ASPIRIN PURITY BY pH TITRATION

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Purpose:

To study pH variation during an acid/base titration and use this to determine the purity of your synthesized aspirin

Concepts:

- pH
- Nernst Equation
- Calibration and use of the pH meter
- Molar Mass
- Effective Molar Mass
- Titration
- Stoichiometry
- Equivalence Point
- Titration of a mixture

Techniques:

- Weighing by Difference
- Using a pH Meter
- Graphing

Apparatus:

- pH Meter
- Buret

NERNST EQUATION describes dependence of electrode voltages on concentration and temperature

For normal pH electrodes,

$$E = E^0 - \frac{2.303\,RT}{N_A e}\log_{10}\frac{1}{[H^+]}$$

where: E = **VOLTAGE DIFFERENCE** between reference and indicator electrodes

E^0 = **CONSTANT** depending only on **TYPES** of **ELECTRODES**

T is ***Absolute*** Temperature

R is gas constant

N_A is Avogadro's number

e is absolute value of electron charge

CALIBRATION (STANDARDIZATION)

Like all measuring devices, must calibrate pH METER before using it.

Immerse pH electrode into one or more (buffer) solutions of accurately known pH.

Set ***Calibration Control*** on meter so reading agrees with pH of standard buffer

Remember to rinse electrode after standardization

SAMPLE TABLE FOR pH TITRATION

Buret Rdg	Cum Vol	pH	Incr		Buret Rdg	Cum Vol	pH	Incr
4.35	**0.00**	2.94			27.10	22.75	6.35	
6.46	2.11	3.15			27.20	22.85	7.00	
8.72	4.37	3.31			27.27	22.92	8.93	**1 drop**
….	….	….			27.32	22.97	9.40	
24.81	20.46	4.12			27.39	23.04	10.49	
25.72	21.37	4.70			27.46	23.11	11.57	
26.39	22.04	5.20			….	….	….	….

Start using 1 drop increments about 2 mL before calculated end point.

Phenolphthalein titration:

0.2433 g requires **21.67** mL of NaOH

How much should I weigh to use **25** mL?

0.2433 g / **21.67** mL = X / (**25** ±3)

I actually weigh out **0.2742** g

pH Titration: **0.2742** g will require:

21.67 X **0.2742** / **0.2433** = 24.42 mL of NaOH

WHAT WE ARE LOOKING FOR

Your synthesized **aspirin (ASA)** most likely contains some unreacted **salicylic acid (SA)** –

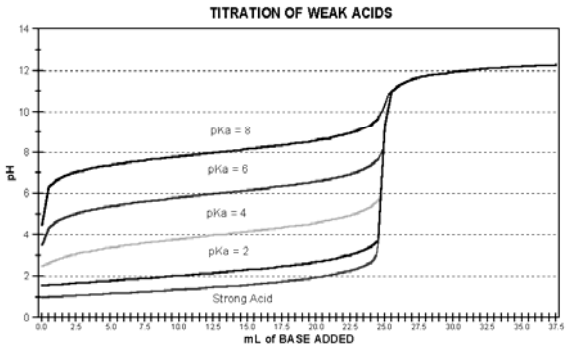
(*Did the **$FeCl_3$** test show any **violet** color?*)

If the sample is **dry**, then it can contain only:

	Molar Mass	pK_a
Aspirin	180.15	**3.50**
Salicylic Acid	138.12	2.99

Titration of these acids *individually* with NaOH should allow them to be easily distinguished.

From Last Semester HOW DOES THE STRENGTH (pK_a) OF AN ACID AFFECT ITS TITRATION CURVE?



What about a mixture of the two?

End point in acid-base titration is characterized by rapid increase in pH

This will only occur after **both** acids are consumed, the stronger acid being consumed first.

Total amount of NaOH is the amount necessary to react with both acids.

Suppose our sample weighs w_{SA+ASA} and contains n_{SA} moles of SA and n_{ASA} moles of ASA

From the **known** number of moles of NaOH used in the titration, n_{NaOH}, we can determine

$\Rightarrow \quad n_{NaOH} = V_{NaOH} \times M_{NaOH} = n_{SA} + n_{ASA}$

the sum of the moles of acid in the original sample.

