Chemistry 218
Chemical Principles II

Procedures Only

Laboratory Manual 2019-21

(38 Pages)

Athabasca University

Contents

[1] These labs require *formal reports;* all others require only a *short* report.

Experiment D1: Reaction Kinetics I— Determination of a Rate Law Procedure

A. Preparation of Solutions

The following standard solutions are required in both this experiment and the one that follows: potassium iodide, sodium thiosulfate, potassium chloride, ammonium peroxydisulfate, and ammonium sulfate.

In consultation with the instructor, students may organize themselves in groups of three in order to prepare a communal supply of these solutions.

Note: collaboration is permitted only to reduce the tedium of preparing several solutions. All subsequent work must be carried out on an individual basis.

The solutions should be prepared in the usual manner (see Experiment A1, *Chemistry 217*, if necessary). Use a general-purpose balance to measure out the approximate mass into a weighing vial. Weigh the vial and its contents on an analytical balance, then transfer the solid into a volumetric flask. Determine the mass of the "empty" weighing vial, and then add distilled water to the solid in the flask until the level of the solution reaches the graduation mark on the neck of the flask. Ensure that the solutions are thoroughly mixed by inverting the flasks several times. Remember that these solutions will be shared by two other people, so make sure that you have correctly calculated the mass of solid required in each case. (Maybe your collaborators will check your calculations for you.) You must use the same solutions throughout this experiment and the next one. If you run out of solution you will not be able to complete the experiment. Thus, try to minimize any waste. Each group of three students should prepare the following volumes of solutions:

Sol'n	Solute	Formula	Volume Required	Final Concentration	Molar Mass	grams Required ?*
A	potassium iodide	KI	1 L	[0.2 mol × L^{-1}]		
B	sodium thiosulfate**	$Na_2S_2O_3$ or $Na_2S_2O_3\ 5H_2O$	500 mL	[0.01 mol × L^{-1}]		
C	potassium chloride	KCl	500 mL	[0.2 mol × L^{-1}]		
D	ammonium peroxydisulfate	$(NH_4)_2S_2O_8$	1 L	[0.1 mol × L^{-1}]		
E	ammonium sulfate	$(NH_4)_2SO_4$	500 mL	[0.1 mol × L^{-1}]		
*use the formula: grams Required = C (mol/L) × MM (g/mol) × V (L) **sodium thiosulfate may be available in two forms, anhydrous or pentahydrate						

In addition to the above, solutions of starch indicator and copper (II) sulfate (0.1 mol × L^{-1}) will be required. These will be provided by the instructor.

B. Preliminary Investigation

Before you begin the kinetic study, you should carry out the following preliminary investigations. You may use a calibrated Pasteur pipette to obtain the approximate volume of each reagent. Remember to mix the tubes well after every addition.

1. Place about 2 mL of potassium iodide solution (0.2 mol × L^{-1}) in each of four test tubes. To the first tube add 15 drops of starch solution. To the second tube add about 2 mL of ammonium peroxydisulfate solution (0.1 mol × L^{-1}). Record your observations.

2. Add 1 mL of ammonium peroxydisulfate solution (0.1 mol × L^{-1}) to the first tube, and 15 drops of starch solution to the second tube. Record any differences between the two solutions.

3. To the third tube, add 5 drops of sodium thiosulfate (0.01 mol × L^{-1}) and 15 drops of starch solution. Add 2 mL of ammonium peroxydisulfate, and observe the reaction mixture carefully.

4. To the fourth test tube, already containing 2 mL of potassium iodide solution (0.2 mol × L^{-1}), add 15 drops of starch solution, 2 mL of ammonium peroxydisulfate solution (0.1 mol × L^{-1}), and slowly add 1–2 mL of sodium thiosulfate solution (0.1 mol × L^{-1}). Observe what happens.

