DEPARTMENT OF CHEMISTRY & CHEMICAL ENGINEERING

CHM-302: Organic Synthesis & Reaction Kinetics

Experiment 04: Catalyzed Esterification & Recrystallization

Term: Fall 2026
Duration: 3.5 Hours
Lab Location: Hall 402
Total Points: 50 Pts

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Instructor: Dr. Marcus Vance **Head TA:** Elena Rostova **Pre-Lab Due:** Oct 28, 2026 **Format:** Pair Work

Student 1 Name: _____ **Student ID:** _____
Student 2 Name: _____ **Bench #:** _____

1 Executive Summary & Learning Objectives

This laboratory assignment focuses on the acid-catalyzed esterification of salicylic acid with acetic anhydride to yield acetylsalicylic acid (aspirin), followed by crude isolation, purificative recrystallization in an ethanol-water solvent system, and quantitative assessment of chemical purity via micro-melting point determination and ferric chloride (Fe^{3+}) complexation spectroscopy.

Key Pedagogical Objectives:

1. Perform nucleophilic acyl substitution under anhydrous conditions using concentrated acid catalysis.
2. Master vacuum filtration techniques and compute accurate theoretical, crude, and purified percent yields.
3. Understand recrystallization mechanics based on temperature-dependent solubility differentials.
4. Assess organic product purity using colorimetric complexation assays and melting point range analysis.

2 Chemical Hazards & Laboratory Safety Protocols

MANDATORY SAFETY DIRECTIVES & GHS HAZARDS

All operations involving acetic anhydride and concentrated sulfuric acid MUST be conducted inside operational fume hoods. Wear splash goggles, neoprene/nitrile gloves, and lab coat at all times.

Reagent	CAS #	Primary GHS Hazard Statements	PPE Requirement
Salicylic Acid	69-72-7	Acute Tox. 4 (Oral), Eye Dam. 1 (H318, H302)	Nitrile Gloves, Safety Glasses
Acetic Anhydride	108-24-7	Flam. Liq. 3, Skin Corr. 1B, Acute Tox. 4 (H226, H314)	Fume Hood, Heavy Nitrile
Sulfuric Acid (18 M)	7664-93-9	Skin Corr. 1A, Met. Corr. 1 (H314, H290)	Double Gloves, Face Shield
Acetylsalicylic Acid	50-78-2	Acute Tox. 4, Skin Irrit. 2 (H302, H315)	Standard Lab Coat, Goggles

Emergency Procedure: Flush chemical skin exposure with water for 15+ minutes. Benchtop acid spills must be neutralized with sodium bicarbonate ($NaHCO_3$) prior to wipe-down. Waste solutions containing heavy metals ($FeCl_3$) must be poured into Hazardous Metal Waste Container B.

3 Theoretical Reaction Scheme & Stoichiometric Matrix

Reaction Scheme: Acid-Catalyzed Acetylation of Salicylic Acid

$$C_7H_6O_3\,(s) + C_4H_6O_3\,(l) \xrightarrow[85\ ^\circ C]{H_2SO_4} C_9H_8O_4\,(s) + C_2H_4O_2\,(l)$$

Salicylic Acid (2.50 g) + Acetic Anhydride (5.00 mL) $\xrightarrow{H_2SO_4}$ Acetylsalicylic Acid + Acetic Acid

Reagent Physical Property Table

Chemical Compound	MW (g/mol)	Density (g/mL)	m.p. (°C)	b.p. (°C)	Reaction Role
Salicylic Acid	138.12	1.443	158.6	211.0	Limiting Reagent
Acetic Anhydride	102.09	1.082	–73.1	139.8	Excess Reactant / Solvent
Sulfuric Acid (98%)	98.08	1.840	10.3	337.0	Acid Catalyst
Acetylsalicylic Acid	180.16	1.400	135.0–136.0	Decomposes	Target Product
Water (Deionized)	18.02	1.000	0.0	100.0	Quenching Solvent

4 Detailed Experimental Work Plan

Part A: Synthesis of Crude Acetylsalicylic Acid

1. Accurately weigh approximately $2.50\,\text{g}$ of salicylic acid to the nearest $0.001\,\text{g}$ on an analytical balance. Record exact mass in Data Sheet 5.1.
2. Transfer solid into a dry $125\,\text{mL}$ Erlenmeyer flask equipped with a magnetic stir bar.
3. In the fume hood, add $5.00\,\text{mL}$ of acetic anhydride via volumetric pipette. Wash down any solid adhering to flask walls.
4. Carefully add 5–8 drops of concentrated sulfuric acid (H_2SO_4, $18\,\text{M}$) using a Pasteur pipette while swirling.
5. Clamp flask in a warm water bath (75–85°C) on a hotplate-stirrer. Heat with constant stirring for 15 minutes.

