Potentiometric Titration of Acid-Base

Collect

- One 25 mL buret
- One 100 mL volumetric flask
- Two 125 mL Erlenmeyer flasks (check if broken)
- One magnetic stirring bar (from TA)
- Share: 5 mL pipet and pipet filler
- Share: pH 7.00 and pH 4.00 standard buffer solution
Objective & Techniques

I. Objective:

- To prepare and to standardize secondary-standard solutions
- To determine the equivalence point and concentration of acetic acid by using the electric potential method
- To determine the dissociation constant of acetic acid, $K_a$

II. Techniques:

- Use of analytic balance and prepare solutions
- Use of the volumetric flask, graduated pipet, and burets
- Calibration and operation of pH-meter
- Determine the equivalence point by titration curves
Standardization of Acid or Base

- **Primary standard:** substance with high purity and high molar mass
- **Secondary standard:** standardized acid or base
- Common primary standard base: sodium carbonate (Na$_2$CO$_3$)
- Common primary standard acid: potassium hydrogen phthalate (KHP)
- KHP is a monoprotic weak acid with structure

The neutralization rxn of KHP with NaOH in a 1:1 stoichiometric ratio

\[
\text{HOOC}_6\text{H}_4\text{COOK}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow
\]

\[
\text{C}_6\text{H}_4(\text{COO})_2^-(\text{aq}) + \text{K}^+(\text{aq}) + \text{Na}^+(\text{aq}) + \text{H}_2\text{O}(\text{l})
\]

\[
C_{\text{NaOH}} \cdot V_{\text{NaOH}} = n_{\text{KHP}} = \frac{\text{Mass}_{\text{KHP}}}{204.22}
\]
The Equivalence Point

- The pH value of the reacting solution changes significantly near the equivalence point.
- Base on the color change of the acid-base indicator or monitoring the change in pH values to determine the equivalence point.

### Indicator

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Acid form</th>
<th>pH range</th>
<th>Basic form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl orange</td>
<td>Red</td>
<td>3~4</td>
<td>Orange</td>
</tr>
<tr>
<td>Bromothymol blue</td>
<td>Yellow</td>
<td>6~7</td>
<td>Blue</td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>Colorless</td>
<td>8~10</td>
<td>Pink red</td>
</tr>
</tbody>
</table>

**Weak acid / strong base titration curve**
Acid-Base Indicator

- Acid-base indicator: a weak organic acid or base
- Weak acid \((HIn)\) and its conjugate base \((In^-)\) with different colors

\[
HIn + H_2O \rightleftharpoons H_3O^+ + In^- 
\]

- Acidic Color \(HIn\)
- Color Change Range
- Basic Color \(In^-\)
- \(pK_a - 1\)
- \(pK_a + 1\)
- pH increases

- According to the pH range of the equivalence point
  - Strong acid/weak base titration: pH < 7
  - Weak acid/strong base titration: pH > 7
  - Strong acid/strong base titration: pH = 7

- Choose the appropriate indicator to match the end-point with the equivalence point
Equivalence Point

1. Acid-base titration curve
   The point on the curve with the maximum slope is the equivalence point

2. First derivative of titration curve
   The maximum point is the equivalence point

3. Second derivative of the titration curve
   X-intercept of line A-B is the equivalence point
Dissociation Constant of a Weak Acid

- Acid-base neutralization rxn:
  \[ \text{HA(aq)} + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O(l)} + \text{A}^-(\text{aq}) \]
- Dissociation of weak acid
  \[ \text{HA(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{A}^-(\text{aq}) \]

\[ K_a = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]} \]
- At half-equivalence point
  \[ [\text{HA}] = [\text{A}^-], [\text{H}_3\text{O}^+] = K_a \]
  therefore, \( \text{pH} = \text{p}K_a \)

For example
- Equivalence volume = 37.50 mL
- Half-equivalence volume = 18.75 mL
- \( V = 18.00, \text{pH} = 4.60 \)
- \( V = 19.10, \text{pH} = 4.65 \)
- pH of the half-equivalence point = 4.63
- \( \text{p}K_a = \text{pH} = 4.63, K_a = 2.3 \times 10^{-5} \)
pH Meter

pH meter consists of three parts:

- **pH electrode**
  - **Reference electrode** (usually made of silver with silver chloride), the potential is a fixed value
  - **Indicator electrode** (usually made of glass), the potential changes with the concentration of H\(^+\)
- **Thermoprobe**: used to measure the temperature of soln
- **Voltmeter**: used to measure the potential difference (\(E_m\)) between the two electrodes
Cell Potential and pH Value

\[ E_m = K - 2.3RT(pH)/nF \]

\[ E_m = mT(pH) + K \]