Test Tube		Observations
1	2 mL KI + 15 drops starch + 1mL $(NH_4)_2S_2O_8$	
2	2 mL KI + 2 mL $(NH_4)_2S_2O_8$ + 15 drops starch	
3	2 mL KI + 5 drops $Na_2S_2O_3$ + 15 drops starch + 2 mL $(NH_4)_2S_2O_8$	
4	2 mL KI + 15 drops starch + 2 mL $(NH_4)_2S_2O_8$ 1–2 mL $Na_2S_2O_3$	

C. Kinetic Study

You are going to carry out seven kinetic runs (trials), using different concentrations of reactants in each run. The procedure to be followed is described in general terms below; in each individual run you must determine the volumes of reagents to be used from Table D1.1. All the solutions should be at room temperature, and all glassware must be scrupulously clean. The total volume of the reaction mixture is 56.0 mL in each case, and this is achieved by adding the appropriate volume of potassium chloride (0.2 mol × L^{-1}) to the potassium iodide solution and/or ammonium sulfate (0.1 mol × L^{-1}) to the peroxydisulfate solution. These reagents are used rather than water so that the ionic strength of the reaction mixture is approximately the same in each run. Be sure to record the precise concentrations of the potassium iodide and ammonium peroxydisulfate solutions, as these will be the concentrations used in your calculations.

1. Set up two burettes held by a burette clamp on a retort stand as shown in Figure D1.1. Fill one of these burettes with potassium chloride solution (0.2 mol × L^{-1}) and the other with ammonium sulfate (0.1 mol × L^{-1}). Use these burettes to add potassium chloride to the potassium iodide solution and ammonium sulfate to the ammonium peroxydisulfate solution whenever this is called for in Table D1.1.

2. Using a volumetric pipette, measure out the required volume of potassium iodide solution (0.2 mol × L^{-1}) into a 125-mL Erlenmeyer flask. **Note:** If 20 mL of solution is required, use the 10-mL volumetric pipette twice; if 15 mL of solution is required, use the 10-mL volumetric pipette once and the 5-mL volumetric pipette once, and so on.

3. The 125-mL Erlenmeyer flask containing the potassium iodide will serve as the reaction vessel. To the potassium iodide solution already in the flask, add 5 mL of sodium thiosulfate (0.01 mol × L^{-1}), using a 5-mL volumetric pipette, and 1.0 mL of the 3% starch solution using a 1-mL volumetric pipette. Finally, to this same Erlenmeyer flask, add the volume of potassium chloride (0.2 mol × L^{-1}) specified in Table D1.1.

4. Use a volumetric pipette to add the required volume of ammonium peroxydisulfate (0.1 mol × L^{-1}) to a 50-mL Erlenmeyer flask. To this solution add the volume of ammonium sulfate solution specified in the final column of Table D1.1.

5. Place a thermometer into the reaction vessel (i.e., the 125-mL Erlenmeyer flask) and ensure that you understand how to use the stop-clock that is provided. **Note:** If your own wristwatch has a stopwatch function, you may use that instead.

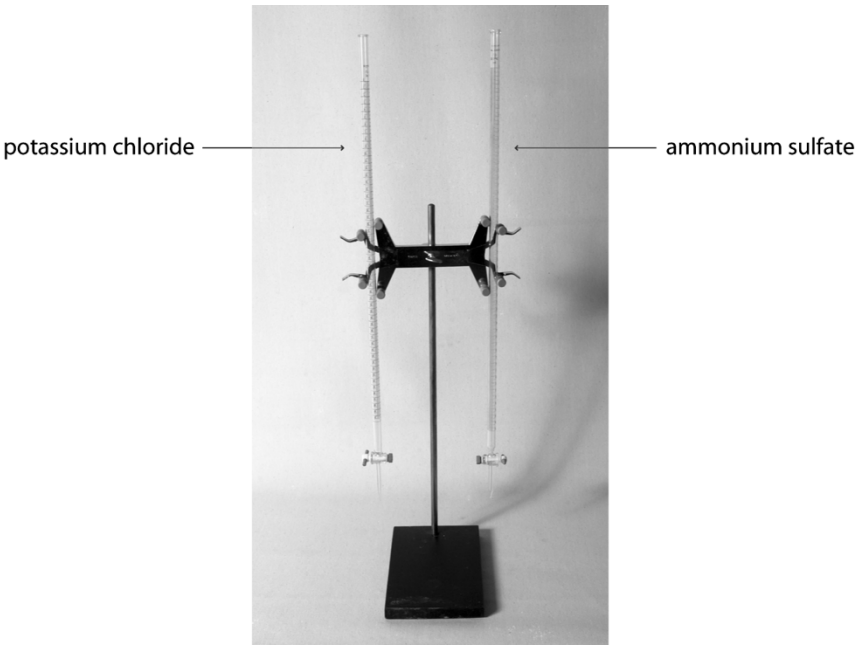
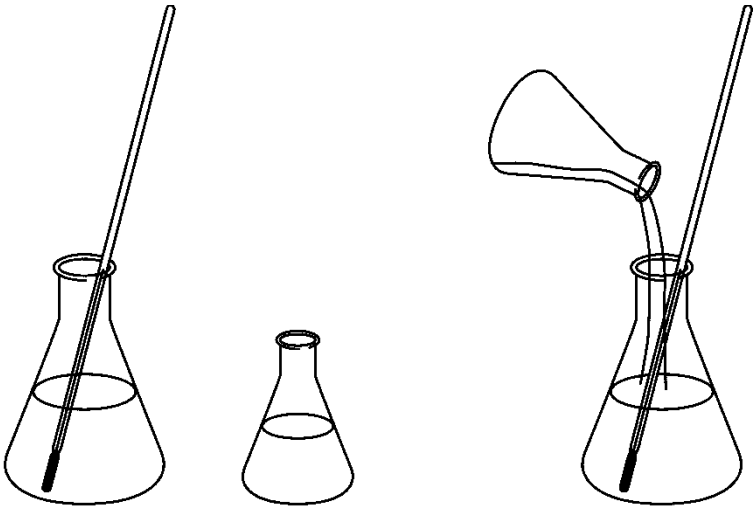


