MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Department of Chemistry
5.311 Introductory Chemical Experimentation

Experiment #3[1]
PREPARATION, CHARACTERIZATION, AND POTENTIOMETRIC TITRATION OF AN UNKNOWN AROMATIC CARBOXYLIC ACID

I. Purpose

This experiment introduces basic manipulative procedures and techniques of preparative chemistry and quantitative volumetric analysis, and provides experience with pH meters. A sample of an alkali or ammonium salt of an unknown aromatic carboxylic acid is converted to the acid, isolated, purified and the yield and melting point determined. Carbonate-free sodium hydroxide solution, which is prepared and standardized against pure potassium acid phthalate, is used to determine the equivalent weight of the purified acid by titration. The apparent pK_a of the unknown acid is determined by potentiometric titration with a glass electrode. Finally, a proton NMR spectrum of the acid is recorded and interpreted to verify the proposed structure.

II. Safety

You will be handling a number of chemicals during this experiment, some of which must be treated with care to avoid damage to yourself or your surroundings. None of these chemicals should be ingested or allowed to contact your skin or eyes. The chemicals are described in this section and denoted by an asterisk when they are used in the procedure. A more comprehensive description of each chemical is included in Appendix A.

1. NaOH 50% w/w: Concentrated NaOH is very caustic and should not be allowed to contact hands or clothing. If it gets on your skin, rinse immediately with plenty of water. Dilute NaOH is less hazardous.
2. Ether: Ether is a highly volatile, flammable liquid. It is used as an anesthetic and should not be inhaled. Prolonged breathing of vapors causes headaches.
   Ether should be used only in the hood to avoid exposure.
3. HCl: Concentrated HCl is a very acidic liquid. Contact with the skin will cause burns. If any gets on you or your clothing, rinse immediately with water. Dilute HCl (3N or less) is less hazardous.
4. Ethanol: Ethanol is a flammable liquid. The type used in this laboratory is not safe to drink, even if it were legal for you to do so (which it is not for a number of reasons!).

[1] The second derivative and the Gran's plot segment added by Mirce D. Gheorghiu

5. Melting Point Standards: the standard compounds used to calibrate your thermometer are organic chemicals varying in melting point. None are particularly hazardous, but they should handled with appropriate care.
6. Soda Lime: Soda lime is a mixture of calcium oxide and sodium hydroxide. The same precautions as apply to sodium hydroxide in solution apply here. These chemicals are caustic and prolonged skin contact will cause burns. If any gets on your skin, rinse well with water.
7. $CaCl_2$: Calcium chloride is a hygroscopic salt, which is not particularly hazardous in small quantities. It is used on roads to prevent icing and is hazardous to cars over the long term. If any gets on your skin, rinse well with water.
8. Potassium Acid Phthalate: KHP is not particularly hazardous and should be handled with the usual precautions. LD_{50} orally in rats 8.0 g/kg
9. Phenolphthalein: This chemical is an organic dye. It should be handled with the usual precautions. Medicinally it is a potent laxative.

III. Procedure for Preparation and Characterization

The preparative directions will give satisfactory yields and purity with any of the compounds supplied. They are not necessarily optimal for any given compound. The analytical procedures will give precise and accurate results with any of the compounds supplied. Careful attention to detail is necessary to get good yields and accurate analysis. One of the keys to success in this course is efficient use of your time. For example it is valuable to recognize which operations may be conducted simultaneously.

Reading assignments pertaining to both theoretical and technical aspects of the experiment are presented at the beginning of each section (TM refers to Techniques Manual; SWH, Skoog, D.A. West, D.M., and Holler, F.J., *Fundamentals of Analytical Chemistry*, 8th edition, Saunders: Fort Worth, 2004)

A. Isolation and Purification of Acid

1. General References

a. Reading

Collecting, washing, and drying crystals	TM 17:13-15
Procedure of extraction	TM 16:11-13; Mohrig 8:56-71
Drying agents	TM 10:42-43; Mohrig 8:72-76
Simple distillation	TM 15: 6-9; Mohrig 11:109-118
Ground glass equipment	TM 10: 7-10: Mohrig 2:16-23
Recrystallization	TM 17:1-15; Mohrig 9:78-92

b. Demonstrations

Crystallization and top-loading balance
Extraction

c. Digital Laboratory Techniques Manual

2. Titration
5. Reaction Work-Up I
6. Reaction Work-Up II
7. Filtration
9. Recrystallization
11. Balances
12. Melting Point
14. Distillation

2. Preparation of the Acid from its Salt.

A 6 g sample of the salt of an unknown aromatic carboxylic acid is provided. Record the sample number and weight in the laboratory notebook. Transfer the salt to a 150-mL beaker containing 25 mL of distilled water. Rinse out the vial with 2-3 mL of water and add the rinse water to the beaker. Heat the mixture on a hot plate until a homogeneous solution is obtained. Filter the solution if any undissolved material remains. If additional water is required to effect solution, it may be added in 15-20 mL increments with continued heating.

