Determination of the pK_a of an Acid

To use the analytical technique of **titration** to determine the **pK_a** of **acetic acid**.

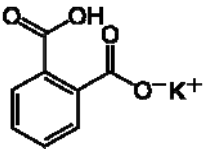
Acids are compounds that contain ionizable hydrogen atoms within the molecule. Strong acids ionize totally, weak acids only slightly. The value of **K_a**, the equilibrium constant for the dissociation (ionization) of the acid, is an indication of the strength of the acid. We can also use the **pK_a**, the **negative log** of the **K_a** as an indication of acid strength.

An acid may contain one or more "ionizable" hydrogen atoms in the molecule. The **equivalent mass** of an acid is the mass that provides one mole of hydrogen ions **H^+**. It can be calculated from the **molar mass divided by the number of ionizable hydrogen atoms** in a molecule. For example, hydrochloric acid, **HCl** contains one ionizable H atom and has a molar mass of 36.46g/mol. Thus its **equivalent mass is also 36.46g/mol**. Sulfuric acid **H_2SO_4** has 2 ionizable H atoms and a molar mass of 98.08g/mol. Thus its **equivalent mass is 49.04g.mol**. So **36.46g HCl** or **49.04g H_2SO_4** would provide one mole of H^+ ions during titration.

Titration involves the addition (from a buret) of a **measured volume of a solution** of known concentration (the titrant) to a solution containing the substance being analyzed (the analyte). The point in the titration where **enough titrant has been added to react exactly with all the analyte** is called **the equivalence point.** This point is marked by the **color change** of an indicator at **the endpoint, which exactly matches the equivalence point**. The equivalent mass may be determined by titrating with a standard solution of NaOH, since one mole of NaOH will react with (neutralize) one mole of hydrogen ions at the equivalence point.

For this acid-base titration, the concentration of the NaOH solution must be accurately known. Thus to **"standardize" the NaOH solution**, that is to find its **exact molarity**, the NaOH is titrated against a known mass of a solid acid, **potassium acid phthalate, KHP**.

KHP has one ionizable hydrogen atom with formula **$KHC_8H_4O_4$**:



Three samples of dried KHP will be weighed, dissolved in water and titrated with NaOH solution using the indicator phenolphthalein. From the three titrations, the average molarity of the NaOH will be calculated by utilizing the formulas: At equivalent point: **$Moles_{acidKHP} = Moles_{baseNaOH}$** and **$Molarity_{acid}$ X $Volume_{acid}$ = $Molarity_{base}$ X $Volume_{base}$**

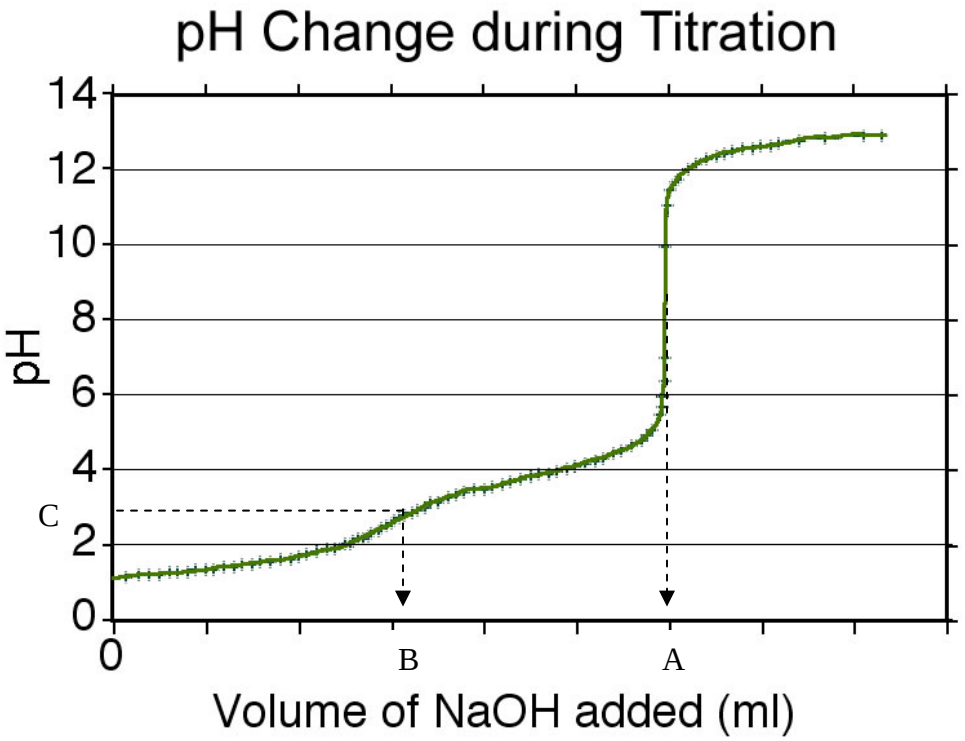
To determine the **pK_a** of **acetic acid CH_3COOH**, a pH meter will be used to record the pH of the acetic acid solution **as the NaOH titrant is added**. A graph of **pH** (vertical y-axis) **vs. volume of NaOH** added (horizontal x-axis) will be plotted. There will be a significant change in pH in the vicinity of the equivalence point. Note that the equivalence point will probably NOT be at pH 7, but will be on the basic side due to acetate ion being a weak base. The value of the equilibrium constant for the dissociation of the weak acid can be obtained from the graph.

