Strength of Vinegar by Acid-Base Titration
Test Exercise – 100 points

Questions?
How, and with what accuracy and precision can you determine the concentration of a solution of NaOH?
Using that NaOH solution, with what accuracy and precision can you determine the concentration of a solution of acetic acid?

Organization of this Pre-lab Lecture

TITRATION
A reaction conducted by slow addition of a precisely measured volume of a reagent solution of known concentration to a fixed amount of another substance with which the reagent reacts until a SIGNAL indicates that a significant chemical change has occurred.

We call the appearance of the signal the END POINT of the titration.

END POINTS & EQUIVALENCE POINTS
The point at which an observable signal occurs is called END POINT.

Our interest is the point at which a stoichiometric amount of the reagent in the buret has been consumed by the reagent in the beaker.

This is called the EQUIVALENCE POINT.

Stoichiometric: having consumed an equivalent number of moles.

e.g., in the titration of a fixed amount of HCl with NaOH

\[ \text{HCl} + \text{NaOH} = \text{NaCl} + \text{H}_2\text{O} \]

Equivalence point is: mol NaOH added = mol HCl

Concepts:
Strong/Weak Acids Acid Dissociation/K_a End point
Equivalence point Stoichiometry Indicator
Titration curves Logarithmic Measures pH & pK_a
Primary Standard

Techniques:
Titration / Back-titration Standardization
pH Measurement Weighing by Difference
Preparing solutions of Precise Concentration in a Volumetric Flask

Apparatus:
Analytical Balance Buret Pipet
pH Meter Volumetric Flask
END POINTS & EQUIVALENCE POINTS

For a signal to be useful, it must be an accurate indication of completion of reaction, i.e., it must signal the EQUIVALENCE POINT. Signal agents (indicators) are chosen so that, as closely as possible, END POINT = EQUIVALENCE POINT.

STRONG AND WEAK ACIDS

Acids and bases can be characterized by the extent to which they dissociate in solution.

**STRENGTH**
- **FULLY DISSOCIATED**
- **PARTIALLY DISSOCIATED**

Hydrochloric Acid is a **STRENGTH** acid.

\[
\text{HCl (g) + H}_2\text{O (l)} \rightarrow \text{HCl (aq)} \rightarrow \text{H}^+ (aq) + \text{Cl}^- (aq)
\]

Acetic Acid is a **WEAK** acid.

\[
\text{HOAc (l) + H}_2\text{O (l)} \rightarrow \text{HOAc (aq)} \rightarrow \text{H}^+ (aq) + \text{OAc}^- (aq)
\]

DISSOCIATION CONSTANTS / pH / pKₐ

A **QUANTITATIVE** measure of strength or weakness of an acid (or base) is its **DISSOCIATION CONSTANT**, \( K_a \). For the reaction

\[
\text{HA (aq)} \rightarrow \text{H}^+ (aq) + \text{A}^- (aq)
\]

The acid dissociation constant, \( K_a \), is defined as

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

Both \([\text{H}^+]\) and \( K_a \) vary over many orders of magnitude. So, it is convenient to represent them by their logarithms instead.

\[
pH = -\log_{10}[\text{H}^+] \quad [\text{H}^+] = 10^{-pH}
\]

\[
pK_a = -\log_{10} K_a \quad [\text{H}^+] = 10^{-pK_a}
\]

STANDARDIZATION

The analytical determination of the purity or concentration of a substance through its reaction with a substance of certified composition and purity (Primary Standard).

* NIST, US Pharmacopeia, American Chemical Society, etc.

Chemical Grades: USP, NF, Reagent, Primary Standard, Secondary Standard

This **STANDARDIZATION** involves reaction of the base, aqueous NaOH, with a **PRIMARY STANDARD**, the weak acid:

potassium hydrogen phthalate (KHP)

THE STOICHIOMETRY OF OUR REACTIONS

KHP is a monoprotic weak acid. One available proton.

\[
\text{H}_2\text{C}_8\text{H}_4\text{O}_4^- + \text{OH}^- \rightarrow \text{C}_8\text{H}_4\text{O}_4^- + \text{H}_2\text{O}
\]

The stoichiometry of the reaction is: \( pK_a = 5.4 \)

\[
1 \text{ mol KHP} \leftrightarrow 1 \text{ mol NaOH}
\]

Acetic acid, \( \text{CH}_3\text{COOH} \), is also a monoprotic weak acid.

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

\[
1 \text{ mol CH}_3\text{COOH} \leftrightarrow 1 \text{ mol NaOH}
\]

It's \( pK_a = 4.7 \)

ACID/BASE INDICATORS

An Acid/Base Indicator is an organic dye whose color is different in solutions of different pH.