Slowly pour the solution into a 250-mL Erlenmeyer flask containing 5 mL of conc. (s.g. 1.19) hydrochloric acid diluted with 25 mL of ice water. (**CAUTION!** Avoid breathing the fumes of concentrated HCl. The dilution should be performed in the hood.) Swirl the flask continuously during the addition to ensure good mixing. Check the pH of the solution using pH paper from your desk. It should be pH 2. If not, add more acid.

When the addition has been completed, let the Erlenmeyer flask stand for 15 min. in an ice bath to effect maximum separation of the acid. Collect the product by suction filtration on a Büchner funnel.[2]

Wash the product with portions of 5 mL of ice cold distilled water to remove any salts and the excess hydrochloric acid (check the pH of water drops on the stem of the Büchner funnel until they are no longer acid on the pH paper). **If the aromatic acid contains HCl absorbed on the crystals, all the titrations that follow are going to provide you altered results**. Avoid drawing excessive amounts of air through the filtered product to prevent contaimination with dust from laboratory air. Save the filtrate and washings.

Weigh a clean, dry 80 x 40 mm crystallizing dish on the top-loading laboratory balance. Transfer the crude acid crystals to it as completely as possible using a small spatula to dislodge any product that adheres to the filter. Air-dry the product overnight or for at least 2 hours in a 50˚C oven.[3]

Weigh the dish and dried product and record the yield of crude product in the notebook. Set aside a few crystals for melting point determination (to be performed later).

While the first crop of crude product is drying, transfer the filtrate to a separatory funnel and extract two times with 50 mL portions of diethyl ether. Combine the extracts and wash with 50 mL of saturated aqueous sodium chloride.

Run the ether phase into a 125 mL Erlenmeyer, add 1 - 2 g of anhydrous sodium sulfate, stopper and let stand with occasional swirling for 20 min. to remove water. Filter through a fluted paper filter into a tared 250 mL round bottom flask. Evaporate the solvent on a rotary evaporator to dryness. Weigh the flask. If the residue amounts to more than 0.1 g, add to the first crop and recrystallize, saving enough material to run a melting point.

3. Purification of Product by Recrystallization

Directions are given for recrystallization from an ethanol-water mixture, which may or may not be the best solvent system for the compound you have. As a general practice, try

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[2] **Caution!** Be sure you have a trap between the aspirator and your suction flask; see TM 17:10 or 17:14.

[3] Caution should be exercised in oven-drying unknown organic compounds. Try putting a few crystals in first to check that the product does not melt at oven temperature. The drying times given should ordinarily be sufficient for these compounds but you should confirm that no significant loss of weight takes place on further drying before reporting the yield.

recrystallizing a very small amount of an unknown compound from the common solvents: water, ethanol, ethyl acetate, hexane to determine what conditions might give the best results before trying to work up the whole batch. In conducting the small scale recrystallizations, estimate the ratio of sample to solvent. A dilution of 20 mg/0.5 mL solvent is a good initial concentration. Record all observations in the notebook. As experience is gained with a variety of compounds, one develops a feel for the sort of solvent to use for a given type of compound and molecular weight range. A melting point should be run on the crystals obtained in the preliminary small-scale recrystallization to assure that the solvent has not reacted with the sample and has produced an entirely different product. However, time for this procedure has not been allotted. You may assume that all the unknowns are unreactive with the solvents.

The following is a typical procedure for recrystallization from ethanol-water. However, these conditions may not be optimal for your compound. Dissolve the crude crystals in the minimum amount of boiling denatured ethanol in a 125 mL Erlenmeyer flask. Use a hot plate! Ethanol is flammable and should not be heated over an open flame.

If the solution is colored, add a pinch of charcoal. Filter the hot solution by gravity using a 65 mm short-stem filter funnel with a fluted filter, preheating the funnel with the vapors from the boiling solution. Catch the filtrate in a 125 mL Erlenmeyer. Record in your notebook the mass of the crude acid and the approximate volume of solvent required for solution.

Separation of crystals before the hot solution has passed through the filter can be avoided by adding a 10% excess of solvent after the minimum amount has been determined. The filtrate may also be heated just to boiling to dissolve any deposited material and may be used to wash crystals from the stem of the funnel.

If the preliminary experimentation indicted that ethanol is a good solvent for the product, reheat the filtrate just to boiling and add water slowly until a slight cloudiness appears. Add a few drops of ethanol to obtain a clear solution and set the hot solution aside to stand undisturbed and cool slowly.[4]

Note the appearance of the crystals as they begin to form and record their characteristics in your notebook. When crystallization appears to be complete, cool in an ice bath for 10-15 min. and collect the product by suction-filtration on a Büchner funnel, using a small spatula to dislodge crystals that adhere to the flask. Catch the filtrate in a clean, dry filter flask. If crystals remain after the flask has been emptied, the filtrate can be poured back into the flask to help complete the transfer. A small amount of fresh, cold (0 ºC) 95% ethanol should be used as a final wash to free the crystals of mother liquor.