Figure D1.1: Burettes arranged to deliver potassium chloride and ammonium sulfate.

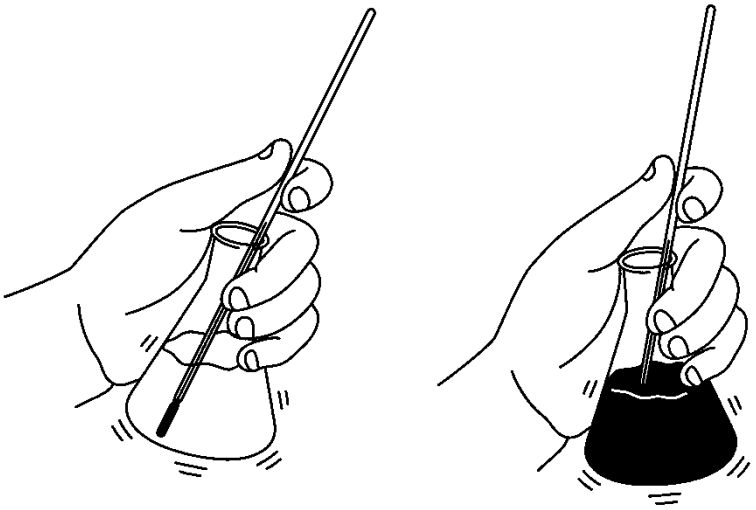
6. Pour the solution from the 50-mL Erlenmeyer flask into the reaction flask (i.e., the 125-mL Erlenmeyer flask) and swirl to mix the solution thoroughly. Start the stop-clock immediately (see Figure D1.2). Continue swirling the solution in the reaction vessel until a permanent blue-black colour appears. When this happens, immediately stop the stop-clock. Record the temperature of the reaction mixture.



125 mL Erlenmeyer flask containing potassium iodide, sodium thiosulfate, starch indicator, and (if necessary) potassium chloride. The reaction vessel.

50 mL Erlenmeyer flask containing ammonium peroxydisulfate and (if necessary) ammonium sulfate.

Mix the two solutions.



Stir thoroughly. Start clock.

Watch for appearance of blue colour.

Figure D1.2
Starting the reaction

7. Carefully clean your Erlenmeyer flasks with soap and water, rinse them with distilled water, and then give them a final rinse with acetone. There is no need to clean your volumetric pipettes, provided that there are sufficient pipettes for you to use a different one for each solution. (Share with your neighbour if necessary.) Prepare the solutions for the next run using the information given in Table D1.1.

