Principles of Neutralization Titrations

Titration Curves for Weak Acids

Four distinctly different types of calculations are needed to compute values for a weak acid (or a weak base) titration curve:

1. At the beginning, the solution contains only a weak acid or a weak base, and the pH is calculated from the concentration of that solute and its dissociation constant.

2. After various increments of titrant have been added (up to, but not including, the equivalence point), the solution consists of a series of buffers. The pH of each buffer can be calculated from the analytical concentrations of the conjugate base or acid and the concentrations of the weak acid or base that remains.

3. At the equivalence point, the solution contains only the conjugate of the weak acid or base being titrated (that is, a salt), and the pH is calculated from the concentration of this product.

4. Beyond the equivalence point, the excess of strong acid or base titrant suppresses the acidic or basic character of the reaction product to such an extent that the pH is governed largely by the concentration of the excess titrant.

Example Generate a curve for the titration of 50.00 mL of 0.1000 M acetic acid (HOAc) with 0.1000 M sodium hydroxide at 25°C.

Changes in pH during the Titration of a Weak Acid with a Strong Base

	pH	
Volume of NaOH, mL	50.00 mL of 0.1000 M HOAc with 0.1000 M NaOH	50.00 mL of 0.001000 M HOAc with 0.001000 M NaOH
0.00	2.88	3.91
10.00	4.15	4.30
25.00	4.76	4.80
40.00	5.36	5.38
49.00	6.45	6.46
49.90	7.46	7.47
50.00	8.73	7.73
50.10	10.00	8.09
51.00	11.00	9.00
60.00	11.96	9.96
70.00	12.22	10.25

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Initial pH

First, we must calculate the pH of a 0.1000 M solution of HOAc using Equation 9-22.

$$[H_3O^+] = \sqrt{K_a c_{HOAc}} = \sqrt{1.75 \times 10^{-5} \times 0.1000} = 1.32 \times 10^{-3}\,M$$

$$pH = -\log(1.32 \times 10^{-3}) = 2.88$$

pH after Addition of 10.00 mL of Reagent

A buffer solution consisting of NaOAc and HOAc has now been produced. The analytical concentrations of the two constituents are

$$c_{HOAc} = \frac{50.00\ mL \times 0.1000\ M - 10.00\ mL \times 0.1000\ M}{60.00\ mL} = \frac{4.000}{60.00}\,M$$

$$c_{NaOAc} = \frac{10.00\ mL \times 0.1000\ M}{60.00\ mL} = \frac{1.000}{60.00}\,M$$

Now, for the 10.00 mL volume, we substitute the concentrations of HOAc and OAc$^-$ into the dissociation-constant expression for acetic acid and obtain

$$K_a = \frac{[H_3O^+](1.000/60.00)}{4.00/60.00} = 1.75 \times 10^{-5}$$

$$[H_3O^+] = 7.00 \times 10^{-5}$$

$$pH = 4.15$$

pH after Addition of 25.00 mL of Reagent

As in the previous calculation, the analytical concentrations of the two constituents are

$$c_{HOAc} = \frac{50.00\ mL \times 0.1000\ M - 25.00\ mL \times 0.1000\ M}{75.00\ mL} = \frac{2.500}{75.00}\,M$$

$$c_{NaOAc} = \frac{25.00\ mL \times 0.1000\ M}{75.00\ mL} = \frac{2.500}{75.00}\,M$$

Now, for the 25.00 mL volume, we substitute the concentrations of HOAc and OAc$^-$ into the dissociation-constant expression for acetic acid and obtain

$$K_a = \frac{[H_3O^+](2.500/75.00)}{2.500/75.00} = 1.75 \times 10^{-5}$$

$$pH = pK_a = -\log(1.75 \times 10^{-5}) = 4.76$$

At this half-titration point, the neutralical concentrations of the acid and conjugate base cancel in the expression for $[H_3O^+]$.