A significant fraction of the product may be left in the filtrate and should be recovered. This may be done by evaporating the filtrate to a small volume and cooling the solution until crystallization takes place or by precipitating with water and recrystallizing from a smaller volume of the same or another solvent (Techniques Manual Chapter 17). Always save the filtrate

[4] Some compounds, particularly those which melt below 100 ºC, may separate as an oil when water is added and the mixture cools. Although the oil may solidify at room temperature, the product is likely to be impure and recrystallization from a hydrocarbon solvent, such as hexane, or hexane-ethyl acetate should be tried. It is essential that the product separate from the solvent in a crystalline form from the outset and not as an oil which then solidifies.
Go ahead with part B while waiting for things to cool, crystallize, dry in the oven, etc. A major saving in time and increase in working efficiency is possible through planning.

from a recrystallization until you are sure it contains nothing worth recovering. At least a portion of the material should be recrystallized again to establish that the melting point does not change.

Transfer the combined lots of recrystallized product to a preweighed, dry crystallizing dish and dry to constant weight in air or in a 50 ºC oven. Transfer the recrystallized acid to one or more labeled weighing bottles and dry for an hour in the 110 ºC oven if the melting point is 130 ˚C or higher. If the melting point is lower than 130 ºC, dry for an hour in the 50 ºC oven. At the end of the drying period, remove the weighing bottles from the oven and let them cool in a small desiccator charged with calcium chloride. Observe the precautions involved in the use of desiccators mentioned in Chapter 6 of the Techniques Manual and Skoog et al., pp. 31. Stopper the weighing bottles the first time the desiccator is opened after they are cool. Leave the dried samples in your desiccator until needed for the various measurements to follow. Do not waste sample. Record the yield of purified material obtained.

4. Determination of Melting Point

A Mel-Temp® apparatus with a digital thermometer and a 90-mm melting point capillary is used. Calibrate the thermometer by taking the melting points of four pure compounds that melt over the range of 50-200°C. Pure melting point standards* are provided in the laboratory. Prepare a graph of reported versus observed melting points for a particular Mel-Temp and digital thermometer. For future reference, **record the identification number of the Mel-Temp and thermometer**. Consult the Chemical Rubber Company HANDBOOK OF CHEMISTRY AND PHYSICS to verify the melting points of the standards used.

*Students will be divided into teams. Each team will calibrate one Melt-Temp with each member of the team determining one point (i.e. melting point standard) on the curve for this instrument. You will use the same Melt-Temp apparatus for entire term.

To load the melting point capillary. push the open end into some of the crystals (which must be carefully dried beforehand), invert and tap the sealed end gently on the desk top until the crystals slide down. The crystals should not occupy more than 2-3 mm of the tube. If you have difficulty getting the crystals to go to the bottom of the tube, take a 65 mm long stem funnel and place it upside down on the bench top. Drop the capillary tube down the stem. The impact will not have enough force to break the tube, but it will force the crystals to the bottom.

If you have no previous knowledge of the melting point, it saves time, to do a rough determination by setting the Variac to about 60 and scanning the 50-250 °C range (5 °C to 10 °C per minute). When the approximate melting range has been found, a new tube should be prepared and the run repeated using a much slower (<1 °C per min) rate of temperature increase. Melting point ranges should not exceed four degrees for the former and two for the latter. Always recrystallize a product to constant melting point.

Determine the uncorrected melting point of the unknown acid and compare to the calibration plot. Record in the notebook these results together with any pertinent observations made during heating i.e., evidence of decomposition, color changes, etc. When submitting your notebook pages, include a table showing yields and corrected melting points of the crude and purified products as well as the thermometer calibration curve.

B. Standardization of 0.1 M Sodium Hydroxide

1. General References

a. Reading

Primary standards, end points, and Equivalent weight	SWH Chapter 6 & Appendix 7*
Calculation of concentrations of standard solutions and results of titrations	SWH Chapter 13
Titrations	SWH Chapters 13, 14
Potentiometric Titrations	SWH Chapter 21 (623-629)
Preparation of standard solutions of base	SWH Chapter 16
Precision weighing and desiccation	TM 6: 5-11, SWH Chapter 35
Burettes	TM 7: 6-9
Ordinary titrations	TM 8: 6-7
Titrations sensitive to atmospheric interference (CO_2)	TM 8: 8-9
Confidence limits, uncertainty of mean	TM 3:5-8
Propagation of errors	TM 3:4-5

* Skoog, D.A. West, D.M., and Holler, F.J., *Fundamentals of Analytical Chemistry*, 8th edition., Saunders: Fort Worth, 2004)

2. Preparation of 0.1XXX M sodium hydroxide

N.B. *To minimize the waste*, each student will use ca. 150 mL of the 0.1XXX M NaOH solution. It is sufficient for 9 students to share a 2 liter bottle. If the group is larger, make a second 2 L NaOH solution. The TA will ask for volunteers to make the 0.1XXX M solution. However, everyone must know all the details how to make the solution starting from the 50% NaOH solution available in the lab and how to store the solution.

