Strength of Vinegar by Acid-Base Titration

Test Exercise – 100 points

1

? QUESTIONS ?

How are acid/base titrations conducted?

What is **standardization**?

How do you standardize a solution of a base?

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?

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Concepts:

Strong/Weak Acids	Acid Dissociation/K_a	End point
Equivalence point	Stoichimetry	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

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Organization of this Pre-lab Lecture

Titration		Procedure 2 – NaOH Standardization
End Points & Equivalence Points		Backtitration
Strong and Weak Acids		Calculations 2 – NaOH Standardization
Dissociation Constants / pH / pK_a		What does the End Point Look Like?
Standardization		Procedure 3 - Unknown
Stoichiometry of our Reactions		Calculations 3 - Unknown
Acid/Base Indicators		Procedure 4 – Measure pH / Calculate K_a / pK_a
How pH varies when NaOH is added to Acetic Acid		Analysis of Errors - Standardization
Procedure 1 – Preparation of KHP Solution		Analysis of Errors - Unknown
Calculations 1 – KHP Solution		Pitfalls to Avoid

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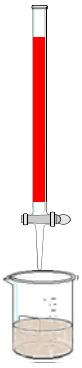
TITRATION



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.

The *SIGNAL* is often a **COLOR CHANGE**, but may be an observable change in another property.

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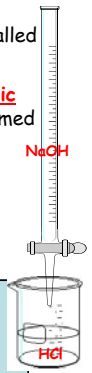
END POINTS & EQUIVALENCE POINTS

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

$HCl + NaOH = NaCl + H_2O$

Equivalence point is: mol NaOH added = mol HCl

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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***

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STRONG AND WEAK ACIDS

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

STRONG ⇔ **Fully *Dissociated***
WEAK ⇔ **Partially *Dissociated***

Hydrochloric Acid is a **STRONG** acid

$HCl\ (g) + H_2O\ (l) \rightarrow HCl\ (aq) \rightarrow H^+\ (aq) + Cl^-\ (aq)$

Acetic Acid is a **WEAK** acid

$HOAc\ (l) + H_2O\ (l) \rightarrow HOAc\ (aq) \rightarrow H^+\ (aq) + OAc^-\ (aq)$

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DISSOCIATION CONSTANTS / pH / pK_a

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

$$HA\ (aq) \rightarrow H^+\ (aq) + A^-\ (aq)$$

The acid dissociation constant, K_a, is defined as

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

Both $[H^+]$ and K_a vary over many orders of magnitude.

So, it is convenient to represent them by their logarithms instead.

$pH = -\log_{10}[H^+]$ $\qquad [H^+] = 10^{-pH}$

$pK_a = -\log_{10} K_a$ $\qquad [H^+] = 10^{-pK_a}$

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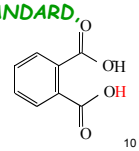
STANDARDIZATION

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)



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THE STOICHIOMETRY OF OUR REACTIONS

KHP is a monoprotic weak acid. One available proton.

$$HC_8H_4O_4^- + OH^- \rightarrow C_8H_4O_4^{=} + H_2O$$

The stoichiometry of the reaction is: **pK_a is 5.4**

1 mol KHP ⇔ 1 mol NaOH

Acetic acid, CH_3COOH, is also a monoprotic weak acid.

$$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$$

1 mol CH_3COOH ⇔ 1 mol NaOH

It's pK_a is 4.7

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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.,

$$HIn \rightleftarrows In^- + H^+$$
Green Yellow

(The equilibrium lies to the left in acidic solutions.)

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.

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

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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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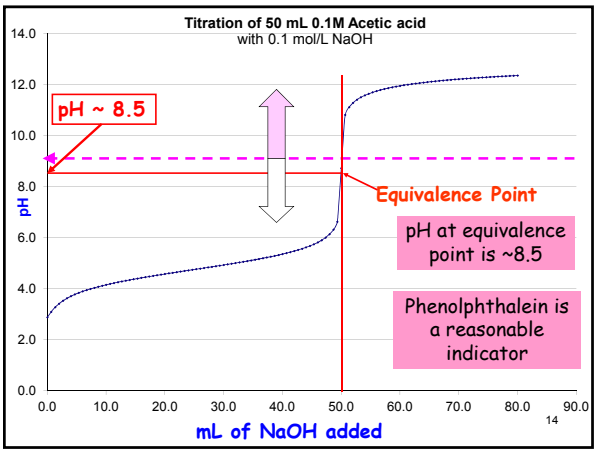

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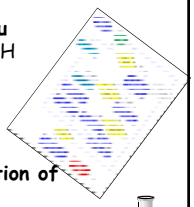
PROCEDURE 1 – PREPARE KHP

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**

Must transfer ALL the solution

** Follow manual procedure

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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

Follow the procedure described in the lab manual for the use of the volumetric flask!