But the (**known**) weight of the original sample was:

$$w_{SA+ASA} = n_{SA} \times 138.1 + n_{ASA} \times 180.1$$

w_{SA} w_{ASA}

We have two (linear) equations in two unknowns

These can be solved simply. The EMM formula

$$\%ASA = \frac{100\,(EMM - 138.1)}{180.1 - 138.1} =$$

is one way of representing the solution using the quantity, **EMM**

$$= \frac{w_{SA+ASA}}{n_{SA} + n_{ASA}} = \frac{w_{SA+ASA}}{n_{NaOH}}$$

**** Equations involving EMM apply ONLY when EMM is between 138.1 and 180.1***

In normal (indicator only) titrations, can determine (only) number of available moles of acid in a sample – i.e., EMM

e.g., if **25.00 mL** OF **0.100 M** NaOH is required to react with **425 mg** of a sample, the number of moles of acid in the sample is

25.00 mL X 0.100 mmol / mL = 2.50 mmol

and sample behaves like an acid of EFFECTIVE MOLAR MASS (EMM)

EMM = **425 mg / 2.50 mmol = 170 mg / mmol**

Consistent with sample being largely ASA (MM = 180) with some SA impurity (MM = 138)

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 obtain 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

Make abscissa of graph *CUMULATIVE VOLUME* of added NaOH
Remember to subtract the initial buret reading

Record NaOH STOCK SOLUTION *CONCENTRATION*
You need it to calculate EMM's

SAVE REMAINDER OF SYNTHESIZED ASPIRIN FOR FUTURE EXERCISE

pH METERS MAY NEED OCCASIONAL RECALIBRATION – between users

SUMMARY OF PROCEDURE

1.) Working in **ASSIGNED PAIRS**, perform ***NORMAL TITRATIONS*** on samples of:
AUTHENTIC SALICYLIC ACID (SA)
AUTHENTIC ACETYLSALICYLIC ACID (ASA)
You will be given vials of pure SA and ASA

2.) Compute EMM's for both of the above

3.) Working ALONE from here on, titrate YOUR SAMPLE OF ASA with standardized NaOH, using phenolphthalein as an indicator

Agreement of your EMM's with expected values for SA and ASA is a measure of your titration technique.

4.) From this, **determine EMM and the AMOUNT of YOUR SAMPLE OF ASA** needed to consume 25 mL of the same NaOH solution

5.) Weigh out your ASA sample and calculate how much NaOH it will require.

6.) Set up pH meter, check calibration

7.) TITRATE YOUR SAMPLE OF ASA with standardized NaOH, using ***pH METER***

Weigh all samples on **ANALYTICAL BALANCE** by **DIFFERENCE**

DO NOT TRANSFER ANY COMPOUND TO BALANCE PAN!

Even though you share pH meters,

Don't do simultaneous pH titrations

Datasheet and graph for this exercise may be turned in *at the beginning of the next lab*

Do NOT record pH titration data on data sheet – only in lab notebook

Calculations

Regular titration of synthesized ASA

Weight of sample		**205.6 mg**
Volume of NaOH		**22.61 mL**
Conc of NaOH		**0.05246**
EMM =	mmol NaOH	

205.6 / (22.61 * 0.05246) = 177.4 mg

What weight is required for 25 ± 3 mL of NaOH?

(25 ± 3) * **205.6/22.61** = (25 ± 3)*9.093 = **227±27mg**

Suppose you ***actually*** weigh **211.5 mg** of sample.
Where will the end point be?
22.61 * 211.5 / 205.6 = 23.26 mL NaOH

Should begin 1 drop increments at ~21 mL

Calculations - Continued

After doing the pH titration on your sample, you will have three quantities that let you determine the purity of your synthesized ASA:

Your **EMM_{sa}** for SA and
Your **EMM_{asa}** for ASA (from the regular titrations),
Your **EMM_s** for your synthesized aspirin.

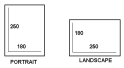
You should calculate your purity using these numbers, i.e.,

YOUR VALUES

$$\%ASA = \frac{100\,(EMM_s - EMM_{sa})}{EMM_{asa} - EMM_{sa}}$$

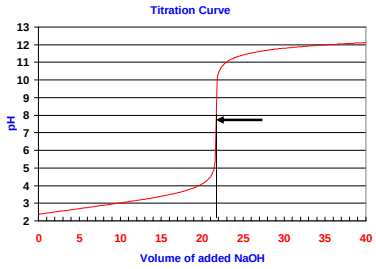
REMINDERS ABOUT GRAPHING (SUPL-004)

- Use rational number of boxes per unit (1, 2, 5, 10, 20, ……) for pH and volume
- Arrange graph so that maximum total area of graph paper is utilized
- Draw a smooth curve through the experimental points
- Label equivalence (end) point and half-titration 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*



You must plot the pH *vs* volume of NaOH added BY HAND – not on a computer

pH axis does not need to start at 0



NEXT WEEK

Next Week's Exercise uses same pH TITRATION TECHNIQUE to IDENTIFY AN

UNKNOWN ACID

TEST EXERCISE

READ SUSB-014
DO PRELAB