Make a storage bottle for dispensing standard sodium hydroxide and protecting it from atmospheric carbon dioxide, following the design in Figure 1. The bottle is a 2 liter polyethylene bottle, which takes a No. 6 1/2 2 holes rubber stopper. Insert a No. 5 corkborer in the hole in the stopper, slide the polyethylene tubing into the corkborer and then withdraw the corkborer to leave the polyethylene tubing fitting snugly in the hole at the proper place.

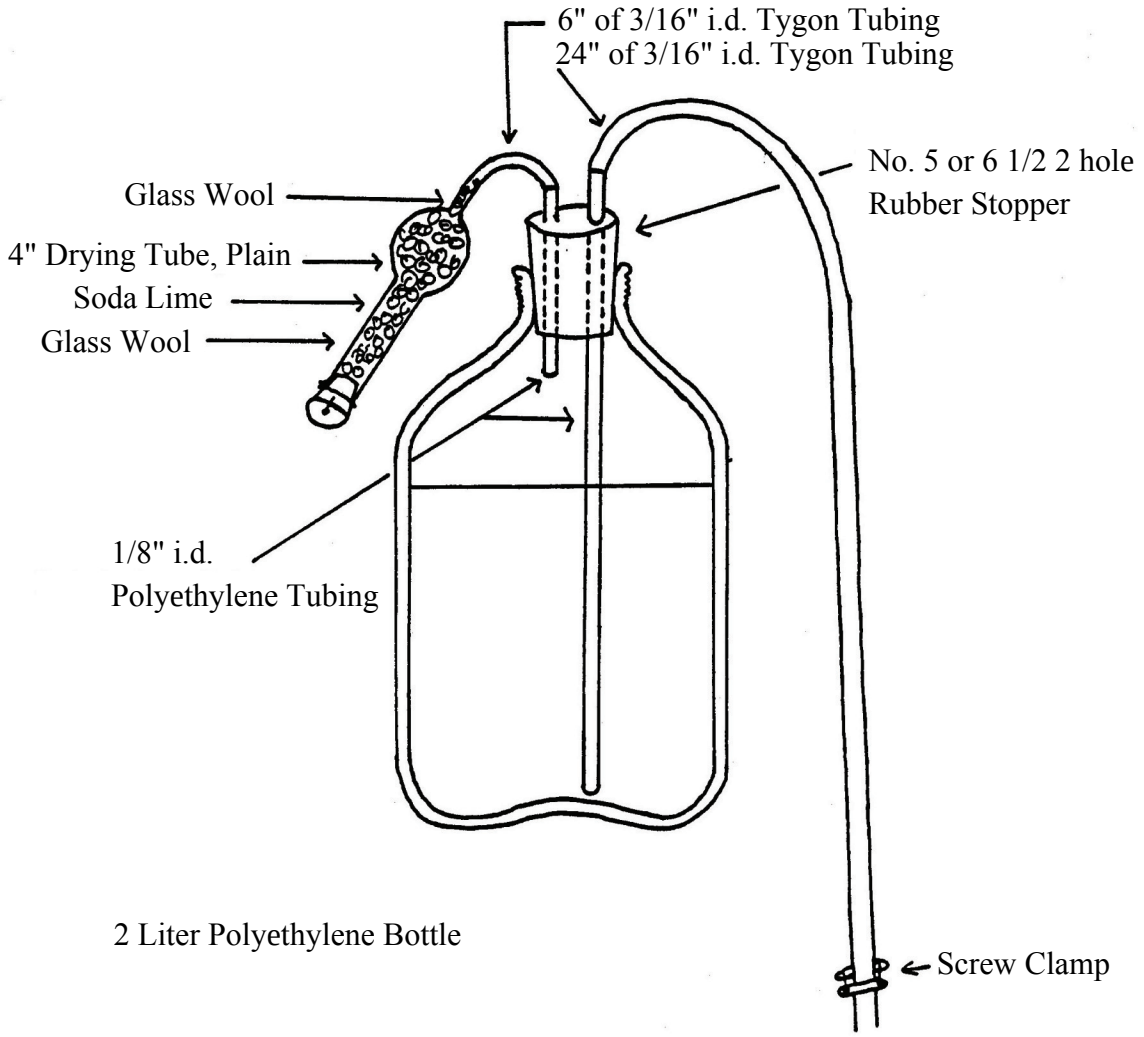


Fig. 1. Siphon storage bottle for standard NaOH

Fill the absorption tube with soda-lime to absorb carbon dioxide from the air as it is drawn into the bottle. The siphon, when ready for use, may be started by holding the outlet of the Tygon delivery tube against an aspirator inlet until the flow begins, then pinching the outlet shut and raising the bottle above the level of the outlet.

