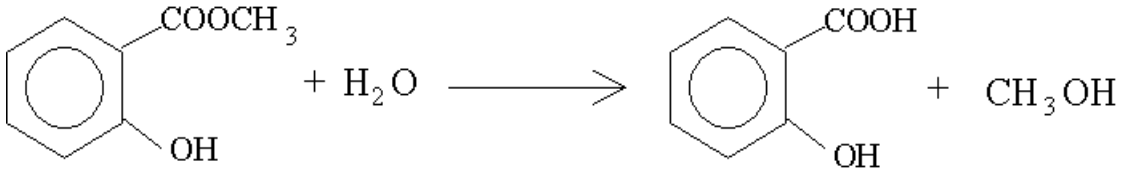
SYNTHESIS OF SALICYLIC ACID

The purpose of this experiment is to synthesize salicylic acid, a white organic solid that was extracted from willow bark by Hippocrates in the fifth century BC. At that time salicylic acid was known to ease pains and reduce fevers. Hippocrates' discovery was lost over time, but re-discovered in the mid 1700's. In the early 1800's it was discovered that the component which made this miracle drug effective was salicylic acid. Salicylic acid, however, caused upset stomachs, but when reacted with acetyl chloride a new compound was produced which had similar medicinal properties as salicylic acid, but did not cause stomach upset. This new compound, acetylsalicylic acid, was given the name aspirin, and was originally produced by the German company, Bayer.

The salicylic acid prepared in this experiment will be the starting material for the preparation of aspirin by our Chemistry 131 students.

Salicylic acid can be prepared by heating methyl salicylate with water. Methyl salicylate, commonly called oil of wintergreen, is used as a flavoring agent and as an ingredient in commercially available liniments. Salicylic acid has some pain relieving abilities, but its chief use is as the starting materials in preparing aspirin (acetylsalicylic acid). When methyl salicylate is heated with water, the formation of salicylic acid occurs very slowly. Replacing the water with an aqueous solution of sodium hydroxide can speed up this hydrolysis reaction. Once the reaction is complete, the sodium hydroxide can be chemically removed by reaction with sulfuric acid. The overall reaction for this experiment is (using condensed structural formulas),



The experiment will be carried out in three steps: hydrolysis of methyl salicylate in NaOH solution, acidification to form crude salicylic acid, and recrystallization to form purified salicylic acid.

This experiment will give you experience in performing a laboratory synthesis, in using a Bunsen burner, in conducting a vacuum filtration, and in re-crystallizing a solid product. You will also calculate the percent yield for your synthesis.

BEFORE YOU BEGIN:

1. Watch the demonstration on the use of the Bunsen burner and practice adjusting your burner before you begin the reaction.

2. Be sure you understand how to perform vacuum filtration.

3. Observe the safety precautions involved in using sodium hydroxide, sulfuric acid, and the other chemicals used in this experiment. Material Safety Data Sheets (MSDS) will be available for your reference.

PROCEDURE: Gloves MUST be worn for steps 4 through 13.

1. Using your graduated cylinder, pour 25 mL of water into a clean 150 mL beaker and mark this volume on the outside of the beaker with a marker (not tape). Empty the water, dry the beaker, and then record its mass. You will be asked to show this notebook entry to your instructor as you do step 2.

2. Dispense about 1.5 mL of methyl salicylate into your **preweighed** 150 mL beaker.

3. Weigh the beaker and methyl salicylate and calculate the exact mass of methyl salicylate.

4. Add 15 mL of 6M NaOH from a clean graduated cylinder. (A white precipitate will form immediately. However, this precipitate is an intermediate and not the final product.) Then add deionized water up to your 25 mL mark on the beaker. Stir with a glass stirring rod. (Rinse the graduated cylinder promptly into a waste beaker.)

5. Set up a ring stand with an iron ring, and place a piece of wire gauze on the ring. Adjust the height of the ring so that the wire gauze will be near the top of the flame from the Bunsen burner. Do not light the burner until you have made this adjustment.

6. Place the beaker on the wire gauze and position a second iron ring just below its lip. Arrange the snorkel vent so its opening will be about four inches above the top of the beaker. Leave the glass stirring rod in the beaker to help prevent "bumping" which is a sudden burst of bubbles from overheating. Heat the mixture to a *gentle* boil, stirring the solution occasionally as the precipitate dissolves. You should move the burner away, touching only the base, to control heating at the slowest possible boil.

7. Gently boil the solution for 15 minutes. Some solid will reappear; use a stream of deionized water from a plastic wash bottle to rinse solids from the inner walls of the beaker into the solution. Between evaporation and rinsing, try to keep the total volume of solution at about 25 mL, as indicated by your mark.

8. When the solution has been boiled for 15 minutes, remove the flame, cool 2 – 3 minutes on the wire gauze, then on the benchtop, and then cool in an ice bath until it is only warm to the touch.

9. While your solution is cooling, set up your apparatus for vacuum filtration.

10. Place your beaker in an acid-resistant pan. Pour about 40 mL of 2M H_2SO_4 into a graduated cylinder inside the same pan, and then *cautiously* add it to the beaker with stirring. A white precipitate of the crude product should form during the addition. Rinse the graduated cylinder immediately into a waste beaker.

11. Again, cool the beaker in the ice bath until it is cold. At the same time, cool 20 mL of deionized water in an Erlenmeyer flask. You will use this cold water to wash the precipitate after it is filtered.