Indicators are often weak acids*, e.g.,

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

* We use amounts of indicator sufficiently small so as not to interfere with the acid we are titrating.

(We use PHENOLPTHALEIN which is COLORLESS in acidic solutions and PINK in basic solutions.)

The color change to pink occurs when pH increases from \(< 9\) to \(> 9\).
How does the pH vary when NaOH is added to Acetic Acid

Graphs which show the dependence of pH on the volume of base added to an acid are called **Titration Curves**.

Titration curve for Acetic Acid with NaOH looks like this

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**PROCEDURE 1 - PREPARE KHP**

It does not matter in which order you
A.) Prepare KHP & Standardize NaOH
B.) Titrate Unknown
C.) Determine pH of unknown

**A. STANDARDIZATION**

Prepare solution of known concentration of primary standard, KHP
- Weigh sample **BY DIFFERENCE**
- Dissolve fully in **ERLENMEYER**
- Bring to total volume in **VOLUMETRIC FLASK**

**Follow manual procedure**

**CALCULATIONS - KHP SOLUTION**

| Weight of vial + KHP          | 15.4371 g |
| Weight of vial + remaining KHP | 12.3495 g |
| Weight of KHP transferred     | 3.0876 g  |
| Volume of KHP Solution        | 0.2500 L  |

Molarity of KHP Solution:
$$\frac{3.0876 \text{ g}}{204.22 \text{ g/mol}} \times \frac{1}{0.2500 \text{ L}} = 0.06047 \text{ M}$$

**PROCEDURE 2 - NaOH STANDARDIZATION**

Determine concentration of stock NaOH Solution (Nominally 0.1 M)

Titrate measured volumes of standard KHP solution (known concentration) with measured volumes of NaOH Solution (unknown concentration)

(Delivered from buret 1)

(Received from buret 2)
Having determined concentration of KHP solution, calculate volume of ~ 0.1 M NaOH needed to react with 40 mL of KHP.

40 mL of our KHP solution (0.06047 M) contains:

40 mL \times 0.06047 \text{ mmol/mL} = 2.4 \text{ mmol of KHP}

That will require \(2.4 \text{ mmol of NaOH}\)

What volume of 0.1 M NaOH will contain 2.4 mmol of NaOH?

\[
2.4 \text{ mmol} = 0.1 \text{ (mmol/mL)} \times V \text{ (mL)}
\]

\[
V = \frac{2.4}{0.1} = \sim 24 \text{ mL}
\]

We now know when to begin to add the NaOH from the buret slowly!

**Calculations - NaOH Standardization**

**Molarity of KHP Solution:** 0.06047 M

<table>
<thead>
<tr>
<th>KHP buret reading, final</th>
<th>37.44 mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>KHP buret reading, initial</td>
<td>3.68 mL</td>
</tr>
<tr>
<td>Volume of KHP titrated</td>
<td>33.76 mL</td>
</tr>
<tr>
<td>NaOH buret reading, final</td>
<td>28.73 mL</td>
</tr>
<tr>
<td>NaOH buret reading, initial</td>
<td>4.52 mL</td>
</tr>
<tr>
<td>Volume of NaOH used</td>
<td>24.21 mL</td>
</tr>
<tr>
<td>mmol of KHP titrated</td>
<td>2.042 mmol</td>
</tr>
<tr>
<td>mmol of NaOH used</td>
<td>2.042 mmol</td>
</tr>
</tbody>
</table>

\[
33.76 \text{ mL} \times 0.06047 \text{ M} = \frac{2.042 \text{ mmol}}{24.21 \text{ mL}} \]

**Stoichiometry is 1 to 1**

**Molarity of NaOH**

\[
\frac{2.042 \text{ mmol}}{24.21 \text{ mL}} = 0.08435 \text{ M}
\]

Suppose 2nd and 3rd titrations produce 0.08592 M and 0.08539 M for the NaOH concentration.

Are our three values for NaOH concentration in reasonable agreement?

Average = \(\frac{(0.08435 + 0.08592 + 0.08539)}{3} = 0.08522 \text{ M}\)

Avg Dev = \(\frac{(0.00087 + 0.00070 + 0.00017)}{3} = 0.00058 \text{ M}\)

Pct Dev = \(100 \times \frac{0.00058}{0.08522} = 0.68\%\)

**Backtitration**

In the **Standardization**, both reagents are delivered by a buret. Can "Backtitrate".

I.e., if end point is overshot, can recover by adding more KHP and continuing titration, e.g.,

1. Add measured volume of KHP (~40 mL)*
2. Titrate to Phenolphthalein Endpoint
3. If you overshoot endpoint, add more KHP
4. Titrate to Phenolphthalein Endpoint again

* Instead of ~35 mL

Do at most 3 titrations for the standardization

**Procedure 3 - Unknown**

Unknowns are solutions of acetic acid in water.