Prepare approximately 0.1XXX M sodium hydroxide as follows. Put 1.5 liters of distilled water in the 2 liter polyethylene bottle.[5] Measure out 9 mL of 50% w/w sodium hydroxide in a 10 mL graduated cylinder and pour into the water in the bottle.[6] Both the solution bottle and the 50% sodium hydroxide bottle should be closed immediately with their polyethylene screw caps. **Mix the dilute sodium hydroxide solution very thoroughly by**

[5] Many textbooks recommend boiling the water beforehand to remove dissolved carbon dioxide. In practice this is only necessary if very dilute solutions of hydroxide are to be prepared (0.01 M or less).

[6] Solid sodium hydroxide is always coated with sodium carbonate and is not suitable for making up these solutions. Sodium carbonate is virtually insoluble in very concentrated sodium hydroxide so that dilution of the unshaken 50% reagent is a very convenient way of obtaining carbonate free base. **Concentrated sodium hydroxide will dissolve human skin**!!

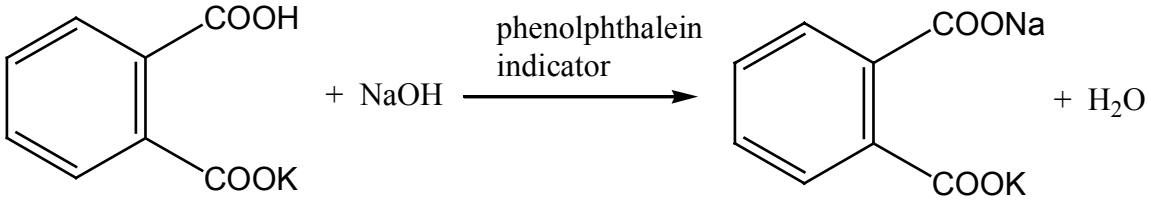
vigorous shaking with repeated inversions for at least 30 sec.[7] Replace the screw cap with the siphon assembly and close the delivery tube with a small screw clamp.

3. Standardization of 0.1XXX M sodium hydroxide

Note: If you are scheduled to do the potentiometric titration first, go immediately to Section IV. When you have completed the potentiometric titration, return to this section.

Put 3-4 grams of reagent grade potassium acid phthalate[8] into an unstoppered weighing bottle and place in the 110 ºC drying oven for an hour. At the end of the drying period, dessicate as described for the unknown acid. Weigh by difference at least three samples of the potassium acid phthalate into labeled or numbered 250 mL Erlenmeyer flasks. Sample masses should be 0.2000-0.3000 g (analytical balance) for the phthalate. Estimate all masses to 0.1 mg and record all data immediately in the notebook.

Dissolve the phthalate samples by swirling with 50-75 mL of water. Warming may be necessary. It is essential that the samples dissolve completely; even a few small, undissolved particles can cause a serious titration error. Add 3-4 drops of phenolphthalein indicator and titrate with the sodium hydroxide solution in a 25 mL Teflon stoppered burette following the instructions in Chapter 8 of the Techniques Manual. The titration may be carried out rapidly at first but the end point (stoichiometric point) should be approached carefully. With low-carbonate sodium hydroxide, the endpoint should be sharp and easily located to within a fraction of a drop.[9] Try to obtain the same intensity of pink color at the endpoint for all your titrations.



Potassium Hydrogen Phthalate
F.W. 204.23

Make all burette readings by estimating to the nearest 0.01 mL, allowing time for drainage. Run sufficient titrations to assure a precise and presumably accurate standardization.

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[7] It is always important to mix a standard solution very thoroughly and it is surprising how much mixing is necessary. Unless this is done, significant differences in concentration can persist and cause lack of agreement in subsequent titrations. In the present instance, the dense, viscous concentrated hydroxide solution needs to be dispersed throughout the solution by repeatedly inverting the bottle with vigorous shaking.

[8] Potassium acid phthalate (KHP) is a primary standard: (i) it is available in high purity, (ii) is soluble in water, (iii) stable in air, (iv) absence of hydrated water (v) low cost, (vi) large formula weigh so the relative error associated with weighing is minimized. The drying removes superficial moisture.

[9] The phenolphthalein endpoint is taken as the first distinct pale pink color which persists for 10 seconds or more after thorough mixing. The color is not permanent but will fade in a matter of minutes or less as a result of absorption of carbon dioxide from the air.

The standardization titration should be repeatable to within 2 p.p.t. (parts per thousand) or 0.2%. If three titrations do not result in the desired precision, it will be necessary to conduct additional titrations. Include with your notebook pages a table giving the calculated molarity of the sodium hydroxide from each titration, the average and the 95% confidence limits. Estimate what you think the reading uncertainties in weighing, and using the burette and the uncertainties in endpoint location ought to be. How do these compare with the observed precision? See Data Analysis, Appendix B.