- \( E_m \): measured cell potential
- \( K \): constant, determined by the type of electrode used
- \( R \): gas constant
- \( T \): absolute temperature of the solution
- \( pH \): pH value of solution
- \( n \): number of moles of electrons transferred through the electrodes during a reaction
- \( F \): Faraday constant

The relationship between measured cell potential and pH value
Outline of Procedures

I. Preparation of NaOH(aq)

II. Standardization of NaOH with KHP

III. Calibration of pH-meter

IV. Titration of vinegar
**Procedure I. Prepare 0.1 M NaOH**

1. Take 10 mL of 1 M NaOH
2. Place in a 100 mL volumetric flask
3. Add water till mark

---

1. Invert the flask several times
2. Mix thoroughly
3. Pour into beaker

---

1. Use approx. 5 mL of 0.1 M NaOH
2. Rinse buret twice and fill with solution

---

Read initial volume of buret \( (V_i) \) to 0.01 mL
Procedure II. Standardize NaOH with KHP

- Measure ca. 0.2~0.22 g KHP with analytical balance
- **Place in a 125 mL Erlenmeyer flask**
- Record accurate weight

(1) Dissolve with 50 mL distilled water

(2) Add 2 d. of phenolphthalein

(3) Titrate with 0.1 M NaOH

- Titrate the solution to appear **pink** and persist for 30 s
- Record $V_i$ and $V_f$
- Carry out a duplicate test
- Calculate average concentration of NaOH
Procedure III. Prepare pH-Meter

- Push the “POWER” button, warm up for 10 minutes
- Remove the electrode cap by rotating it
- Use washing bottle to clean the electrodes
- Blot dry with a tissue
Procedure III. Calibrate pH-Meter

(1) Collect pH 7.00 and 4.00 standard buffer solution
(2) Switch to “Temp” function to check if the temp is close to r.t.
(3) Switch to “pH” function

- Immerse thermoprobe and electrodes into pH 7.00 buffer solution
- Adjust Calib knob until meter shows ‘7.00’

- Rinse thermoprobe and electrodes
- Immerse in pH 4.00 buffer solution
- Adjust Slope knob until meter shows ‘4.00’
Notice: Operation of pH-Meter

- Use 100 mL beaker for titration
- Place the electrode on the holder
- **When testing, both thermoprobe and the electrode** should be placed in soln.
- The *salt bridge* of electrode should be fully immersed in the test solution
- Position the electrode in the soln. so that the stirring bar will not strike the electrode
- Turn the magnetic stirring bar on during titration
- Every time the testing solution is changed, the electrode should be rinsed with DI water and blot dry with tissues
- When the electrode is not in use, it needs to be immersed in **clean DI water**
- When the electrode is not in use for long periods of time, it should be immersed in **3 M KCl** solution
**Procedure IV. Titration of Vinegar**

**Sampling**

1. Transfer **2.5 mL** vinegar into a 100 mL beaker
2. Record brand and acidity of vinegar

**Titrate**

1. Add **40 mL** of distilled water
2. 2 d. of phenolphthalein
3. Place stirring bar, the electrode, and thermoprobe in soln

- Fill up the buret with standardized 0.1 M NaOH(aq) before titration
- Add ~1 mL aliquots of NaOH and record $V_i$, $V_f$, and pH value after each addition
- **At pH 5.5~10**: add titrant in 0.2 mL increments
- **At pH > 10**: add titrant in 1 mL increments
- When pH > 11: stop titration
- Observe and record the change in color of solution during titration
After Experiment

- Rinse and check the pH electrode
- Place electrode in plastic-cap that containing 3 M KCl
- Turn the pH meter off
- Hand in magnetic stirring bar
- Wash buret and invert to dip dry
- Waste liquids (salts) can be discarded in sin after neutralization
Data Analysis

- Calculate **average standardized concentration of NaOH**

- Tabulate the **experimental data**, give **3 plots in Excel**, and calculate **3 equivalence points**

- Calculate the **molar concentration of acetic acid in vinegar (C_M)**
  \[ C_1 V_1 = C_M V_2 \]

- Calculate the **percent concentration** and compare with labels (assume density is same as water)

  For example:
  \[
  C_M = 0.737 \text{ M} \\
  \frac{0.737 \text{ mol/L} \times 60.0 \text{ g/mol}}{1000 \text{ mL/L} \times 1.0 \text{ g/mL}} \times 100\% = 4.4\%
  \]

- Determine **K_a of acetic acid** from the half-equivalence point
### Worksheet

First derivative:

