Collect

- One 50 mL buret
- One 100 mL volumetric flask
- Two 125 mL Erlenmeyer flasks (check if broken)
- One magnetic stirring bar (from TA)
- One 5 mL pipet and pipet filler (shared)
- pH 7.00 and pH 4.00 standard buffer solution (shared by two groups)
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. Skills:

- 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 ($\text{Na}_2\text{CO}_3$)
- 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

$$\text{HOOCC}_6\text{H}_4\text{COOK}(aq) + \text{NaOH}(aq) \rightarrow$$

$$\text{C}_6\text{H}_4(\text{COO})_2^{2-}(aq) + \text{K}^+(aq) + \text{Na}^+(aq) + \text{H}_2\text{O}(l)$$
The Equivalence Point

- The pH 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.

<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

\[
\text{HIn} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{In}^-
\]

<table>
<thead>
<tr>
<th>Acidic Color</th>
<th>Color Change Range</th>
<th>Basic Color</th>
<th>pH increases</th>
</tr>
</thead>
<tbody>
<tr>
<td>HIn</td>
<td></td>
<td>In⁻</td>
<td></td>
</tr>
<tr>
<td>pK_a - 1</td>
<td></td>
<td>pK_a + 1</td>
<td></td>
</tr>
</tbody>
</table>

- 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 Weak Acid

- Acid-base neutralization rxn:
  \[ \text{HA}(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(l) + \text{A}^-(aq) \]
- Dissociation of weak acid
  \[ \text{HA}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq) \]
  \[ K_a = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]} \]
- At half-equivalence point
  \[ [\text{HA}] = [\text{A}^-], \ [\text{H}_3\text{O}^+] = K_a \]
  therefore, \( \text{pH} = \text{pK}_a \)

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
- \( \text{pK}_a = \text{pH} = 4.63, K_a = 2.3 \times 10^{-5} \)
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

Fig. T16-1  pH meter in lab (SUNTEX SP-701)
$E_m$ vs. pH of pH Meter

$E_m = K - 2.3RT(pH)/nF$

$E_m = mT(pH) + K$

- $E_m$: 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 in the 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 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 rinse the electrodes
- Blot dry with a tissue
- Press “HOLD” when cleaning the electrodes and the screen will freeze

Cap of electrode  Control knobs  pH Electrode  Thermoprobe
Procedure III. Calibrate pH-Meter

(1) Collect pH 7.0 and 4.0 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 in Using pH Meter

- Use 100 mL beaker for testing
- 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 properly so that the stirring bar will not strike the electrode
- Turn the magnetic stir on
- Rinse the electrode with D.I. water and blot dry with tissues when changing the test soln
- Immerse the electrode in clean D.I. water when not in use
- Immerse the electrode in 3 M KCl soln when not in use for long period of time
Procedure IV. Titration of Vinegar

**Sampling:**
1. Transfer **3.0 mL** vinegar into a 100 mL beaker
2. Record brand and acidity of vinegar

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

**Titrate**
- Titrate with standardized 0.1 M NaOH
- Add ~1 mL aliquots of NaOH and record $V_i$, $V_f$, and **pH value** after each addition
- **At pH 6~10:** add titrant in **0.2 mL** increments
- **At pH > 10:** add titrant in **1 mL** increments
- When pH is ~12: stop titration
- Observe and record the change in color of solution during titration
After Experiment

- Rinse and check pH electrode before use
- Immerse the electrode into clean D.I. water (or Place electrode in plastic-cap filled with 3 M KCl)
- Turn the pH meter off
- Hand in magnetic stirring bar to TA
- Waste liquids (salts) can be discarded in sink 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 **mass 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>
<th>( V_2 )</th>
<th>( \Delta(\Delta pH/\Delta V)/\Delta V_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.10</td>
<td>4.99</td>
<td>15.63</td>
<td>0.09</td>
<td>16.13</td>
<td>0.02</td>
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<tr>
<td>16.15</td>
<td>5.08</td>
<td>16.63</td>
<td>0.11</td>
<td>17.11</td>
<td>0.02</td>
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<td>17.10</td>
<td>5.18</td>
<td>17.60</td>
<td>0.12</td>
<td>18.14</td>
<td>0.03</td>
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<td>18.10</td>
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<td>18.68</td>
<td>0.16</td>
<td>19.21</td>
<td>0.05</td>
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<td>19.75</td>
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<td>20.23</td>
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<tr>
<td>20.25</td>
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<td>21.15</td>
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<td>22.00</td>
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<td>22.10</td>
<td>5.05</td>
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<td>22.50</td>
</tr>
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<td>24.10</td>
<td>0.32</td>
<td>24.58</td>
<td>-0.14</td>
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</table>

Second derivative

\[
V_1 = \frac{(15.10 + 16.15)}{2} = 15.63
\]

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

- **Half-equivalence point**
- **Equivalence point**
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></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>
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<td>1</td>
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