I. Titrating a Strong Acid with a Strong Base

Problem: titrate a given volume $V_{acid}$ containing a strong acid with concentration $C_{acid}$ using a strong base with concentration $C_{base}$

The total volume during the titration:

$$V_{total} = V_{acid}^0 + V_{base added}$$

The initial number of moles of acid:

$$n_{acid} = C_{acid}^0 \times V_{acid}^0$$

The number of moles of base added:

$$n_{base} = C_{base}^0 \times V_{base added}$$

Calculation of $[H^+]$ and/or $[OH^-]$:

**BEFORE** the end-point ($n_{acid} > n_{base}$):

$$[H^+] = \frac{n_{acid} - n_{base}}{V_{total}}$$

**AT** the end-point ($n_{acid} = n_{base}$):

$$[H^+] = [OH^-] = \sqrt{K_w} = 10^{-7} M$$

**AFTER** the end-point ($n_{acid} < n_{base}$):

$$[OH^-] = \frac{n_{base} - n_{acid}}{V_{total}} \quad [H^+] = \frac{K_w}{[OH^-]}$$
I. Titrating a Strong Acid with a Strong Base

The Excel used in examples in this presentation is on the course website.

<table>
<thead>
<tr>
<th>Input parameters</th>
<th>V added (mL)</th>
<th>V total (mL)</th>
<th>millimoles base</th>
<th>[H+] (M)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial acid concentration (M) - cell B3 renamed into &quot;acid&quot;</td>
<td>0.1</td>
<td>0.4</td>
<td>25.4</td>
<td>4.00E-02</td>
<td>9.69E-02</td>
</tr>
<tr>
<td>Initial base concentration (M) - cell B4 renamed into &quot;base&quot;</td>
<td>0.1</td>
<td>0.8</td>
<td>25.8</td>
<td>8.00E-02</td>
<td>9.38E-02</td>
</tr>
<tr>
<td>Initial acid solution volume (mL) - cell B5 renamed into &quot;Vacid&quot;</td>
<td>25</td>
<td>1.2</td>
<td>25.2</td>
<td>1.20E-01</td>
<td>9.06E-02</td>
</tr>
<tr>
<td>Kw - cell B8 renamed into &quot;Kw&quot;</td>
<td>1.00E-14</td>
<td>1.6</td>
<td>25.6</td>
<td>1.60E-01</td>
<td>8.80E-02</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.2</td>
<td>2.00E-01</td>
<td>8.52E-02</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.4</td>
<td>2.40E-01</td>
<td>6.25E-02</td>
</tr>
<tr>
<td>Millimoles of acid in the initial solution = acid*Vacid (cell B9 renamed into &quot;mmoles&quot;)</td>
<td>2.5</td>
<td>2.8</td>
<td>27.8</td>
<td>2.80E-01</td>
<td>7.99E-02</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.2</td>
<td>3.20E-01</td>
<td>7.73E-02</td>
</tr>
</tbody>
</table>

Titration of strong acid with strong base

Cells contain the following:
- Column D is filled to the desired volume values
- Column H = -log(Column G)
- E2=D2+Vacid
- F2=D2*base*1000

Below/above equivalence:
- G2 = |F(moles-F2)/(moles-F2)|*E2/Kw*E2/(F2-moles)

At equivalence:
- G66 = 1E-7

Equiv. point at pH = 7
II. Titrating a Weak Acid with a Strong Base

Now the acid HA is weak \((K_a < 10^{-4})\), and we have to account for the fact that both HA and A⁻ are present in solution. The following is an approximate solution:

The total volume during the titration:

\[
V_{\text{total}} = V_{\text{acid}}^0 + V_{\text{base added}}
\]

Initial moles of acid; moles of added base:

\[
\begin{align*}
n_{\text{acid}} &= C_{\text{acid}}^0 \times V_{\text{acid}}^0 \\
n_{\text{base}} &= C_{\text{base}}^0 \times V_{\text{base added}}
\end{align*}
\]

**NO BASE ADDED:**

\[
[H^+] \approx \sqrt{C_{\text{acid}}^0 \times K_a}
\]

**BEFORE** the end-point

(HA / A⁻ buffer)

\[
\begin{align*}
[HA] &\approx \frac{n_{\text{acid}} - n_{\text{base}}}{V_{\text{total}}} \\
[A^-] &\approx \frac{n_{\text{base}}}{V_{\text{total}}} \\
[H^+] &= \frac{K_a \times [HA]}{[A^-]}
\end{align*}
\]