Part B: Quenching, Precipitation & Vacuum Isolation

1. Remove flask from water bath. Slowly add $2.0\,\text{mL}$ of ice-cold deionized water to decompose unreacted acetic anhydride (**CAUTION:** exothermic reaction; vapor evolution).
2. Once reaction subsides, add $40\,\text{mL}$ of ice-cold water. Chill mixture in an ice-water bath for 15 minutes to maximize precipitation.
3. Assemble a Büchner funnel with Whatman No. 1 filter paper on a filter flask attached to vacuum aspirator.
4. Filter crude aspirin under vacuum. Wash filter cake twice with $5\,\text{mL}$ portions of ice-cold water. Draw air through cake for 5 minutes.

Part C: Purification via Recrystallization & Characterization

1. Transfer crude solid to a $50\,\text{mL}$ beaker. Dissolve in minimum volume (~ 5–$7\,\text{mL}$) of warm 95% ethanol heated to 60°C.
2. Add $20\,\text{mL}$ of warm deionized water. Cover beaker with watch glass and allow to cool undisturbed to room temperature, then transfer to ice bath.
3. Collect purified needle crystals via vacuum filtration. Dry in oven at 60°C for 25 minutes.
4. Determine melting point range using Mel-Temp apparatus. Perform FeCl_3 test (1 drop $1\%\text{FeCl}_3$ in ethanol) to test for residual salicylic acid.

5 Primary Experimental Data & Observations Sheet

Table 5.1: Gravimetric Synthesis Data

Measurement Parameter	Unit	Recorded Value
Mass of Salicylic Acid ($\text{C}_7\text{H}_6\text{O}_3$)	g	.
Volume of Acetic Anhydride ($\text{C}_4\text{H}_6\text{O}_3$)	mL	.
Calculated Density of Acetic Anhydride	g/mL	1.082
Mass of Acetic Anhydride Used	g	.
Theoretical Yield of Acetylsalicylic Acid	g	.
Mass of Watch Glass + Filter Paper	g	.
Mass of Watch Glass + Filter Paper + Crude Aspirin	g	.
Mass of Isolated Crude Acetylsalicylic Acid	g	.
Mass of Watch Glass + Filter Paper + Purified Aspirin	g	.
Mass of Isolated Purified Acetylsalicylic Acid	g	.
Crude Percent Yield	%	.
Purified Percent Yield	%	.

Table 5.2: Analytical Purity & Characterization

Sample Tested	Observed m.p. (°C)	FeCl_3 Color Test Result	Phenol Assessment
Pure Salicylic Acid Standard	158.5 – 159.5	Intense Dark Violet	High Phenolic Content
Commercial Aspirin Tablet (Control)	134.5 – 135.5	Clear / Pale Yellow	No Phenolic Impurity
Crude Aspirin Sample	–		
Purified Recrystallized Aspirin	–		

6 Mandatory Pre-Lab Analytical Questions

Complete these pre-lab questions individually before arriving at the laboratory session. Submit your completed responses to the TA at the beginning of the lab.

Q1. Stoichiometric Yield Calculation:
A student reacts $2.75\,\text{g}$ of salicylic acid with $5.50\,\text{mL}$ of acetic anhydride in the presence of 5 drops of sulfuric acid.

(a) Determine the limiting reactant showing full dimensional analysis.

(b) Calculate the theoretical yield of acetylsalicylic acid in grams.

(c) If $2.82\,\text{g}$ of purified aspirin is recovered, calculate the overall percent yield.

Q2. Mechanistic Pathway:
Draw the complete curved-arrow mechanism for the acid-catalyzed acetylation of salicylic acid by acetic anhydride. Clearly indicate all proton transfers, tetrahedral intermediates, and resonance structures of the protonated anhydride catalyst complex.

Q3. Quenching Side Reactions:
Why is water added at the end of the reaction heating period? Write the balanced chemical equation for the hydrolysis of excess acetic anhydride and explain why this operation is conducted in the fume hood.

Q4. Recrystallization Solvent Selection:
Explain why a solvent pair of ethanol and water is superior to pure water or pure ethanol for the recrystallization of aspirin, referencing polar solubility parameters and temperature coefficients.

Q5. Purity Assay Chemistry:
Describe the chemical basis of the iron(III) chloride (FeCl_3) colorimetric test. What functional group coordinates with Fe^{3+} to form the violet complex, and why does pure aspirin yield a negative test?

7 Student Safety Commitment & TA Verification

Safety Compliance Declaration

By signing below, I certify that I have read and fully understood the GHS safety data sheets for all chemical reagents used in Experiment 04. I agree to abide by all laboratory safety regulations, wear required PPE, perform acid heating operations exclusively within chemical fume hoods, and properly segregate hazardous organic waste.

Student 1 Signature: _____ **Date:** _____

Student 2 Signature: _____ **Date:** _____

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TA Pre-Lab Check (Sign-off): _____ **Bench Safety Approved:** [ ] Yes [ ] No