Since **$HA + H_2O$ <---> $H_3O^+ + A^-$**

Then the equilibrium expression is: $$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

When the acid is half neutralized, [**HA**] = [A^-], so these terms cancel (equal 1) and **K_a** = [H_3O^+]. Therefore, when the acid is half neutralized, the **$pH = pK_a$**

The point where the **pH is equal to pK_a** pH can be found from the graph:



A = volume of NaOH at equivalence point

B = ½ the volume of A or the volume when half-neutralized

C = **pH** when half neutralized, or **pK_a**

EQUIPMENT

analytical electronic balance
waxed weighing paper
microspatula
dessicator
ring stand
buret clamp
50mL buret
(3) 250mL Erlenmeyer flasks
10.0mL pipet
pipet bulb
pH meter
(3) 100mL beakers
50mL graduated cylinder

CHEMICALS

potassium acid phthalate, $KHP_{(s)}$
distilled water (in wash bottle)
phenolphthalein
~0.12M $NaOH_{(aq)}$
~0.08M $CH_3COOH_{(aq)}$

PROCEDURE

Part 1: Standardization of ~0.12M NaOH Solution:

1. Rinse (3) 250mL Erlenmeyer flasks with tap water, then rinse each with about **10ml distilled water.** Let drain.

2. Using **KHP** which has been dried in an oven and stored in a dessicator, accurately weigh **0.4 to 0.5grams** onto a folded piece of waxed weighing paper with a microspatula. Wash the KHP carefully into one of the rinsed Erlenmeyer flasks using distilled water from wash bottle.

3. With graduated cylinder, add **about 40mL of distilled water** to the KHP and swirl until completely dissolved.

4. With gloved hand, clean a **50ml buret** by rinsing it **3 times** with small (about 7mL) **portions of NaOH solution** (don't forget to rinse through the tip into WASTE beaker) and then fill it above the **0.0mL line** with your NaOH solution. With WASTE beaker placed under the buret tip, open the stopcock briefly to remove any bubbles from the tip (or shake the buret vertically). Adjust titrant to **0.0mL** line **record this initial volume** of titrant under **1st titration** on Data Table.

5. Add **3 drops phenolphthalein** to the acid KHP in the flask and then add **~10mL** of titrant, **swirling constantly**. Place a piece of white paper towel under the flask. Now add very small amounts of the NaOH, swirling constantly, until the first trace of pink color persists for a second, then drop by drop, pausing between drops. The addition of the final drop will turn the entire solution pink, the endpoint, and will persist for 30 seconds. **Record final volume** of titrant.

6. Repeat **Steps #2, 3, 5** two more times. Note **final volume of last titration** is the **initial volume of the next titration**.

7. Calculate the **average Molarity** of your **NaOH solution**.

Part 2: Determination of the Molarity and pK_a of acetic acid:

1. Take 10.0mLpipet and pipet bulb to fume hood and accurately measure **20.0mL** of the **~0.08M CH_3COOH solution** and transfer to **100mL beaker** labeled **"pH meter titration".**

2. Fill buret to **0.0mL line** with NaOH. Take **buret stand**, **buret** and **beaker of acetic acid** solution to one of the pH meters.

3. Remove pH probe from the **yellow buffer** solution and **rinse probe with distilled water** and dry gently with paper towel.

4. Set up the electrode so that it is submerged in the acid solution. **Turn switch** on back from "**standby'** to "**pH**". Record **pH** of acid solution for **0.0mL titrant** on Data Table.

5. Position buret over beaker with acid solution, and titrate the acid solution with NaOH solution, (gentle swirling) **recording the volume of base and pH of the solution every 1mL** during the initial part of the titration. As you approach a **pH of 5.0-5.5**, **decrease the volume of base added to "0.5mL"**. (turn the page and READ!!!)

6. Now as you approach the **equivalence point** (**around pH of 6** when # $moles_{base\ ion}$ = #$moles_{acid\ ion}$), **decrease the volume of base added to "0.1mL".** There will be a **sharp increase in pH** with small additions of NaOH. Continue the titration curve at least **3mL beyond** the equivalence point.

7. Graph your data, with **pH on y-axis** and **volume NaOH on x-axis**. Make graph large enough to reflect the care you took with the measurements of pH and volume of NaOH. **From the graph**, determine the **pK_a** that is, the **pH** when the acid is half neutralized.

8. Determine the **volume of base** needed to reach the equivalence point. Use this value and the **molarity of the NaOH** calculated in Part 1, along with the **volume of the acid** you placed into the beaker to calculate the **exact molarity of the acetic acid** solution.