**AT** the end point:

(A⁻ hydrolysis)

\[
\begin{align*}
[HA] &\approx 0 \\
[A^-] &\approx \frac{n_{\text{acid}}}{V_{\text{total}}} \\
[OH^-] &\approx \sqrt{\frac{K_w \times [A^-]}{K_a}} \\
[H^+] &= \frac{K_w}{[OH^-]}
\end{align*}
\]

**AFTER** the end-point:

(dominated by the excess base)

\[
\begin{align*}
[OH^-] &= \frac{(n_{\text{base}} - n_{\text{acid}})}{V_{\text{total}}} \\
[H^+] &= \frac{K_w}{[OH^-]}
\end{align*}
\]
## II. Titrating a Weak Acid with a Strong Base

<table>
<thead>
<tr>
<th>Input parameters</th>
<th></th>
<th>V added (mL)</th>
<th>V total (mL)</th>
<th>millimoles base</th>
<th>[H+] (M)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial acid concentration (M) - cell B3 renamed into &quot;acid&quot;</td>
<td></td>
<td>0.1</td>
<td>0.4</td>
<td>25.4</td>
<td>0.00E+00</td>
<td>1.32E-03</td>
</tr>
<tr>
<td>Initial base concentration (M) - cell B4 renamed into &quot;base&quot;</td>
<td></td>
<td>0.1</td>
<td>0.8</td>
<td>25.3</td>
<td>8.00E-02</td>
<td>5.26E-04</td>
</tr>
<tr>
<td>Initial acid solution volume (mL) - cell B5 renamed into &quot;Vacid&quot;</td>
<td></td>
<td>25</td>
<td>1.2</td>
<td>25.2</td>
<td>1.20E-01</td>
<td>3.45E-04</td>
</tr>
<tr>
<td>pKa value of the acid - cell B6 renamed into &quot;pKa&quot;</td>
<td></td>
<td></td>
<td>4.76</td>
<td>1.6</td>
<td>25.6</td>
<td>1.60E-01</td>
</tr>
<tr>
<td>Kw - cell B8 renamed into &quot;Kw&quot;</td>
<td>= 1.00E-14</td>
<td>2</td>
<td>27</td>
<td>2.00E-01</td>
<td>2.00E-04</td>
<td>3.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.4</td>
<td>27.4</td>
<td>2.40E-01</td>
<td>1.64E-04</td>
<td>3.79</td>
</tr>
<tr>
<td>Millimoles of acid in the initial solution = acid*Vacid (cell B9 renamed into &quot;mmoles&quot;)</td>
<td></td>
<td>2.5</td>
<td>2.8</td>
<td>27.8</td>
<td>2.80E-01</td>
<td>1.38E-04</td>
</tr>
<tr>
<td>Ka = 10^(-pKa) - cell B10 renamed into &quot;Ka&quot;</td>
<td></td>
<td>1.74E-05</td>
<td>3.2</td>
<td>29.2</td>
<td>3.20E-01</td>
<td>1.18E-04</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.6</td>
<td>32.6</td>
<td>3.60E-01</td>
<td>1.03E-04</td>
<td>3.99</td>
</tr>
</tbody>
</table>

### Titration of a weak acid with a strong base

- **Column D is filled to the desired volume values**
- **Column H = -log(Column G)**
- **E2=D2+Vacid**
- **F2=D2*Kw**

**No base added:**
- **Cell G2 = SQRT(acid*Ka)**

**Below equivalence:**
- **Cell G3 = (mmoles-F3)/F3*Ka**

**At equivalence:**
- **Cell G65 = SQRT(Kw*Ka*E65/mmoles)**

**Above equivalence:**
- **Cell G66 = E66/(F66-mmoles)*Kw**

### Graph: Titration of a pKa = 4.76 acid with a strong base

- **pH ~ pKa at half-titration point**
- **Equiv. point at pH > 7**

### Graph Data:

<table>
<thead>
<tr>
<th>Volume of base added (mL)</th>
<th>pH after the addition</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.00E-01</td>
</tr>
<tr>
<td>5</td>
<td>1.05E-01</td>
</tr>
<tr>
<td>10</td>
<td>1.10E-01</td>
</tr>
<tr>
<td>15</td>
<td>1.15E-01</td>
</tr>
<tr>
<td>20</td>
<td>1.20E-01</td>
</tr>
<tr>
<td>25</td>
<td>1.25E-01</td>
</tr>
<tr>
<td>30</td>
<td>1.30E-01</td>
</tr>
<tr>
<td>35</td>
<td>1.35E-01</td>
</tr>
<tr>
<td>40</td>
<td>1.40E-01</td>
</tr>
<tr>
<td>45</td>
<td>1.45E-01</td>
</tr>
<tr>
<td>50</td>
<td>1.50E-01</td>
</tr>
</tbody>
</table>
More Advanced: "Exact" Solution

We are going to calculate pH for a mixture of NaOH and HA with the following effective initial concentrations (the ratios of volumes account for the dilution occurring during titration).