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$$c_{NaOAc} = \frac{50.00 \text{ mL} \times 0.1000 \text{ M}}{100.00 \text{ mL}} = 0.0500 \text{ M}$$

Thus,

$$OAc^- + H_2O \rightleftharpoons HOAc + OH^-$$

$$[OH^-] = [HOAc]$$

$$[OAc^-] = 0.0500 - [OH^-] \approx 0.0500$$

Substituting these quantities into the base dissociation-constant expression for OAc^- gives

$$\frac{[OH^-]^2}{0.0500} = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.71 \times 10^{-10}$$

$$[OH^-] = \sqrt{0.0500 \times 5.71 \times 10^{-10}} = 5.34 \times 10^{-6} \text{ M}$$

$$pH = 14.00 - [-\log(5.34 \times 10^{-6})] = 8.73$$

pH After Addition of 50.10 mL of Base

After the addition of 50.10 mL of NaOH, the excess base and the acetate ion are both sources of hydroxide ion. The contribution from the acetate ion is small, however, because the excess of strong base suppresses the reaction of acetate with water. This fact becomes evident when we consider that the hydroxide ion concentration is only 5.34×10^{-6} M at the equivalence point; once a tiny excess of strong base is added, the contribution from the reaction of the acetate is even smaller. We have then
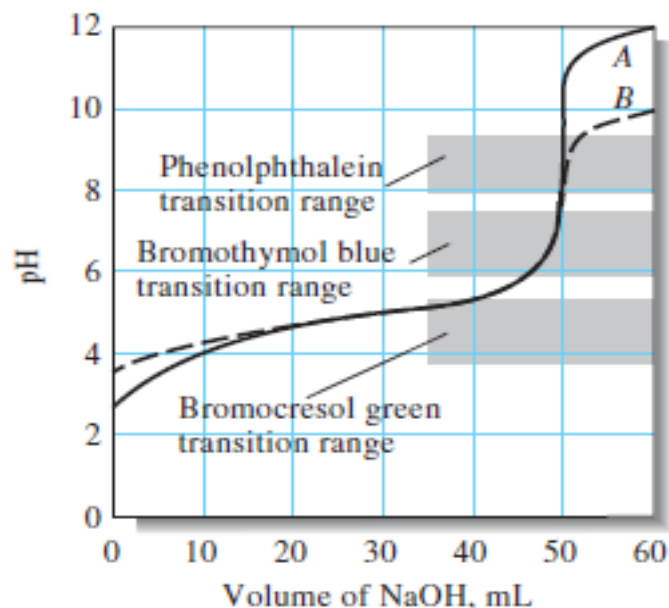
$$[OH^-] = c_{NaOH} = \frac{50.10 \text{ mL} \times 0.1000 \text{ M} - 50.00 \text{ mL} \times 0.1000 \text{ M}}{100.10 \text{ mL}}$$

$$= 9.99 \times 10^{-5} \text{ M}$$

$$pH = 14.00 - [-\log(9.99 \times 10^{-5})] = 10.00$$

Note that the titration curve for a weak acid with a strong base is identical with that for a strong acid with a strong base in the region slightly beyond the equivalence point.

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Curve (A) for the titration of acetic acid with sodium hydroxide.
Curve A: 0.1000 M acid with 0.1000 M base.
Curve B: 0.001000 M acid with 0.001000 M base.

The Effect of Concentration

Figure above is a plot of the data in previous Table. Note that the initial pH values are higher and the equivalence-point pH is lower for the more dilute solution (Curve *B*).

At intermediate titrant volumes, however, the pH values differ only slightly because of the buffering action of the acetic acid/sodium acetate system that is present in this region.

Figure above is graphical confirmation that the pH of buffers is largely independent of dilution. Note that the change in [OH⁻] in the vicinity of the equivalence point becomes smaller with lower analyte and reagent concentrations.

This effect is analogous to the effect for the titration of a strong acid with a strong base.

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The Effect of Reaction Completeness

Titration curves for 0.1000 M solutions of acids with different dissociation constants are shown in **Figure below.**
Note that the pH change in the equivalence-point region becomes smaller as the acid becomes weaker—that is, as the reaction acid and the base becomes less complete.

