Chapter 14
Principles of Neutralization
Titrations

Standard Solutions

- The standard reagents used in acid/base titrations are ALWAYS strong acids or bases: HCl, HClO₄, H₂SO₄, NaOH and KOH.
- Standard acids are prepared by diluting of concentrated acids.
- HNO₃ is not used as a standard acid.
- Weak acids and bases are NEVER used as standard reagents—they react incompletely with analytes.

Acid-Base Indicators

\[ \text{Hln(aq)} \xrightarrow{\text{(acid color)}} \text{H}^+(\text{aq})+\text{ln}^-(\text{aq}) \]

\[ K_a = \frac{[H^+][\text{ln}^-]}{[\text{Hln}]} = \frac{K_a}{[H^+]} = \frac{[\text{ln}^-]}{[\text{Hln}]} \]

Add a few drops of the phenolphthalein indicator to an acidic solution (pH=1):

\[ \frac{K_a}{[H^+]} = \frac{1 \times 10^{-3}}{1 \times 10^{-1}} = \frac{[\text{ln}^-]}{[\text{Hln}]} = \frac{1}{1000000} \]

The ratio shows that the predominant form of the indicator is Hln, resulting in an acid color solution.
As OH⁻ is added to this solution, [H⁺] decreases and the equilibrium shift to right, changing HIn to In⁻. A color change from colorless or slightly red to reddish purple will occur.

For most indicators, about 1/10 of the initial form must be converted to the other form before a new color is apparent.

**Indicator pH Range: pKₐ ± 1**

\[
pH = pK_a + \log \left( \frac{[In^-]}{[HIn]} \right)
\]

For a acid solution

\[
pH = pK_a + \log \left( \frac{1}{10} \right) = pK_a - 1
\]

For a basic solution

\[
pH = pK_a + \log \left( \frac{10}{1} \right) = pK_a + 1
\]
Titration Errors with Acid-Base Indicators

- Systematic (determinate) Errors: Difference between the color change of indicator and the equivalence point.
  -- blank titration correction

- Personal (Indeterminate) Errors: Uncertainty of color change (±0.5 to ±1 pH; best ±0.1 pH), Insensitivity of eyes to color change.
  Colorless → Red/Red → colorless?
  -- use reference color solution
Titrations and pH Curves

- The equivalence point is defined by stoichiometry, not by the pH.
- The pH value at equivalence point is affected by the acid strength or base strength.
- The strength of a weak acid or weak base have significantly effect on the shape of pH curves.

Determine the Equivalence Point of an Acid-Base Titration

- Use a pH meter to monitor the pH and then plot a titration curve.
- Use an acid-base indicator, which marks the endpoint of a titration by changing color.

Titration of Strong Acids and Strong Bases

- \( \text{HCl} + \text{NaOH} \leftrightarrow \text{NaCl} + \text{H}_2\text{O} \)
   \( \text{HCl} \rightarrow \text{H}^+ + \text{Cl}^- \)
   \( \text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^- \)
   \( \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^- \)
- In HCl: \( [\text{H}^+] = c_{\text{HCl}} + [\text{OH}^-] \approx c_{\text{HCl}} \)
- In NaOH: \( [\text{OH}^-] = c_{\text{NaOH}} + [\text{H}^+] \approx c_{\text{NaOH}} \)
- Equivalent point: pH = 7
Titrating a Strong Acid with a Strong Base

- Ex. 14-1 Generate the hypothetical titration curve for the titration of 50 mL of 0.0500 M HCl with 0.1000 M NaOH.

- How many mL of 0.1000 M NaOH are needed to complete the reaction? (to reach the equivalent point)

\[(C_1V_1)_\text{HCl} = (C_2V_2)_\text{NaOH}\]

\[V_2 = \frac{(0.0500 \times 50)}{0.1000} = 25 \, \text{mL}, \, \text{pH} = 7.0\]

Calculating pH During a SA-SB Titration

- Initial pH: For a strong acid, which is completely dissociated, \(\text{pH} = -\log [\text{H}_3\text{O}^+]\).

- pH before the equivalence point: Subtract the number of moles of \(\text{H}_3\text{O}^+\) reacted from the concentration originally present; divide by the total volume to obtain \([\text{H}_3\text{O}^+]\); determine pH.

- pH at the equivalence point: The solution contains only \(\text{Na}^+\), \(\text{Cl}^-\), and \(\text{H}_2\text{O}\), and is therefore neutral, so \([\text{H}_3\text{O}^+] = 1.0 \times 10^{-7}; \text{pH} = 7.00\).

- pH after the equivalence point: Subtract the number of moles of \(\text{H}_3\text{O}^+\) reacted from the total number of moles of \(\text{OH}^-\) added to obtain the number of moles of \(\text{OH}^-\) in excess; divide by the total volume to obtain \([\text{OH}^-]\); determine pOH and pH.