The following equilibria are to be considered:

\[
\text{HA} \Leftrightarrow \text{A}^- + \text{H}^+ \quad K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}
\]

\[
\text{H}_2\text{O} \Leftrightarrow \text{OH}^- + \text{H}^+ \quad K_w = [\text{H}^+][\text{OH}^-]
\]

Mass balance equation:

\[
C_{\text{weak}} = [\text{HA}] + [\text{A}^-] = [\text{A}^-] \times \left( \frac{[\text{H}^+]}{K_a} + 1 \right)
\]

Charge balance equation:

\[
C_{\text{base}} + [\text{H}^+] = [\text{OH}^-] + [\text{A}^-]
\]

Combination of the above equation results in 3\text{rd} order equation for [H\text{\textsuperscript{+}}] which can be trivially solved in MathCAD (using "root" function):
Comparison of Strong vs Weak Acid Titration

25 mL of 0.1 M acids titrated with a 0.1 M strong base

Above the equivalence point, when an excess base has been added, the curves become identical.

Below the equivalence point the curves are quite different (recall that pH ≈ pKₐ at the half-titration point).
III. Titrating a Mixture of a Strong & Weak Acids

This is the kind of titration you will be performing in lab 2. There are two equivalence points; one for the strong acid and one for the weak acid. After all of the strong acid is titrated, the calculation is the same as for the weak acid case. Below the first equivalence point one must account for H\(^+\) from both untitrated strong acid and ionization of weak acid. Here is an approximate solution:

At any time below the first equivalence point, the total remaining acid concentrations are:

\[
C_{\text{strong}} \approx \frac{(n_{\text{strong acid}} - n_{\text{base added}})}{V_{\text{total}}} \quad C_{\text{weak}} \approx \frac{n_{\text{weak acid}}}{V_{\text{total}}}
\]

\(H^+\) ion has two sources: 

\([H^+] = C_{\text{strong}} + [A^-]\) 

\(A^-\) and HA are at equilibrium

\(C_{\text{weak}} = [HA] + [A^-]\) 

\(K_a = \frac{[H^+][A^-]}{[HA]}\)

After some algebra, this leads to a quadratic equation for \([H^+]\). This equation is solved in the Excel worksheet that is available on the course website.

\([H^+]^2 + [H^+] \times (K_a - C_{\text{strong}}) - K_a \times (C_{\text{strong}} + C_{\text{weak}}) = 0\)
III. Titrating a Mixture of a Strong & Weak Acids

Titration of a pKa = 4.76 acid with a strong base

2nd order equation for $[\text{H}^+]$ solved at and below the 1st equiv. point

pH ~ pKa when 50% weak acid is titrated

2nd equiv. point at pH > 7
Mixture vs Individual Acids

Different acid solutions titrated with a 0.1 M strong base

- Blue line: 25 mL of 0.1 M pKa = 4.76 acid
- Red line: 25 mL of 0.1M strong acid
- Green line: 25mL mixture of 0.1M strong & 0.1M weak acids

Volume of added base (mL)

pH
Differentiation of Vector Data

- Physical meaning of the derivative
  - Slope of the tangent line = rate of change
  - Equals zero at function maximum or minimum
  - Positive when the function is increasing
  - Negative when it is decreasing

- Finite difference approximation
  - Works well only for “well-behaved” data sets
  - For titration data, $V = [V_1, V_2, V_3, \ldots, V_n]$ and $pH = [pH_1, pH_2, pH_3, \ldots, pH_n]$ the finite difference approximation can be used as follows:

    \[ \langle V \rangle_{1,2} = \frac{V_2 + V_1}{2} \quad \frac{dpH}{dV} = \frac{pH_2 - pH_1}{V_2 - V_1} \]

    \[ \langle V \rangle_{2,3} = \frac{V_3 + V_2}{2} \quad \frac{dpH}{dV} = \frac{pH_3 - pH_2}{V_3 - V_2} \]

  - The maximal value of the first derivative corresponds to an end point
Example of an Experimental Titration Plot

1st derivative = maximum
2nd derivative = zero
at both end-points