<table>
<thead>
<tr>
<th>$V_{NaOH}$</th>
<th>pH</th>
<th>$V_1$</th>
<th>$\Delta pH/\Delta V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.10</td>
<td>4.99</td>
<td>15.63</td>
<td>0.09</td>
</tr>
<tr>
<td>16.15</td>
<td>5.08</td>
<td>16.63</td>
<td>0.11</td>
</tr>
<tr>
<td>17.10</td>
<td>5.18</td>
<td>17.60</td>
<td>0.12</td>
</tr>
<tr>
<td>18.10</td>
<td>5.30</td>
<td>18.68</td>
<td>0.16</td>
</tr>
<tr>
<td>19.25</td>
<td>5.48</td>
<td>19.75</td>
<td>0.21</td>
</tr>
<tr>
<td>20.25</td>
<td>5.69</td>
<td>20.70</td>
<td>0.31</td>
</tr>
<tr>
<td>21.15</td>
<td>5.97</td>
<td>21.58</td>
<td>0.72</td>
</tr>
<tr>
<td>22.00</td>
<td>6.58</td>
<td>22.10</td>
<td>5.05</td>
</tr>
<tr>
<td><strong>22.20</strong></td>
<td>7.59</td>
<td><strong>22.30</strong></td>
<td><strong>9.55</strong></td>
</tr>
<tr>
<td><strong>22.40</strong></td>
<td>9.50</td>
<td><strong>22.50</strong></td>
<td><strong>2.75</strong></td>
</tr>
<tr>
<td>22.60</td>
<td>10.05</td>
<td>23.10</td>
<td>0.95</td>
</tr>
<tr>
<td>23.60</td>
<td>11.00</td>
<td>24.10</td>
<td>0.32</td>
</tr>
</tbody>
</table>

Second derivative:

<table>
<thead>
<tr>
<th>$V_2$</th>
<th>$\Delta(\Delta pH/\Delta V)/\Delta V_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.13</td>
<td>0.02</td>
</tr>
<tr>
<td>17.11</td>
<td>0.02</td>
</tr>
<tr>
<td>18.14</td>
<td>0.03</td>
</tr>
<tr>
<td>19.21</td>
<td>0.05</td>
</tr>
<tr>
<td>20.23</td>
<td>0.11</td>
</tr>
<tr>
<td>21.14</td>
<td>0.46</td>
</tr>
<tr>
<td>22.20</td>
<td>8.25</td>
</tr>
<tr>
<td><strong>22.40</strong></td>
<td>-34.00</td>
</tr>
<tr>
<td>22.80</td>
<td>-3.00</td>
</tr>
<tr>
<td>23.60</td>
<td>-0.63</td>
</tr>
<tr>
<td>24.58</td>
<td>-0.14</td>
</tr>
</tbody>
</table>

\[ V_1 = \frac{(15.10 + 16.15)}{2} = 15.63 \]
\[ V_2 = \frac{(15.63 + 16.63)}{2} = 16.13 \]
Graphs of the Titration of Vinegar

Half-equivalence point

Equivalence point

V

V_1

V_2
## Data Processing When $V_i$ is not 0.00 mL

- **$V_i = 11.00$**
- **Subtract $V_i$**
- **Round to two decimal places**

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$V_{NaOH}$ (mL)</td>
<td>$V$ (mL)</td>
<td>pH</td>
<td>$V1$ (mL)</td>
<td>dpH/dV</td>
<td>$V2$ (mL)</td>
</tr>
<tr>
<td>2</td>
<td>11.00</td>
<td>0.00</td>
<td>3.03</td>
<td>0.50</td>
<td>0.37</td>
<td>1.00</td>
</tr>
<tr>
<td>3</td>
<td>12.00</td>
<td>1.00</td>
<td>3.40</td>
<td>1.50</td>
<td>0.18</td>
<td>2.00</td>
</tr>
<tr>
<td>4</td>
<td>13.00</td>
<td>2.00</td>
<td>3.58</td>
<td>2.50</td>
<td>0.18</td>
<td>3.00</td>
</tr>
<tr>
<td>5</td>
<td>14.00</td>
<td>3.00</td>
<td>3.76</td>
<td>3.50</td>
<td>0.12</td>
<td>4.00</td>
</tr>
<tr>
<td>6</td>
<td>15.00</td>
<td>4.00</td>
<td>3.88</td>
<td>4.50</td>
<td>0.10</td>
<td>5.00</td>
</tr>
<tr>
<td>7</td>
<td>16.00</td>
<td>5.00</td>
<td>3.98</td>
<td>5.50</td>
<td>0.10</td>
<td>6.00</td>
</tr>
<tr>
<td>8</td>
<td>17.00</td>
<td>6.00</td>
<td>4.08</td>
<td>6.50</td>
<td>0.09</td>
<td>7.00</td>
</tr>
<tr>
<td>9</td>
<td>18.00</td>
<td>7.00</td>
<td>4.17</td>
<td>7.50</td>
<td>0.11</td>
<td>8.00</td>
</tr>
<tr>
<td>10</td>
<td>19.00</td>
<td>8.00</td>
<td>4.28</td>
<td>8.50</td>
<td>0.07</td>
<td>9.00</td>
</tr>
<tr>
<td>11</td>
<td>20.00</td>
<td>9.00</td>
<td>4.35</td>
<td>9.50</td>
<td>0.08</td>
<td>10.00</td>
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<tr>
<td>12</td>
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<td>10.00</td>
<td>4.43</td>
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<td>0.04</td>
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</tr>
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<td>4.47</td>
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<tr>
<td>14</td>
<td>23.00</td>
<td>12.00</td>
<td>4.55</td>
<td>12.50</td>
<td>0.07</td>
<td>13.00</td>
</tr>
</tbody>
</table>
## Vinegar Titration Data

