Purpose:
To conduct a pH titration, to use it to determine the Molar Mass and pKa of an unknown acid & from these two quantities, identify of the acid.

Concepts:
- pH, pK\textsubscript{a}
- Titration Curve
- Molar Mass
- Equivalence/End Point
- Strong vs Weak Acids

Techniques:
- Weighing by Difference
- Titration
- Use of a pH Meter
- Calibration of pH Meter
- Graphing
- Handling the Glass Electrode

Apparatus:
- Buret
- Analytical Balance
- pH Meter
- Glass Electrode

Weak Acids, pH and pK\textsubscript{a} - Some Definitions

- \text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-
- \text{[H}^+\text{][A}^-\text{]} \rightleftharpoons \text{[HA]} \\
- \text{pK} = -\log_{10} K
- \text{pK} = -\log_{10} K\text{a}

- Weak Acid = \text{K}a \text{ is small (i.e., K}a \text{<< 1)}
- pK\text{ is large (i.e., pK}a \text{ > 0)}

- Monoprotic Acid = an acid with only 1 replaceable hydrogen atom, e.g., HCl, CH\textsubscript{3}COOH
- Polyprotic Acid = an acid with 2 or more replaceable hydrogen atoms, e.g., H\textsubscript{2}SO\textsubscript{4}, HCOOHCH\textsubscript{2}COOH

Last Semester: Titration of a weak acid (vapor) with a strong base.

Organization of the Lecture

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This Exercise: Titration of a weak acid (unknown) with a strong base.

Are there any points of interest in addition to the end point?

For sufficiently weak acids, \([ HA ]\) will be equal to \([ A^- ]\) when half of the acid has been neutralized. I.e., when the volume of NaOH added is \(\frac{1}{2}\) that required to completely neutralize the acid.

\[
\begin{align*}
HA & \rightleftharpoons H^+ + A^- \\
K_a &= \frac{[H^+][A^-]}{[HA]}
\end{align*}
\]

The Half Titration Point

At the point where \([ HA ] = [ A^- ]\),

\[
[H^+] = K_a
\]

\[
\text{pH} = \text{pK}_a
\]

This is called the Henderson-Hasselbalch equation.

An incidental observation.

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

Taking the logs of both sides of the equation gives us:

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

Multiplying by \(-1\) and rearranging we get:

\[
\text{pH} = \text{pK}_a + \log \frac{[A^-]}{[HA]}
\]

The Half Equivalence Point

How good is our approximation that \(\text{pH at half-equivalence point} = \text{pK}_a\)?

For the concentrations used in this exercise and the \(pK_a's\) of the possible unknown weak acids, the error in the approximation is less than 2% for \(pK_a's \sim 3\)

is less than 1% for \(pK_a's > 4\)

\*

A web supplement discusses this approximation.

http://www.ic.sunysb.edu/Class/che134/lectures/phpkahalftr.pdf

Which features of Titration Curves are primarily affected by the \(pK_a\) of the Acid?

\[
\text{pH} = \text{pK}_a + \log \frac{[A^-]}{[HA]}
\]
How Strength of an Acid affects its Titration Curve

In normal titrations (indicator only), we can determine (only) total number of available moles, \( n \), of acid in a sample – and from that:

- If we know the weight, we can compute the Molar Mass \((\text{w}/n)\)
- If we know the Molar Mass, the weight of acid \((w = \text{MM} \times n)\)

\[\text{mmol} \text{ NaOH} \times 25.00\ \text{mL} \times 0.100\ \text{mmol/mL} = 2.50\ \text{mmol}\]

and

\[\text{Molar Mass} = \frac{425\ \text{mg}}{2.50\ \text{mmol}} = 170\ \text{mg/mmol}\]

In a \(\text{pH}\) titration, in addition to the Molar Mass, we have the \(\text{pH}\) of the solution at each point up to, and past the end point, including the half-titration point at which:

\[\text{pH}_{1/2} = pK_a\]

\(pK_a\) can distinguish acids with the same Molar Mass.

