More Stuff about Aqueous Equilibria: CH 17, Part 4

Demo: Strong Acid + Strong Base

0.1 M HCl — 0.1 M NaOH

50 mL — Predicted equivalence point of 50 mL

pH = 7

Titration: Weak Acid + Strong Base

- 50 mL 0.1 M acetic acid ($pK_a = 4.75$) is titrated with 0.1 mL NaOH. (calculate pH initial, after 20 mL, after 50 mL
- Initial pH is determined by the weak acid
  - Use K_a to solve for pH

Weak Acid + Strong base

0.1 M acetic acid

50 mL initial pH = 2.87

After 20 mL NaOH added

initial moles HA = $0.050\,L \cdot 0.1 \frac{mol}{L} = 0.005\ mol$

Moles OH^- added = $0.020\,L \cdot 0.1 \frac{mol}{L} = 0.002\ mol$

$$OH^- + HA \rightarrow A^- + H_2O$$

moles A^- = moles OH^- added = 0.002 mol

equilibrium moles HA = HA moles initial − mol OH^- added

= 0.003 mol

$$pH = pK_a + \log\frac{[A^-]}{[HA]} = pK_a + \log\frac{A^- \text{ mol}}{HA \text{ mol}} = 4.75 + \log\left(\frac{0.002}{0.002}\right)$$

$$= 4.56$$

50 mL NaOH

Initial moles HA = 0.005 mol

$0.050\,L \times \frac{0.1\,mol}{L} = 0.005\,mol\ OH^- = mol\ A^-$

equilibrium moles HA = 0.005 mol (initial HA) − 0.005 mol (OH^-) = 0 mol HA

$\frac{0.005\,mol\,A^-}{0.1\,L} = 0.050\,M\ A^-$

$CH_3COO^- + H_2O \rightleftharpoons OH^- + CH_3COOH$

A^- acetate; HA acetic acid

$pK_b + pK_a = pK_w$

$pK_b = 14 - 4.75$

$pK_b = 9.25$

$K_b \cdot K_a = K_w$

$K_b = 5.6 \times 10^{-10}$

	CH_3COO^-	OH^-	CH_3COOH
I	0.05 M	0	0
C	−x	x	x
E	0.05−x	x	x

$\frac{x^2}{0.05} = 5.6 \times 10^{-10}$

$x = 5.3 \times 10^{-6}$

$pOH = 5.28$

$pH = 8.72$

Weak Acid vs. Strong Acid Titration Curves

(1) A sln. of WA has a higher initial pH than a SA at the same concentration

(2) pH at the midpoint = pK_a

(3) At the equivalence point pH > 7.0 for a weak acid but pH = 7.0 for strong acid

Titration of Weak Base with Strong Acid

- Titration curve looks similar to a WA being titrated by SB, but it is "flipped over"
- pH during the titration:
  - high pH initially
  - pH < 7 at equivalence point (only BH^+ present)
  - low pH at end

Titrations of Polyprotic Acids

- Each H^+ dissociation has an equivalence point
- The pH at the midpoint of each dissociation occurs at the pKa for that step

$$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+ \rightleftharpoons HPO_4^{2-} + H^+ \rightleftharpoons PO_4^{3-} + H^+$$

phosphoric acid

Clicker question:

100 mL of 0.1 M malonic acid is titrated with 0.1 M NaOH. At what point in the titration is true?

Use of Indicators

- Indicators are weak acids that have a different color than their conjugate base form
- Each indicator has a pKa at which it changes colors
- An indicator can be used to find the equivalence point in a titration as long as the end point (where it changes color) is on the steep part of the titration curve!