Initial Point:
Before any base is added, the solution is 0.0500 M in \(\text{H}_3\text{O}^+\), and

\[\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log 0.0500 = 1.30\]

After Addition of 10.00 mL of Reagent:
The hydronium ion concentration is decreased as a result of both reaction with the base and dilution. So the analytical concentration of HCl is

\[\text{no. mmol HCl remaining after addition of NaOH} = \frac{\text{original no. mmol HCl} - \text{no. mmol NaOH added}}{\text{total volume soln}}\]

\[= \frac{(50.00 \, \text{mL} \times 0.0500 \, \text{M}) - (10.00 \, \text{mL} \times 0.1000 \, \text{M})}{50.00 \, \text{mL} + 10.00 \, \text{mL}}\]

\[= \frac{(2.500 \, \text{mmol} - 1.000 \, \text{mmol})}{60.00 \, \text{mL}} = 2.500 \times 10^{-3} \, \text{M}\]

\[\text{[H}_3\text{O}^+] = 2.500 \times 10^{-3} \, \text{M}\]

and \(\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log (2.500 \times 10^{-3}) = 1.60\)
What is the solution pH after addition of 40.00 and 50.00 mL of 0.1000 M NaOH into 50 mL of 0.05000 M HCl?

When 40.00 mL of NaOH added:

\[
[OH^-] = \frac{(0.1000 \times 40.00 - 0.05000 \times 50)}{40 + 50} = 0.0166 \text{ M}
\]

\[
pOH = -\log(0.0166) = 1.78, \text{ pH} = 14 - pOH = 12.22
\]

When 50.00 mL of NaOH added:

\[
[OH^-] = \frac{(0.1000 \times 50.00 - 0.05000 \times 50)}{50 + 50} = 0.025 \text{ M}
\]

\[
pOH = -\log(0.025) = 1.60, \text{ pH} = 14 - pOH = 12.40
\]

### Table 14.2

<table>
<thead>
<tr>
<th>Volume of NaOH, mL</th>
<th>pH 50.00 mL of 0.0500 M HCl with 0.1000 M NaOH</th>
<th>pH 50.00 mL of 0.000500 M HCl with 0.0100 M NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.30</td>
<td>3.30</td>
</tr>
<tr>
<td>10.00</td>
<td>1.60</td>
<td>3.60</td>
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<td>20.00</td>
<td>2.15</td>
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<td>24.00</td>
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<td>4.87</td>
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<td>24.90</td>
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<td>25.00</td>
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<td>26.00</td>
<td>11.12</td>
<td>9.12</td>
</tr>
<tr>
<td>50.00</td>
<td>11.80</td>
<td>9.80</td>
</tr>
</tbody>
</table>

\[
pH = 14.00 - 3.88 = 10.12
\]
Using Charge-Balance Equation to Construct Titration Curve

For HCl titrated with NaOH

CBE: \([H^+] + [Na^+] = [OH^-] + [Cl^-]\)

Where 
\[
[Na^+] = \frac{V_{NaOH}c_{NaOH}}{V_{NaOH} + V_{HCl}}, \quad [Cl^-] = \frac{V_{HCl}c_{HCl}}{V_{NaOH} + V_{HCl}}
\]

\([H_2O^+] = [OH^-] + [Cl^-] - [Na^+]\)

(1) Before equivalence point, \([OH^-] \ll [Cl^-]\), so

\[
[H_2O^+] = \frac{V_{HCl}c_{HCl}}{V_{NaOH} + V_{HCl}} - \frac{V_{HCl}c_{HCl}}{V_{NaOH} + V_{HCl}} - \frac{V_{HCl}c_{HCl}}{V_{NaOH} + V_{HCl}}
\]

(2) At the equivalence point, \([Cl^-] = [Na^+]\), \([H_2O^+] = [OH^-]\)

\[
[H_2O^+] = \sqrt{K_w}
\]

(3) Beyond the equivalence point, \([H_2O^+] \ll [Na^+]\)

\[
[OH^-] = \frac{V_{NaOH}c_{NaOH}}{V_{NaOH} + V_{HCl}} - \frac{V_{HCl}c_{HCl}}{V_{NaOH} + V_{HCl}} = \frac{V_{NaOH}c_{NaOH} - V_{HCl}c_{HCl}}{V_{NaOH} + V_{HCl}}
\]
Titration a Strong Base (NaOH) with a Strong Acid (HCl)

Titrations of Weak Acid with Strong Bases

In weak acid - strong base titrations (or weak base - strong acid) the pH before and at the equivalence point depends on the acid (base) concentrations and $K_a$ ($K_b$).