The Mechanics of \(\text{pH}\) Titration

All the procedures of a normal (indicator) titration.

1. Rinse buret with base solution
2. Eliminate any bubbles in tip
3. Drain/fill to an arbitrary starting volume (not 0.00)
4. Stir/swirl solution constantly to insure complete mixing
5. Adjust amount of acid to require 25 ± 3 mL of base
6. Add base more slowly as you approach the end point - dropwise with stirring when very near end point
7. Record volumes to full precision (xx.xx)

In \(\text{pH}\) titration, also:

8. Calibrate \(\text{pH}\) meter
9. Rinse and insert glass electrode in solution being titrated - make sure tip of electrode is completely immersed
10. Leave glass electrode in solution for entire titration
11. Record volumes & \(\text{pH}\) to full precision at each cumulative volume
12. Monitor \(\text{pH}\) increments to control added volume increments

Recommended Rate of addition of Base

The half-equivalence point determines the \(pK_a\). That point is in the middle of the Buffer region so \(\text{pH}\) changes slowly with added base.

We can use large increments of base in that region

The end point determines the Molar Mass, so we would like precision in the volume of base when it occurs.

Use 2 drop (0.1 mL) increments starting about 2 mL before the expected end point.

How are you supposed to know the end point before titrating?

From the results of a normal (phenolphthalein) titration on a weighed sample of your unknown

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[Diagram of titration curve showing pH changes with added base.]
WHY that volume?
Optimizes buret precision & quantities of reagents and produces an easily interpretable graph

BUT
Molar mass of the acid is unknown.

STEP 1:
Determine how many mg of your acid will be required to use 25 ± 3 mL of NaOH.
Everyone uses ~ 200 mg of acid – weighed out ACCURATELY into a 150 mL beaker.

Titrate to phenolphthalein end-point - No pH METER

What are the proper incremental additions of base?

Suppose in the phenolphthalein titration:
0.2433 g requires 21.67 mL of NaOH
How much should I weigh to use 25 ± 3 mL of NaOH?

0.2433 g / 21.67 mL = X / (25 ± 3)

X = (0.2433/21.67) * (25 ± 3)

X = 0.28 ± 0.03 g

How much should I weigh to use 25 ± 3 mL?

Suppose in the phenolphthalein titration:
21.67 X / 0.2433 = 24.51 mL of NaOH

I actually weigh out 0.2752 g for the pH Titration

Start 2 drop increments at 24.51-2.00 = 22.51 mL ADDED NaOH

What volume will that weight will actually require?

What are the proper incremental additions of base?

Recommended Volume of Base at the End Point

We seek to use about 25 (25 ± 3) mL of NaOH to reach the end point

<table>
<thead>
<tr>
<th>BURET</th>
<th>VOL (mL)</th>
<th>NaOH</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.40</td>
<td>2.00</td>
<td>2.49</td>
<td></td>
</tr>
<tr>
<td>5.42</td>
<td>1.05</td>
<td>2.72</td>
<td></td>
</tr>
<tr>
<td>8.39</td>
<td>2.02</td>
<td>2.90</td>
<td></td>
</tr>
<tr>
<td>8.37</td>
<td>4.00</td>
<td>3.29</td>
<td></td>
</tr>
<tr>
<td>12.39</td>
<td>6.02</td>
<td>3.64</td>
<td></td>
</tr>
<tr>
<td>12.41</td>
<td>9.04</td>
<td>3.93</td>
<td></td>
</tr>
<tr>
<td>14.38</td>
<td>10.01</td>
<td>3.76</td>
<td></td>
</tr>
<tr>
<td>18.44</td>
<td>14.09</td>
<td>4.06</td>
<td></td>
</tr>
<tr>
<td>20.46</td>
<td>16.09</td>
<td>4.21</td>
<td></td>
</tr>
<tr>
<td>20.67</td>
<td>16.90</td>
<td>4.34</td>
<td></td>
</tr>
<tr>
<td>21.46</td>
<td>17.53</td>
<td>4.28</td>
<td></td>
</tr>
<tr>
<td>21.97</td>
<td>18.50</td>
<td>4.32</td>
<td></td>
</tr>
<tr>
<td>22.44</td>
<td>18.97</td>
<td>4.38</td>
<td></td>
</tr>
<tr>
<td>23.45</td>
<td>19.08</td>
<td>4.42</td>
<td></td>
</tr>
<tr>
<td>24.40</td>
<td>20.05</td>
<td>4.50</td>
<td></td>
</tr>
</tbody>
</table>

What are the proper incremental additions of base?