C. Determination of the Equivalent Weight of the Acid[10]

1. General References - cf. references in Section B
2. Equivalent Mass Determination

Weigh by difference at least three samples of your recrystallized, dessicated unknown acid of 0.1500 -0.2000 g each into numbered 125-mL Erlenmeyer flasks. Dissolve the unknown acid samples by warming with swirling in 50 mL of water and adding, 20-30 mL of 95% ethanol with further warming, if necessary.[11] Allow solution to cool room temperature. Add 5 drops of phenolphthalein indicator and titrate with standardized sodium hydroxide as before.

Note: Save the remaining standard sodium hydroxide solution for use in the potentiometric titrations.

Tabulate the results of the individual titrations of the unknown acid (as equivalent masses) and the 95% confidence limits of the mean. Compare the 95% confidence limits of the results to the propagated uncertainty calculated by estimating your uncertainty in the original measurements. Consult the tables for carboxylic acids in the CRC Handbook for the Identification of Organic Compounds. From the melting point, equivalent mass, and any other observations, e.g., solubility characteristics, attempt to identify the unknown acid. Retain the remaining purified acid in an appropriately labeled vial for use in the determination of the apparent pK_a as described in the next section.

IV. Potentiometric Titration

The relative acidity of an acid HA is reflected by its acid dissociation constant,

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[10] This section may be performed concurrently with the standarization, but remember that the accuracy of the values obtained here depends upon the results of the previous section.

[11] Some acids may need an additional 10 mL of alcohol and heating near boiling to effect the complete solution which is necessary for good results.

$$K_a = \frac{a_{H^+} a_{A^-}}{a_{AH}} \qquad (1)$$

where a_x is the thermodynamic activity of the species x. The activity a_x is often written as the product of the concentration [X] and an activity coefficient γ_x : $a_x = \gamma_{H+} [H^+]$, etc. The activity coefficient accounts for the nonideality of the solution, which results from interactions between dissolved species. In extremely dilute solutions all activity coefficients approach a limiting value of unity, so that the activity is approximately given by the concentration. In 5.311 we will work under the assumption that $a_X \sim [X]$, therefore K_a becomes:

$$K_a = \frac{[A^-][H^+]}{[AH]} \qquad (2)$$

Values of K_a are commonly expressed as the negative (base 10) logarithm: $pK_a = -\log(K_a)$. From the expression given above for K_a, we can write (Henderson-Hasselbalch equation):

$$pK_a = pH - \log\frac{[A-]}{[HA]} \qquad (3)$$

Hence, when the acid is present exactly as 50% A^- ion, and 50% acid HA, the pH will be equal to pK_a. When it is 91% in the ionized form:

$$\frac{[A-]}{[HA]} = 10$$

the pH will be one unit smaller (10 times greater $[H^+]$) than pK_a. When it is 9.1% in the ionized form

$$\frac{[A-]}{[HA]} = 0.1$$

the pH will be one unit larger <u>than</u> pK_a.

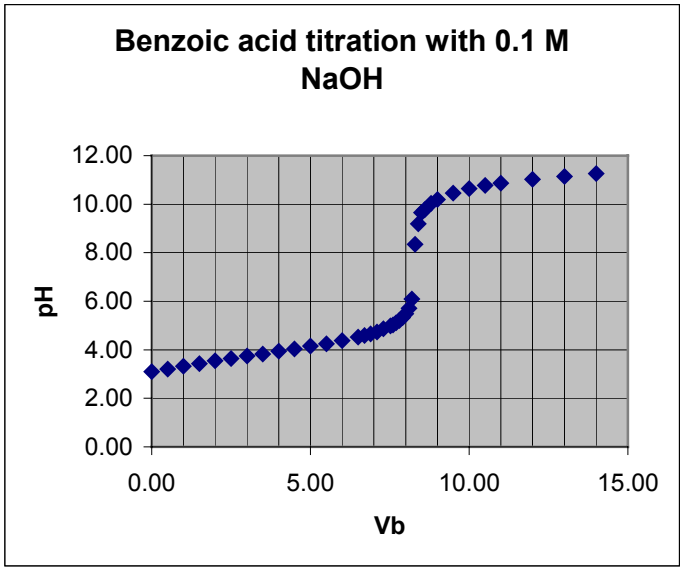

Fig. 2. Typical plot of a potentiometric titration to determine the equivalence point (end point, stochiometric point) and the pK_a value. The case of benzoic acid titrated with 0.0997 M NaOH. The y axis is the pH axis, x axis represents the amount in mL of the added base (volume of base, V_b)

V. **Procedure for Potentiometric Titration**

A. Determination of the apparent pK_a of the unknown aromatic carboxylic acid

1. General References: Skoog, D.A. West, D.M., and Holler, F.J., *Fundamentals of Analytical Chemistry*, 7th edition., Saunders: Fort Worth, 1996)

Activity and Activity Coefficients	SWH Chapter 10
Titration Curves of Weak Acids	SWH 14: 378-383
Silver-silver Chloride Electrodes	SWH Chapter 21
Potentiometric pH Measures with Glass Electrode	SWH Chapter 21
Neutralization Titrations	SWH Chapter 14
Operations of the pH meter	see Appendix 1

2. Determination of pK_a values (**see Appendix 1**)

Use the top loading balances to weigh three samples, ca. 0.1000 g per sample, to an accuracy of +0.0001 g or better. Transfer each sample to a 400-mL beaker and dissolve in 150 mL of water. If necessary, add more distilled water to a total of 200-250 mL (remember: UACAs

have different water solubilities). Heating and swirling will be necessary to dissolve the acid. **Do not add ethanol to effect solution**. Allow the solution to cool to room temperature (ca. 25 °C) before proceeding with the titration. Place a clean magnetic stir bar (size 1") in each beaker of acid.