\[ V_{\text{titrant}} = V_{\text{read}} - V_i \]

**Ex:** \[ 9.30 - 9.30 = 0.00 \]
\[ 11.30 - 9.30 = 2.00 \]

<table>
<thead>
<tr>
<th>( V_{\text{read}} ) (mL)</th>
<th>( V_{\text{titrant}} ) (mL)</th>
<th>pH</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.30</td>
<td>0.00</td>
<td>2.82</td>
<td>Colorless</td>
</tr>
<tr>
<td>11.30</td>
<td>2.00</td>
<td>3.44</td>
<td>Colorless</td>
</tr>
<tr>
<td>13.30</td>
<td>4.00</td>
<td>3.82</td>
<td>Colorless</td>
</tr>
<tr>
<td>15.30</td>
<td>6.00</td>
<td>4.05</td>
<td>Colorless</td>
</tr>
<tr>
<td>17.30</td>
<td>8.00</td>
<td>4.29</td>
<td>Colorless</td>
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<tr>
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<td>9.00</td>
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<td>4.52</td>
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</tr>
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</tr>
<tr>
<td>26.30</td>
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<tr>
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<td>18.20</td>
<td>5.80</td>
<td>Colorless</td>
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</tr>
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<td>18.60</td>
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<td>18.80</td>
<td>6.16</td>
<td>Colorless</td>
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<td>28.30</td>
<td>19.00</td>
<td>6.37</td>
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<td>19.20</td>
<td>6.68</td>
<td>Colorless</td>
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<td>19.40</td>
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<td>Pink</td>
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<td>10.38</td>
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</tr>
<tr>
<td>30.50</td>
<td>21.20</td>
<td>11.03</td>
<td>Pink</td>
</tr>
</tbody>
</table>

Mark half-equivalence point

Mark equivalence point
Vinegar Titration Curve

Vinegar Titration Curve

**Vinegar Titration Curve**

[Graph showing pH vs. V_titrant (mL) with notable points:]

- **Half-equivalence point**: (9.75, 4.49)
- **Equivalence point**: (19.50, 7.76)
Ex.1 Deliver 5.00 mL solution:

- Wash a 10 mL pipet thoroughly.
- Rinse twice with small portion of sample solution.
- Press valve A of pipet filler and squeeze bulb to expel the air inside and create a vacuum.
- Insert the top of pipet into pipet filler, press valve S to draw liquid to equal to the mark of 0.00 mL.
- Hold pipet vertically and transfer liquid into container. (One hand hold pipet and the other hand hold container to operate.)
- Press valve E to drain liquid to the mark of 5.00 mL.
- Wash thoroughly after use.
T13 - Volumetric Flask

- Wash volumetric flask thoroughly and rinse with DI water.
- Transfer the solution to flask with the help of a funnel.
- Fill the flask about half full and swirl the contents to achieve solution.
- Bring the liquid level almost to the mark.
- Use a dropper to add solvent to the mark.
- Stopper the flask and invert the flask repeatedly to assure homogeneous.
- Pour the solution in a beaker for later use; do not store the solution in the flask.
- Wash immediately after use.
T14 - Titration

- Rinse a buret with DI water thoroughly.
- Rinse twice with ca. 5 mL titrant.
- Transfer the titrant to buret via funnel.
- Drain slowly until the tip is free of air bubbles and completely filled with liquid.
- Read and record initial ($V_i$) and final volume ($V_f$) of buret to 0.01 mL.
- Place buret tip well inside the receiving flask during titration.
- Swirl the flask with right hand and control the stopcock with left hand (process done by one person).
- Rinse the buret with tap water, inverted clamped, and left to dry after the experiment.