What are the proper incremental additions of base?

What are the proper incremental additions of base?
**BE SURE TO**

LEAVE ELECTRODE IN SOLUTION WHEN DOING pH TITRATION
- Improves reliability and saves time

STIR THE CONTAINER into which you are titrating to insure good mixing.
- Otherwise, you measure pH of only a small, local part of the solution

RINSE THE pH ELECTRODE WITH DISTILLED WATER and DRY IT CAREFULLY each time you immerse it into a NEW liquid.
- Otherwise, pH electrode can still "see" the last solution with which it was in contact

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**Summary of Procedure**

**STEP 1. Preliminary Titration**
- Allows calculation of weight required for 25 ± 3 mL of base

**STEP 2. Calculated weight of acid that would consume 25 ± 3 mL of base.**

**STEP 3. Weigh out an amount of your acid in the above range on the ANALYTICAL BALANCE BY DIFFERENCE!!!**
- No spatulas, no intermediate containers

**STEP 4. Calculate volume of NaOH required to titrate actual sample.**

**STEP 5. Check pH METER with pH = 4.00 BUFFER**
- If pH differs from buffer by more than 0.10 pH units, recalibrate pH METER

**STEP 6. Titrate using the pH METER**
- Stir solution with stirring rod while titrating
- Get several points along the steepest rise of the pH curve
- Add NaOH slowly 2.00 mL before the volume of added NaOH calculated in Step 4
- Follow titration 10 mL past the End Point

**STEP 7. Remove Glass Electrode from solution**
- Rinse Electrode
- Replace it in its regular container
- Record the concentration of NaOH

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**Reminders about Graphing (SUPL-004*)**
- Use rational number of boxes per unit (1, 2, 5, 10, 20, …) for pH and volume (not 3, 4, 30, 40, …)
- Arrange graph so that maximum total area of graph paper is utilized
- Draw a smooth curve through the experimental points
- Label End Point and Half Equivalence Point clearly
- Interpolate values of these points with precision (significant figures) consistent with your plot
- You should be able to read the ordinate and abscissa to at least the nearest 0.1 mL or 0.1 pH unit

* Available on the web at [http://www.ic.sunysb.edu/Class/che133/susb/supl004.pdf](http://www.ic.sunysb.edu/Class/che133/susb/supl004.pdf)

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**While primary purpose of Part 1 (preliminary titration) is to determine appropriate weight of sample to use for the pH titration,**

The regular titration also provides an estimate of Molar Mass (MM). Can use it to verify MM obtained from pH titration.

If MM’s from regular titration and pH titration differ by 10% or more, you have either made a weighing error, or, may not have plotted pH vs the Delivered Volume.
The pKa values in this table should be viewed as approximate. Measured values may differ from the tabulated values by ±0.5 units or more.

Note on Unknown Acids

We will NOT assign as unknowns polyprotic acids with two pKa's that are both less than 7.

Glutaric Acid $\text{H}_2\text{C}_5\text{H}_6\text{O}_4$ 132.1 4.3, 5.2 $\times$
Potassium dihydrogen phosphate $\text{KH}_2\text{PO}_4$ 136.1 7.2, 12.7 $\checkmark$

Astute students will edit the list of possible unknowns in the manual in accordance with the above!

What can cause Errors in this Exercise?