Position the electrode and 25 mL teflon stopcocked burette, charged with 0.1XXX M sodium hydroxide as indicated in Figure 3. Keep the electrode high enough so that the stirring

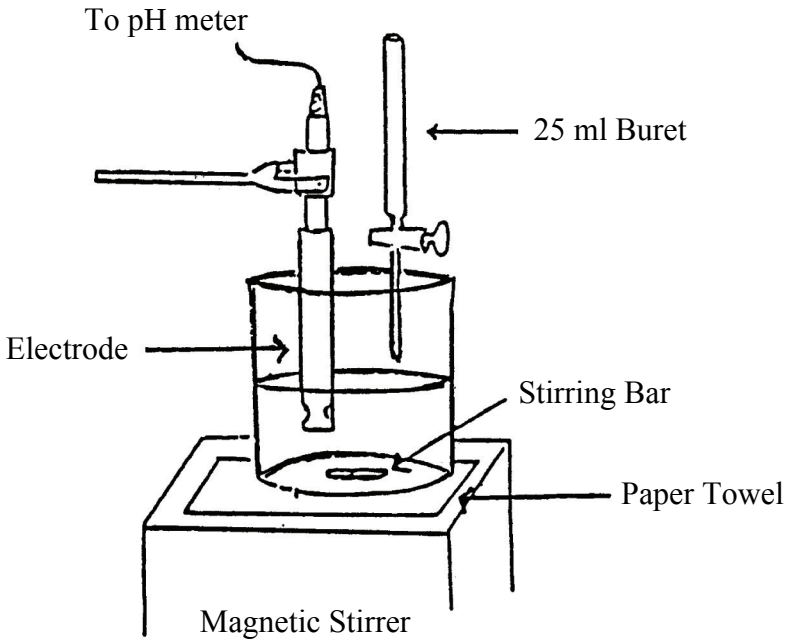

Fig. 3. Apparatus for Potentiometric Titration

bar does not strike it. Insulate the beaker from the magnetic stirrer with a layer of folded paper towels to prevent warming of the solution by the magnetic stirrer. The pH electrode is rinsed with distilled water, wiped gently with Kimwipes® EX-L and placed in the solution so that the solution surrounds the membrane of the glass electrode and no air bubbles are trapped under the polyethylene shield. The temperature of the solution is displayed on the meter., Make sure that is ca. 25 °C.

With continuous stirring, small increments of the standard sodium hydroxide solution are added from a burette. The pH of the solution is measured and recorded in the notebook after each portion has been added. The initial volumes added should be about 0.5 mL. As the equivalence point of the titration is approached, pH changes rapidly. For each 0.3-0.5 jump in pH unit, smaller increments of NaOH solution should be added. Be certain the pH reading has become steady and no bubbles are trapped under the electrode shield before each pH reading is recorded. The titrant could be added dropwise or, better (especially for Gran's plots, see below), by making the tip of burette to touch the inside wall of the titration vessel. Falling drops often lead to splashing on the inside walls of the titration vessel, which need to be rinsed down (therefore, changing the dilution). Do not leave hanging droplet on the burette tip, because it can introduce reading errors of about 0.02 mL.

Carry **one titration** up to pH=12, for which the **equivalence point (V_e) will be located with the second derivative technique**.

The next 2-3 titrations are carried out up to pH=6-7. For these titrations the K_a and V_e will be calculated using Gran's plot (see below).

After the full titration, remember to remove the glass electrode promptly from the final strongly basic solution and to allow it to stand in distilled water for 20-30 min. before attempting additional pH measurements.

You will use two techniques to calculate K_a and V_e: (i) the conventional titration curve method that requires the calculation of the second derivative (SD) of the titration curve followed by extrapolation to $d^2(pH)/d^2(V_b)=0$ and (ii) Gran's plot method.

Both SD and Gran's plot (see Figure 5).[12] are conveniently handled with a spreadsheet like Microsoft Excel (see Lecture handout).

In the conventional titration curve method, the first step involves plotting pH vs. milliliters of added standard base (V_b; see Fig. 2). The next step is the location of the equivalence point that coincides with the V_b at $d^2(pH)/d^2(V_b)=0$.

