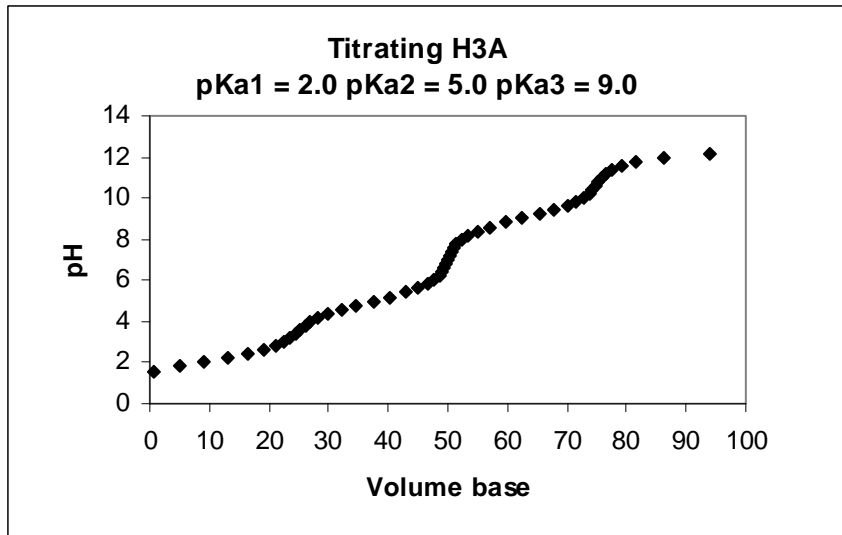


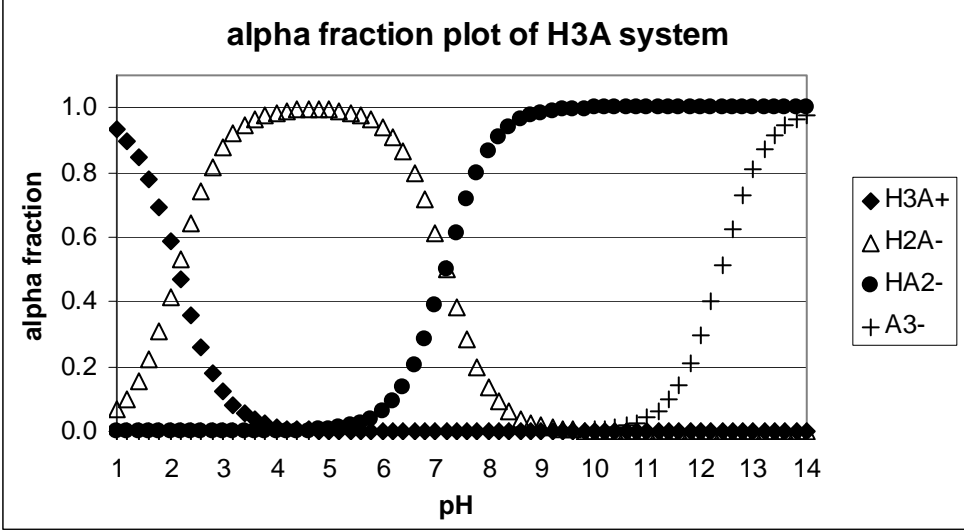
pKa 2.40
4.00E-
K1 03
Ca 0.05
Cb 0.1
Va 50
Vb 25

Weak Base Titrations (0.1 M B with 0.1 M HCl at various Kbs)



Polyprotic tirtrations





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