1. SAMPLE WEIGHT (~200 mg)
   Weigh BY DIFFERENCE !!!!!!!!!!!
   Suppose you use a watch glass to weigh and lose 10 mg of sample in transfer
   $-10 / 200 = -5\%$ ERROR

2. TITRATION (~25 mL)
   Miss End Point by ± 0.50 ml (10 drops)
   ± 0.50 / 25 = ± 2% ERROR IN MM
   ± 0.25 / 12.5 = ± 2% ERROR IN HALF TITRATION VOLUME
   ± 1% ERROR IN pKa

SAMPLE DATA SHEET

| Mass of vial + Acid | 14.6705 g |
| Mass of vial - sample | 14.5581 g |
| Mass of Acid Sample (g) | 0.1124 g |
| Mass of Acid Sample (mg) | 112.4 mg |
| Vol of NaOH @ Equiv Pt | 24.5 mL |
| Concentration of NaOH | 0.0533 M |
| mmol of NaOH | 1.31 mmol |
| mmol of Acid | 1.31 mmol |

Molar Mass = 85.8
pKa = 5.0

From the graph, we have determined:

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>FORMULA</th>
<th>MOLAR MASS</th>
<th>pKₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>$\text{HC}_2\text{H}_3\text{O}_2$</td>
<td>60.0</td>
<td>4.8</td>
</tr>
<tr>
<td>Propanoic acid</td>
<td>$\text{HC}_3\text{H}_5\text{O}_2$</td>
<td>74.1</td>
<td>4.9</td>
</tr>
<tr>
<td>Crotonic acid</td>
<td>$\text{HC}_4\text{H}_5\text{O}_2$</td>
<td>86.1</td>
<td>4.7</td>
</tr>
<tr>
<td>dl-Lactic acid</td>
<td>$\text{HC}_2\text{H}_3\text{O}_3$</td>
<td>90.1</td>
<td>3.9</td>
</tr>
<tr>
<td>Chloroacetic acid</td>
<td>$\text{HC}_2\text{ClH}_3\text{O}_2$</td>
<td>94.5</td>
<td>2.9</td>
</tr>
</tbody>
</table>

Assuming it is monoprotic.
You weigh 223.5 mg of your unknown for the phenolphthalein titration.

It requires 31.50 mL of 0.0553 M NaOH to reach the pink end point.

To use 25 ± 3 mL of the same NaOH, you will need:

\[(25 \pm 3) \times \frac{223.5}{31.50} = 179 \pm 21 \text{ mg}\]

You weigh 188.6 mg of your unknown for the pH titration.

Your expected end point is at:

\[\frac{188.6}{7.163} \text{ mg/mL} = 26.32 \text{ mL of 0.0533 M NaOH}\]

[You begin using 2 drop increments of NaOH around 24.5 mL of NET ADDED NaOH (not buret reading)]

The titration curve has produced:

\[\text{Molar Mass} = 131 \text{ g/mol} \pm ?\]

\[\text{pK}_a = 2.2 \pm ?\]

To what acid do these data correspond?

What are the expected errors in these two numbers?

In the mass range 126 - 146, Table I shows:

- Oxalic acid dihydrate 126.1 1.2, 4.2
- Potassium hydrogen oxalate 128.5 4.2
- Glutaric acid 132.1 4.3, 5.2
- d-l Malic Acid 134.1 3.4, 5.0
- Potassium dihydrogen phosphate 136.1 7.2, 12.7
- Potassium bisulfate 136.2 1.9
- Sodium bisulfate hydrate 137.4 1.9
- Sodium dihydrogen phosphate 138.0 7.2, 12.7
- Adipic acid 146.1 4.3, 4.4

Our numbers are 131 ± 7, 2.2 ± 7.

The precision of the Molar Mass determination is certainly not sufficient to distinguish the two most likely alternatives.

What should you do?

Report:

My unknown is either:
- Potassium Bisulfate or Sodium Bisulfate Hydrate

As long as your unknown is one of the alternatives you name, your answer will be viewed as correct.

(However, you still may be penalized for the precision in your determination - e.g. how close were the Molar Masses from the preliminary and pH titrations?)