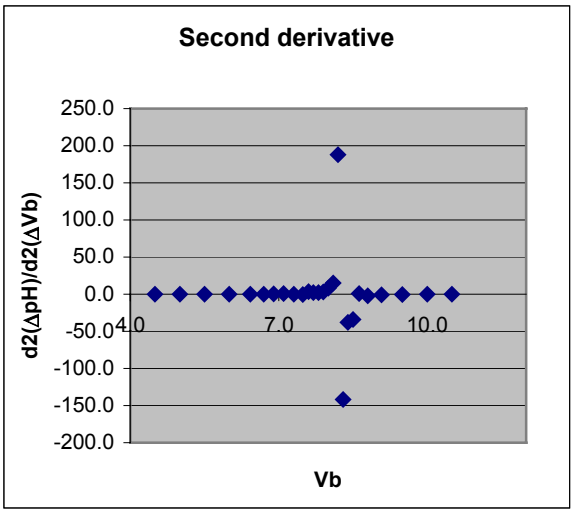

Fig. 4. Plot of second derivative versus added volume of NaOH.

V_{eq} (volume of added base at equivalence point) results from the linear interpolation:

$$V_{eq} = V_{b1} + (V_{b2} - V_{b1}) * \frac{(SD_{eq} - SD_1)}{(SD_2 - SD_1)} \quad (4)$$

The second derivative is zero somewhere between the points of coordinates {SD_1=188; V_1=8.20 mL} and {SD_2=-142; V_2=8.30 mL} (see Figure 3). At SD_{eq}=0, the calculated V_{eq} is 8.22 mL. From V_{eq}, the molarity of the NaOH (related stoichiometrically 1:1 to benzoic acid) and the known mass of benzoic acid that has been titrated, one can calculate the formula weight of benzoic acid and compare it to that obtained by titration with the indicator (see Section C).

[12] Complete details regarding calculation of the second derivative and Gran's plot will provided during the lecture.

Then, calculate the the pH at $V_{eq}/2$ (e.a at 4.11 mL of added NaOH). According to equation (3) $pH=pK_a$ at the equivalence point. Report the 95% confidence limits of the pK_a values.

The next 2-3 titrations will be subjected to Gran's plot[13] method, which has several notable advantages. Gran's method is a useul tool linearizing potentiometric titration curves. The equation (5) is valid only after a few titration readings (not valid if $V_b=0$) and before V_e (for example up to $V_b=0.8V_e$)[15]: **The experimental data can be taken well before the equivalence point. This saves time consumption of reagents (less waste) and improves accuracy (because of the least square regression analysis)**.[16]

$$V_b[H^+] = K_a(V_e - V_b) \qquad (5)$$

$V_b[H^+]$ is plotted against V_b. Only the data that are on the straight line are retained and their range is adjusted for optimum R^2. The slope of the line is $-K_a$ and the V_b intercept is K_a*V_e.

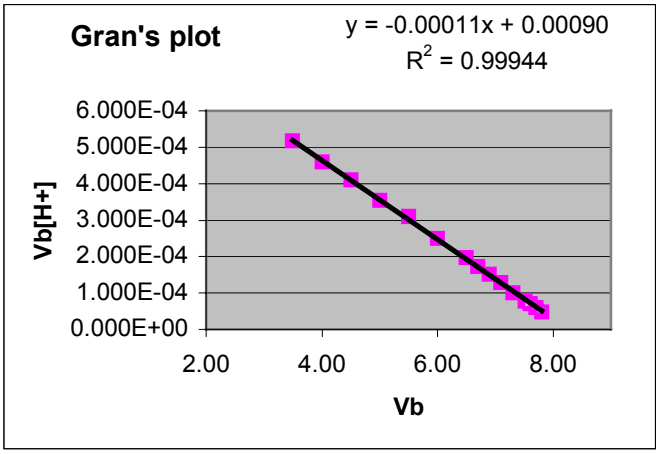

Fig. 5. The linear segment of the titration curve (Gran's plot). The calculated K_a is $1.1*10^{-5}$ and V_e is 8.16 mL of 0.0997 M NaOH (by SD method V_e = 8.22 mL, see above).

VI. ^{1}H-NMR.

Record the ^{1}H-NMR spectrum of the pure acid; recommended solvent $CDCl_3$.or $(CD_3)_2CO$. Comment if the chemical shifts and the coupling constant could account for the chemical structure that you believe correspond to the unknown aromatic carboxylic acid. Attach the NMR as Appendix to the Report.

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[13] Gran, G. *Analyst,* **1952**, *77*, 661.
[14] Because pH changes rapidly for small addition of base, measurements around the equivalence point are prone to experimental error.
[15] See Lecture handout.
[16] Because pH changes rapidly for small addition of base, measurements around the equivalence point are prone to experimental error.

VII. Final Submission

When both titrations have been done, turn in all your remaining purified acid in a labeled bottle and two melting point tubes containing samples of your purified acid. Be sure they are labeled. In the final report, include a table showing mass of crude sample, total amount recrystallized acid recovered, amounts used in the measurements, and the remaining amount turned in.