$\Delta \text{pH}/\Delta \text{vol}$ at the equivalence points of weak acid (base) – strong base (acid) are smaller than for strong acid – strong base titrations.
Plot the titration curve for the titration of 50 mL of 0.10 mol/L acetic acid with 0.10 mol/L NaOH. \( K_a = 1.75 \times 10^{-5}, \ pK_a = 4.76 \)

a) Before the titration starts the weak acid will partially dissociate and the equilibrium \( \text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+ \) establishes itself in the flask. \( K_a = \left[\text{H}_3\text{O}^+\right]\left[\text{CH}_3\text{COO}^-\right]/\left[\text{CH}_3\text{COOH}\right] \)

But the number of moles of protons produced = to the number of moles of conjugate base produced.

\[ \text{\begin{align*} \left[\text{H}_3\text{O}^+\right] &= K_a\left[\text{CH}_3\text{COOH}\right] = \left(1.75 \times 10^{-5}\right)(0.1) = 1.75 \times 10^{-6} \text{ mol/L} \\ \text{pH} &= 2.88 \end{align*}} \]

b) As the titration starts, and up until just before the equivalence point, the reaction: \( \text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \) takes place in the flask and then the equilibrium \( \text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+ \) re-establishes itself in the flask.

\( K_a = \left[\text{CH}_3\text{COO}^-\right]\left[\text{H}_3\text{O}^+\right]/\left[\text{CH}_3\text{COOH}\right] = 1.75 \times 10^{-5} \)

Thus the solution will contain both acetic acid and its conjugate base acetate, that is a buffer will have been created with

\( \left(M_a \times V_i\right)/1000 \text{ moles of acetic acid and} \)

\( \left(M_b \times V_i\right)/1000 \text{ moles of acetate} \)

both in \((V_o + V_i)\) mL of solution.

\[ \text{Moles CH}_3\text{COOH in (V_i + V_j) mL} = \left(M_a \times V_i\right)/1000 - \left(M_b \times V_i\right)/1000 \]

\[ \text{Moles CH}_3\text{COO}^- in (V_i + V_j) mL = \left(M_b \times V_i\right)/1000 \]

\[ \text{Moles CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+ \]

\[ \left[\text{H}_3\text{O}^+\right] = K_a \left[\text{CH}_3\text{COOH}\right]/\left[\text{CH}_3\text{COO}^-\right] \]

At \( V_i = 5 \text{ mL} \), \( \left[\text{H}_3\text{O}^+\right] = 1.75 \times 10^{-6} \text{ mol/L} \) and \( \text{pH} = 3.80 \)

Note 1. In this titration the pH appears to be independent of the concentrations of the acid and base but this is only true because \( M_a = M_b \).

\[ \text{Note 2. When} \ V_i = 0.5 V_e, \ \text{the point of half neutralization} \]

\[ 0.5 M_b V_i = M_a V_i \text{ or } M_b V_i = 2 M_a V_i \]

\[ \left[\text{H}_3\text{O}^+\right] = K_a \text{ and } \text{pH} = pK_a \text{ at 0.5V_e} \]
pH at equivalence point (V_e = V_a)

During the titration:  \( \text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \)

at \( V_e \) all the acetic acid has been neutralized (definition of \( V_e \))

to leave the conjugate base and the equilibrium

\[ \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{CH}_3\text{COOH} \]

establishes itself in the flask.

\[ K_b = K_w / (1.75 \times 10^{-5}) = 5.71 \times 10^{-10}. \]

\[ [\text{OH}^-]^2 = K_b [\text{CH}_3\text{COO}^-] \quad \Rightarrow \quad [\text{OH}^-] = \sqrt{(5.71 \times 10^{-10} \times (0.1 \div 2))} = 5.34 \times 10^{-6} \]

\[ p\text{OH} = 5.27, \quad p\text{H} = 14 - 5.27 = 8.73 \]

pH after equivalence point calculated as for strong acid strong base titration.

(Why? Hint: Use Charge Balance Equation)

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**Table 14.3**

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

<table>
<thead>
<tr>
<th>pH</th>
<th>50.00 mL of 0.1000 M HOAc with 0.1000 M NaOH</th>
<th>50.00 mL of 0.001000 M HOAc with 0.1000 M NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>2.88</td>
<td>2.88</td>
</tr>
<tr>
<td>10.00</td>
<td>4.16</td>
<td>4.16</td>
</tr>
<tr>
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<tr>
<td>50.00</td>
<td>8.73</td>
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</tr>
<tr>
<td>51.00</td>
<td>10.00</td>
<td>10.00</td>
</tr>
<tr>
<td>60.00</td>
<td>11.96</td>
<td>11.96</td>
</tr>
<tr>
<td>70.00</td>
<td>12.22</td>
<td>12.22</td>
</tr>
</tbody>
</table>

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Acetic acid treated with NaOH

The effect of concentrations

Choice of indicators: as for strong acid – strong base titrations

The effect of acid strength - \( K_a \)

The buffering region

\[ K_b = [\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+] / [\text{CH}_3\text{COOH}] \]

\[ = [\text{H}_3\text{O}^+] x [\text{OH}^-] / [\text{CH}_3\text{COOH}] \]

The maximum buffering capacity when \([\text{base}] = [\text{acid}]\)
Using Derivatives To Locate Titration End Points

End point is taken where the slope is greatest

\[ \frac{d\text{pH}}{dV} \]

Or where the second derivative is zero

\[ \frac{d^2\text{pH}}{dV^2} = 0 \]