Choosing an Indicator: The Feasibility of Titration

Figures A and B show that the choice of indicator is more limited for the titration of a weak acid than for the titration of a strong acid.
For example, Figure 14-5 illustrates that bromocresol green is totally unsuited for titration of 0.1000 M acetic acid.
Bromothymol blue does not work either because its full color change occurs over a range of titrant volume from about 47 mL to 50 mL of 0.1000 M base.
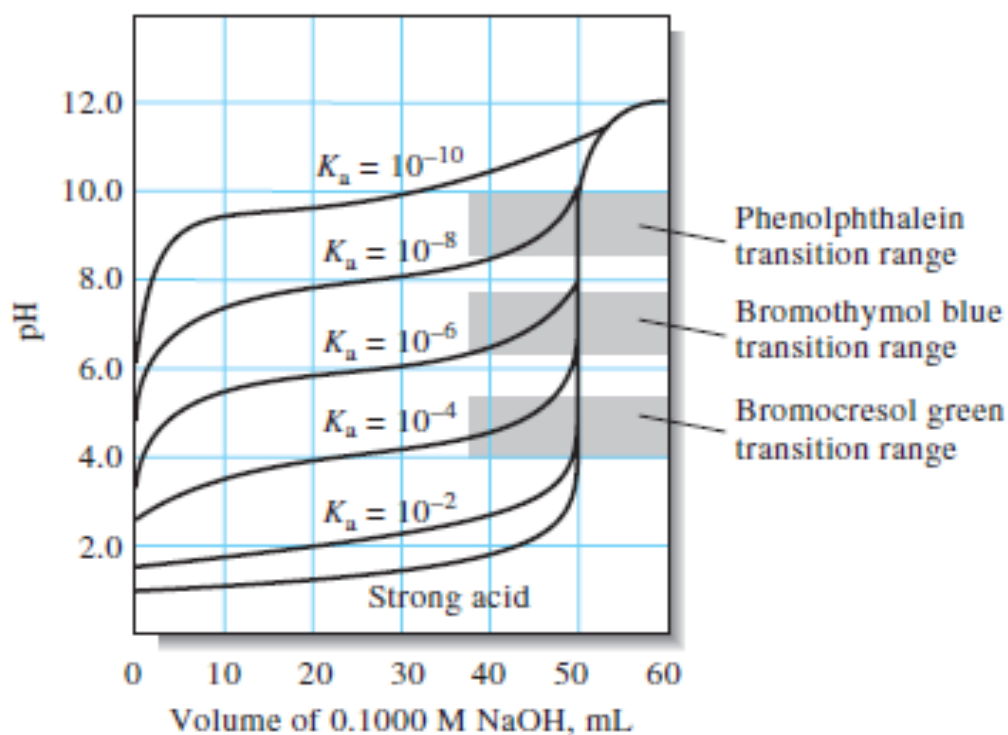On the other hand, an indicator exhibiting a color change in the basic
region, such as phenolphthalein, provides a sharp end point with a minimal titration error.
The end-point pH change associated with the titration of 0.001000 M acetic acid
(curve *B*, Figure A) is so small that there is likely to be a significant titration error regardless of indicator. However, using an indicator with a transition range between that of phenolphthalein and that of bromothymol blue in conjunction with a suitable color comparison standard makes it possible to establish the end point in this titration with decent precision (a few percent relative standard deviation).

Figure B illustrates that similar problems occur as the strength of the acid being titrated decreases. A precision on the order of 2± ppt can be achieved by titrating a 0.1000 M solution of an acid with a dissociation constant of 10^{-8} if a suitable color comparison standard is available. With more concentrated solutions, weaker acids can be titrated with reasonable precision.

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$K_a = 10^{-10}$
$K_a = 10^{-8}$
$K_a = 10^{-6}$
$K_a = 10^{-4}$
$K_a = 10^{-2}$

Phenolphthalein transition range

Bromothymol blue transition range

Bromocresol green transition range

Strong acid

pH

Volume of 0.1000 M NaOH, mL

The effect of acid strength (dissociation constant) on titration curves(B). Each curve represents the titration of 50.00 mL of 0.1000 M weak acid with 0.1000 M strong base.

Titration Curves for Weak Bases

A 50.00-mL aliquot of 0.0500 M NaCN (K_a for HCN $= 6.2 \times 10^{-10}$) is titrated with 0.1000 M HCl. The reaction is

$$CN^- + H_3O^+ \rightleftharpoons HCN + H_2O$$

Calculate the pH after the addition of (a) 0.00, (b) 10.00, (c) 25.00, and (d) 26.00 mL of acid.