We titrate aliquots* of (undiluted) unknown.

In this exercise, an aliquot is a 5 mL pipet-ful (5.00 ± 0.01) of solution.

- Dilute unknown with distilled water (~ 40 mL)
- Add Phenolphthalein as indicator
- Titrate unknown to phenolphthalein end point.

**Remember:** you cannot backtitrate in this case

Since aliquots are identical, you can track the precision of titrations by calculating the percent error in the volumes of NaOH used.

* Aliquots are fixed, repetitive fractions of a solution
CALCULATIONS - UNKNOWN

Volume of Unknown  5.00 mL
Concentration of NaOH solution  0.08522 M

NaOH buret, final  22.47 mL
NaOH buret, initial  3.15 mL
Volume NaOH used  19.32 mL

mmol of NaOH used  19.32 * 0.08522 = 1.646 mmol
mmol of Acetic Acid titrated  = 1.646 mmol
Acetic Acid Concentration  1.646 / 5.00 = 0.329 M

Stoichiometry is 1 to 1

From Standardization

PROCEDURE 4 - MEASURE pH

To determine the K_a (and pK_a) of your unknown, you need to determine the pH of the unknown.

2. Measure pH of undiluted unknown to determine its H^+ concentration using a pH METER

Since HOAc (aq) ionizes to give H^+ and OAc^-, the pH gives us the concentration of the dissociated HOAc in our vinegar, [H^+] = [OAc^-]

Total Acid

I.e., [H^+] = 10^{-2.7} = 2.0 \times 10^{-3}

K_a = \frac{[H^+] \times [OAc^-]}{[HOAc]} = \frac{(2.0 \times 10^{-3})^2}{0.124} = 3.2 \times 10^{-5}

pK_a = -\log_{10}(3.2 \times 10^{-5}) = 4.5

Read & Record Burets

24.64 mL

Begin each titration with buret reading between 0.00 and 5.00 mL

Read & Record Weights

4.6427 g
STANDARDIZATION – Precision

1. **WEIGH** ~3 g of solid KHP using the analytical balance (±0.0004 g)
   
   Precision: $100 \times 0.0004 / 3.0000 = 0.01 \%$

2. **PREPARE A SOLUTION** of KHP using 250 mL volumetric flask (±0.05 mL)
   
   Precision: $100 \times 0.05 / 250.00 = 0.02 \%$

3. **TITRATE** measured volumes of KHP and NaOH using burets (±0.05 mL)
   
   Precision: KHP $100 \times 0.05 / 30.00 = 0.2 \%$
   
   NaOH $100 \times 0.05 / 30.00 = 0.2 \%$

   Concentration of NaOH determined with Precision of approximately $0.01 + 0.02 + 0.2 + 0.2 = 0.43 \%$

ANALYSIS OF ERRORS

TITRATION OF UNKNOWN – Precision

1. **TRANSFER** aliquot of unknown using a 5 mL transfer pipet (Intrinsic error: ±0.01 mL)
   
   Precision: $100 \times 0.01 / 5.00 = 0.2 \%$

2. **TITRATE** aliquot using standardized NaOH, again using a buret (Intrinsic error: ±0.05 mL)
   
   Precision: (Buret)$100 \times 0.05 / 30.00 = 0.2 \%$

3. **STANDARDIZED NaOH** concentration
   
   Precision: $= 0.4 \%$

OVERALL PRECISION of determination of concentration of unknown = $0.2 + 0.2 + 0.4 = 0.8 \%$

PITFALLS TO AVOID

1. Incomplete transfer of solid KHP into flask (caused by weighing using a watch glass or paper)
   
   **Weigh by difference!**

2. Failure to dissolve KHP completely
   
   **Make sure no KHP particles remain undissolved**

3. Incomplete transfer of KHP solution from Erlenmeyer to volumetric flask
   
   **Transfer completely and rinse with distilled water from wash bottle**

4. Failing to bring KHP solution to correct volume
   
   **Use dropper for last 0.5 mL!**

HOW SERIOUS IS OVERTITRATING?

Suppose you over-titrator by 5 drops

I.e., you go past the end point by 5 drops (0.25 mL).

How large an error in accuracy results?

- **Unknowns** range in concentration from 0.5 M to 1.0 M.
- 5 mL of the unknown contains between 2.5 and 5.0 mmol of acetic acid.
- That will require between 25 and 50 mL of ~0.1 M NaOH

The error represented by 0.25 mL will range between $100 \times 0.25 / 25 = 1 \%$ to $100 \times 0.25 / 50 = 0.5 \%$

Errors in identifying the end point are not a major contribution to errors in the accuracy of the concentration of the vinegar unknown.