IDENTIFICATION OF AN UNKNOWN WEAK ACID by pH Titration

TEST EXERCISE (105 points)

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Purpose:

To determine the molar mass *and* pK_a and thereby determine the identity of an unknown acid by pH titration –

Concepts:

pH, pK_a Nernst Equation
Calibration and use of the pH meter
Effective Molar Mass Titration Curve
Stoichiometry Equivalence Point

Techniques:

Weighing by Difference Using a pH Meter
Graphing

Apparatus:

pH Meter Buret Analytical Balance

As usual, we seek to use about 25 **(25 ± 3) mL of NaOH** to reach equivalence point

WHY?

Optimizes buret precision and produces an easily interpretable graph

BUT

Molar mass of the acid is unknown

STEP 1: DETERMINE the relative amount of base that your acid requires

Everyone uses **~ 200 mg** of acid – weighed out ***ACCURATELY*** into a 150 mL beaker.

Titrate to ***phenolphthalein*** end-point - **No pH METER**

e.g. IF **225.1 mg** of *your acid* react with **18.46 mL** of the NaOH,

Your Acid requires 225.1 mg / 18.46 mL
= 12.19 mg / mL NaOH

STEP 2. Using that number, calculate the weight of *your acid* that *would* consume **25 ± 3 mL** of NaOH

e.g. WEIGHT = **(25 ± 3 mL) x 12.19 mg / mL**
= 305 ± 36 mg OF ACID

STEP 3. Weigh out an amount of your acid in the above range on the **ANALYTICAL BALANCE**

BY DIFFERENCE

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

Suppose you weigh out 0.3127 g = **312.7 mg**

That will require:

312.7~~mg~~/ 12.19 ~~mg~~/mL = **25.65 mL** of NaOH

STEP 5. Check the pH METER with the pH = 4.00 BUFFER.

If pH differs from 4.00 by more than 0.10 pH units, ask TA to ***recalibrate pH METER***

STEP 6. Titrate using the pH METER
Be sure to

- **Stir solution** while titrating
- Get several points along the **steepest rise of the pH curve**
- Add NaOH slowly *well before* the **25.65 mL** of ***added* NaOH*** calculated in Step 4
- Follow titration **WELL PAST Equivalence Point** – at least 10 mL –
  i.e to **~36 mL *added* NaOH** in this case

Record the concentration of NaOH

Remember that the 25.65 mL is the *net added volume*, not the *buret reading*

OPTIONAL: Weigh a second sample of the computed amount of your acid and repeat steps 3 – 6.

Do this only after everyone has finished one pH titration.

May wish to repeat normal titration

You obviously must work alone, but pH meters will be shared by as many as three students

Titration curve permits the determination of ***two characteristics*** of the unknown acid

1) **END POINT** determines the **EFFECTIVE MOLAR MASS (EMM)**

2) **pH at HALF EQUIVALENCE POINT** determines **pK_a**

YOU MUST *NOT* SHARE pH METERS DURING A TITRATION

THE SECOND USER MUST WAIT UNTIL THE FIRST USER HAS FINISHED THE pH TITRATION

The Half Titration Point

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

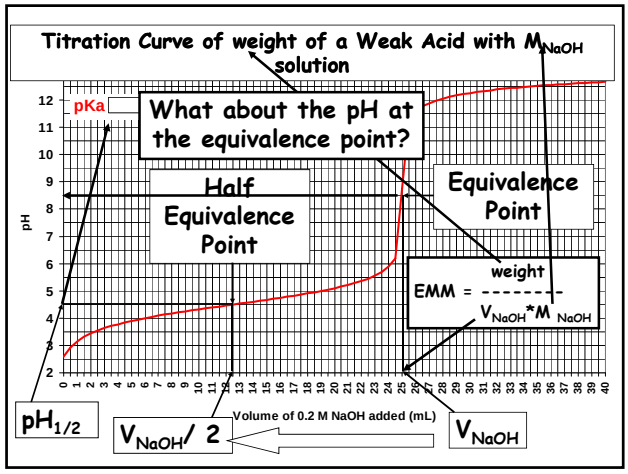
At the

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

In the form:

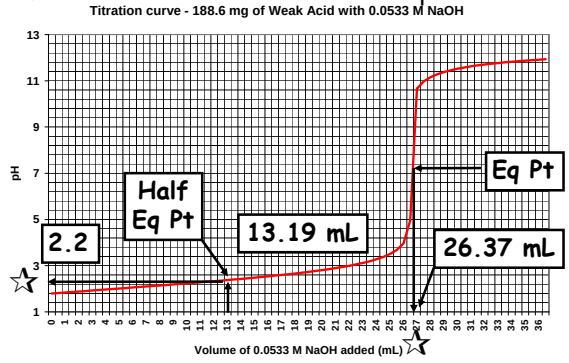
$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

This is the famous *Henderson-Hasselbalch equation.*



EMM (from end point):

E.g., If **188.6 mg** of your unknown requires **26.37 mL** of **0.0533 M NaOH** to reach the end point:



EMM (from end point):

E.g., If **188.6 mg** of your unknown requires **26.37 mL** of **0.0533 M NaOH** to reach the end point:

26.37 mL X **0.0533 mmol/mL** = **1.41 mmol** of NaOH were used, and

EMM = 188.6 mg / 1.41 mmol = 134 mg/mmol

pK_a: from pH (at half equiv pt) ≈ pK_a

In this example, half equivalence point was at:

26.37 mL / 2 = 13.19 mL

pH *at that volume of added NaOH* was **2.2**, pK_a of acid is:

pK_a = 2.2

The tiration curve has produced:

MOLAR MASS = 134 g / mol

&

pK_a = 2.2

To what acid do these data correspond?

What are the errors in these two numbers and what contributes to the errors?

TABLE I: WEAK ACIDS

Glutaric acid	$H_2C_5H_6O_4$	132.1	4.3
dl-Malic acid	$HC_4H_4O_5$	134.1	3.4, 5.0
Potassium dihydrogen phosphate	KH_2PO_4	136.1	7.2, 12.7
Potassium bisulfate	$KHSO_4$	136.2	1.9 ⇦
Sodium bisulfate hydrate	$NaHSO_4.H_2O$	137.4	1.9 ⇦
Sodium dihydrogen phosphate	$NaH_2PO_4.H_2O$	138.0	7.2, 12.7
Our numbers are		**134**	**2.2**

WHAT CAN CAUSE ERRORS IN THIS EXERCISE?

1. SAMPLE WEIGHT (~200 mg)

Weigh **BY DIFFERENCE !!!!!!!!!!**

Suppose you weigh on watch glass 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 EMM

± 0.25 / 12.5 = ± 2% ERROR IN HALF TITRATION VOLUME

&

± 1% ERROR IN pKa

While primary purpose of part 1 (titer determination) is to determine appropriate weight of sample to use for the pH titration,

first titration *also* provides a good estimate of acid EMM. Can use it to verify EMM obtained from pH titration.

If EMM's from regular titration and pH titration differ by 10% or more, it is likely that you have not plotted pH *vs* the appropriate values for the delivered volume.

YOU ARE URGED TO USE THE SAME BALANCE FOR ALL MASS MEASUREMENTS

The Half Equivalence Point

How good is our approximation that

pH at half-equivalence point = pK_a?

For the concentrations used in this exercise and the pK_a's of the unknown acids, the error in the approximation

pH = pK_a at $\frac{1}{2}$ of the volume of base delivered at the equivalence point

is less than 10%

For pK_a's > 4, it is less than 1%

A *web page* deals extensively with this approximation

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 of Acid	**85.83 mg/mmol**
Vol NaOH @ Half Equiv	**12.3 mL**
pH @ Half Equiv	**5.0**
pK_a of Acid	**5.0**

FROM CONTAINER

FROM GRAPH

24.5 X 0.0533 = **1.31**

112.4 / 1.31 = 85.8

The Data are Consistent with Crotonic Acid

(MM = **86.1**; pKa = **4.70**) **[TABLE]**

NEXT EXERCISE

IDENTIFICATION OF PLASTICS

READ **SUSB-013**
And

DO PRE-LAB from **SUSB-013**