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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:	

(3.0876 g / 204.22 g/mol) / (0.2500 L) = 0.06047 M

Weight of KHP | Molar Mass | Volume of Volumetric Flask | 4 Sig Figs

0.015119 Mols of KHP

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PROCEDURE 2 – NaOH STANDARDIZATION

Determine *concentration* of stock NaOH Solution
(*Nominally* 0.1 M)

Titrate

measured volumes of standard KHP solution (*known* concentration)

with

(Delivered from buret 1)

measured volumes of NaOH Solution (*unknown* concentration)

(Delivered from buret 2)

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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 X 0.06047 mmol / mL = 2.4 mmol of KHP

That will require 2.4 mmol of NaOH

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

2.4 mmol = 0.1 (mmol/mL) X V (mL)

V = 2.4 / 0.1 = ~ 24 mL

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

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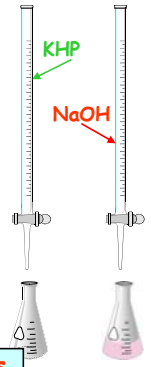
BACKTITRATION

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



*** Instead of ~35 mL**

label the burets.

Do at most 3 titrations for the standardization

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CALCULATIONS – NaOH STANDARDIZATION

Molarity of KHP Solution: 0.06047 M

KHP buret reading, final	37.44 mL
KHP buret reading, initial	3.68 mL
Volume of KHP titrated	33.76 mL
NaOH buret reading, final	28.73 mL
NaOH buret reading, initial	4.52 mL
Volume of NaOH used	24.21 mL

From Part 1

mmol of KHP titrated

33.76 mL X 0.06047 M = 2.042 mmol

mmol of NaOH used 2.042 mmol

Stoichiometry is 1 to 1

Molarity of NaOH

2.042 mmol / 24.21mL = **0.08435 M**

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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 =
(0.08435 + 0.08592 + 0.08539) / 3 = 0.08522 M

Avg Dev =
(0.00087 + 0.00070 + 0.00017) / 3 = 0.00058 M

Pct Dev =
100 X 0.00058 / 0.08522 = 0.68%

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WHAT DOES THE END POINT LOOK LIKE?

Before end point

KHP & Unknown solutions are colorless.

At end point

Just past end point

Way past end point

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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*

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CALCULATIONS - UNKNOWN (36)

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

Stoichiometry is 1 to 1

mmol of NaOH used
19.32 * 0.08522 = 1.646 mmol

mmol of Acetic Acid titrated = 1.646 mmol

3 Sig Figs

Acetic Acid Concentration
1.646 / 5.00 = 0.329 M

From Standardization

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CALCULATIONS - UNKNOWN (36)

Volume of Unknown	5.00 mL	5.00	5.00
Concentration of NaOH solution	0.08522 M		
NaOH buret, final	22.47 mL	21.16	23.72
NaOH buret, initial	3.15 mL	2.37	4.22
Volume NaOH used	19.32 mL	18.79	19.50
mmol of NaOH used			
19.50 * 0.08522 =	1.646 mmol	1.601	1.662
mmol of Acetic Acid titrated =	1.646 mmol	1.601	1.662
Acetic Acid Concentration			
1.662 / 5.00 =	0.329 M	0.320	0.332

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CALCULATIONS - UNKNOWN

Avg Conc of Acetic Acid =

(0.329 M + 0.320 M + 0.332 M) / 3 = 0.327 M

Avg Deviation =

(0.002 + 0.007 + 0.005) / 3 = 0.005 M

Pct Deviation =

100 X 0.005 / 0.327 = 1.5%

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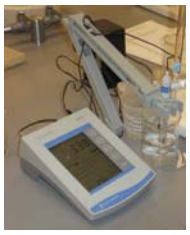
PROCEDURE 4 – MEASURE pH

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

Electronic device designed to measure hydrogen ion concentration in aqueous solutions



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

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CALCULATE pH / pK_a

The titration gives us the TOTAL CONCENTRATION of HOAc in the unknown.

Suppose result of our titration is [HOAc] = 0.124 M and, the measured pH = 2.7

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

From pH

$[OAc^-] = [H^+]$

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

Total Acid

Should subtract 2.0×10^{-3} But to 2 sig figs, can ignore

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

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Read & Record Burets

24.64 mL

Read & Record Weights

4.6427 g

Begin each titration with buret reading between 0.00 and 5.00 mL

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ANALYSIS OF ERRORS

STANDARDIZATION – Precision

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

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

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

Concentration of NaOH determined with ***PRECISION*** of approximately *0.01 + 0.02 + 0.2 + 0.2* = **0.43 %**

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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 X 0.01 / 5.00 = *0.2 %*

2. ***TITRATE*** **aliquot using standardized NaOH, again using a buret** (Intrinsic error: ±0.05 mL)
   Precision: (Buret)100 x 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 %*

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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 !

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5. Incomplete mixing of KHP solution in volumetric flask
   Mix thoroughly both before and after bringing to final volume

6. Improper use of the pipet
   Make sure you use the pipet as instructed

7. Contamination of unknown by allowing contact with syringe while pipeting
   Discard any sample for which this happens

8. Over-titrating unknown
   Stop at earliest detectable pink color which persists for ≥ 30 seconds

GRADE ON THIS EXERCISE WILL DEPEND ON both Accuracy and Precision

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How Serious is Overtitrating?

Suppose you over-titrate 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 X 0.25 / 25 = 1 % to 100 X 0.25 / 50 = 0.5 %

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

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