12. Filter the cold mixture by vacuum filtration. After pouring, wash any product out of the beaker into the filter with several small portions of ice cold deionized water from a wash bottle kept in an ice bath. Turn off the vacuum, wash the crude product in the filter with about a third of the ice water from the Erlenmeyer flask, turn the vacuum on for a few seconds, and repeat until the 20 mL of water is used.

13. Allow the vacuum to continue for several minutes until the surface is dry and no droplets are passing into the suction flask. Clean and rinse the beaker during this time.

14. Using a metal spatula, carefully and gently transfer the precipitate from the filter paper to your clean 150 mL beaker. This can best be accomplished by tilting the Buchner funnel over the beaker.

15. Recrystallize the crude product: Using a clean graduated cylinder, add 40 mL of deionized water to the beaker and do the following:

16. Again, place the beaker (with stirring rod) on the wire gauze using a second ring, and heat the mixture. When it reaches the boiling point, stir the contents of the beaker until **all** the precipitate dissolves. Coax any granular solid on the beaker walls into the solution with a wet stirring rod. Expect some recrystallization on the walls, which will be in the form of fine needles.

17. Remove the flame and the stir rod and allow the solution to cool for 5 minutes without disturbing it. Crystals of salicylic acid should begin to appear. During this time, empty the waste filtrate in your filtration flask into the appropriate container, clean the funnel and replace the filter paper.

18. Cool the beaker for 2 minutes on the bench top, then in the ice bath until it is cold. Also cool 20 mL of deionized water in an Erlenmeyer flask.

19. Filter the cold mixture using vacuum filtration. Wash the crystals with ice cold water as before.

20. Continue the vacuum for 5 min. Clean and dry a 100 mL (not the 150) beaker during this time.

21. Using a pencil, mark your initials on the white, etched area on the beaker. (Do not use tape or marker.) Then weigh and record the mass of the beaker.

22. Carefully transfer the precipitate to your clean, dry beaker. Place your beaker in the location specified by your instructor. (If it is to be oven-dried, the temperature should not exceed 60^{o}C, since it can sublime.)

23. Your product should dry at least 18 hours. Then make arrangements to obtain the mass of the product after drying and the beaker has cooled. If this data is obtained on a different day, make a new date entry in your lab notebook under the previous data, enter the dried mass, and show the gram yield in your notebook.

24. After your product has been weighed, transfer it to the marked container in the laboratory, and clean and return your 100 mL beaker.

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Name_____

Partner _____

POST-LAB REPORT:

1. In sentence format, write a summarizing description (an Abstract) of the experimental procedure you followed. Assume the reader is thoroughly familiar with all the laboratory techniques that you used, and only needs an overview of the method: do not include details the reader could easily assume from your description. (Your abstract will lose points if it is unnecessarily detailed.) The last sentence should include a statement of the gram yield and the percent yield of salicylic acid.

2. Show the calculation of the mass of methyl salicylate you actually used, showing each mass measurement:

3. Complete the following table, using your actual data:

Reactant	mL, M or grams	moles	Limiting (Yes/No)?
methyl salicylate (g)			
sodium hydroxide (mL, M)			
water (the approximate amount present during the boiling hydrolysis)			
sulfuric acid (mL, M)			

4. What is the theoretical yield of salicylic acid? (Show calculations.)
a) in moles b) in grams

5. What was your actual yield of salicylic acid? _____ g
Clearly indicate each mass measurement, and show the calculation below:

6. What is your percent yield of salicylic acid? (Show your calculations.)

7. Each of the following are examples of errors or flaws in this procedure that could affect your actual yield and cause your percent yield to be different from 100%. For each of the following, state whether the given scenario would make the actual and the percent yield appear *greater*, *smaller*, or have *no effect*, compared to results from correctly following the procedure:

Influence	effect on actual yield	effect on percent yield
a) Starting with about 1.3 mL of methyl salicylate instead of 1.5 mL		
b) Spattering and losses in transferring solid		
c) Not enough rinsing of product so impurities remain		
d) When rinsing product, using water at room temperature		
e) Incomplete drying of product		

Name _____

Prelaboratory Assignment – Synthesis of Salicylic Acid

1. Convert the structural formulas that are available above to molecular formulas and determine their molar masses. If you wish, you may check them in your text, the Merck Index or another source.

molecular formula molar mass

a) methyl salicylate

b) salicylic acid

2. Using molecular formulas, rewrite the overall reaction:

Also, record the overall reaction **and the molar masses** in your notebook using molecular formulas.

3. a) Determine the molecular formula of the sodium salt of salicylic acid (sodium salicylate), which is the salt formed when NaOH removes one hydrogen from salicylic acid:

The reaction we will do occurs in two steps, which you will write equations for in #3b and c:
b) Using molecular formulas, write down a balanced molecular equation for the reaction of methyl salicylate with sodium hydroxide to give the sodium salt of salicylic acid. (You will need to figure out the other product.)

c) Write down a balanced molecular equation for the acid-base reaction of the sodium salt of salicylic acid with sulfuric acid to give salicylic acid and sodium hydrogen sulfate ($NaHSO_4$):

4. How many moles of methyl salicylate does the procedure call for? The density of methyl salicylate is 1.18 g/mL at 22° C. Remember that this is only an estimate.

5. If you recover 1.253 g of salicylic acid at the end of the experiment, what is your percent yield? (Assume that methyl salicylate is the limiting reagent.)