Table D1.1 Volumes to be used in kinetic runs

	Volumes to be added **(mL)**					
	Reaction vessel (125-ml Erlenmeyer Flask)				**50-mL Erlenmeyer Flask**	
Run	KI (0.2 M)	$Na_2S_2O_3$ (0.01 M)	Starch (3%)	KCl (0.2 M)	$(NH_4)_2S_2O_8$ (0.1 M)	$(NH_4)_2SO_4$ (0.1 M)
1	25.0	5.0	1.0	0	25.0	0
2	15.0	5.0	1.0	10.0	25.0	0
3	10.0	5.0	1.0	15.0	25.0	0
4	5.0	5.0	1.0	20.0	25.0	0
5	25.0	5.0	1.0	0	20.0	5.0
6	25.0	5.0	1.0	0	15.0	10.0
7	25.0	5.0	1.0	0	10.0	15.0
Optional: You may choose to do the setup for Experiments D1 and D2 all together (see Table D2.1).						

WASTE DISPOSAL: The solutions used up to this point in the experiment may be washed down the drain with large amounts of water. Acetone should be placed in the special container provided.

D: The Effect of a Catalyst

You will now carry out one run in which a catalyst is present in the reaction mixture.

1. Repeat Run 3 as described in Part B, but this time add only 14 mL of potassium chloride to the reaction vessel from the burette. In addition, use a 1-mL volumetric pipette to add 1-mL of copper (II) sulfate solution (0.1 mol × L^{-1}) to the ammonium peroxydisulfate solution in the 50-mL Erlenmeyer flask. Thus, your reaction mixture will consist of the following:

Table D1.2 Volumes to be used in catalyst run

		Volumes to be added **(mL)**					
		Reaction vessel (125-ml Erlenmeyer Flask)				**50 mL Erlenmeyer Flask**	
	Run	KI (0.2 M)	$Na_2S_2O_3$ (0.01 M)	Starch (3%)	KCl (0.2 M)	$(NH_4)_2S_2O_8$ (0.1 M)	**$CuSO_4$** (0.1 M)
(3)	**8**	10.0	5.0	1.0	**14.0**	25.0	**1.0**
Optional: You may choose to do the setup for Experiments D1 and D2 all together (see Table D2.1 on page 12).							

2. Rapidly pour the solution from the 50-mL Erlenmeyer flask into the reaction flask (i.e., the 125-mL Erlenmeyer flask) and swirl to mix the solution thoroughly. Start the stop-clock immediately (see Figure D1.2). Quickly swirl the solution in the reaction vessel until a permanent blue-black colour appears. When this happens, immediately stop the stop-clock and record the time. Also record the temperature of the reaction mixture.

WASTE DISPOSAL: The solutions used in the experiment may be washed down the drain with large amounts of water. Acetone should be placed in the special container provided.

In you lab reports, don't forget about the Post Lab Questions for every experiment!

Experiment D2:
Reaction Kinetics II—The Determination of an Activation Energy Procedure

Before you begin this experiment, check to see that the constant-temperature water baths have been switched on and set to temperatures of 35°C and 50°C. Secondly, check to see that you have a sufficient supply of the solutions that you prepared for use in Experiment D1. All the glassware used in this experiment must be clean and dry.

Note: If you are doing this experiment before you do D1, collaborate with two other people in preparing the solutions listed under Part A of Experiment D1. Do not waste these solutions, as you will use them later when you do Experiment D1. Once the solutions have been prepared, all the kinetic runs must be carried out individually—you may not pool your data.

In this experiment, the composition of the reaction mixture will be the same in each of the four runs. Specifically, it will have the composition shown in the table below.

Table D2.1 Volume to be used in temperature runs

Reaction vessel				50-mL Erlenmeyer	
KI (0.2 M)	$Na_2S_2O_3$ (0.01 M)	Starch (3%)	KCl (0.2 M)	$(NH_4)_2S_2O_8$ (0.1 M)	$(NH_4)_2SO_4$ (0.1 M)
10.0 mL	5.0 mL	1.0 mL	15.0 mL	10.0 mL	15.0 mL

1. Set up two burettes, one containing potassium chloride solution ($0.2\ mol \cdot L^{-1}$) and the other containing ammonium sulfate solution ($0.1\ mol \cdot L^{-1}$), as described in Step 1 in Part B of Experiment D1.

2. Using a volumetric pipette, measure out 10 mL of the potassium iodide solution into a 125-mL Erlenmeyer flask. This flask will serve as the reaction vessel. See Table D2.1 above.

3. To the 125-mL Erlenmeyer flask containing the potassium iodide, add 5 mL of sodium thiosulfate solution using a 5-mL volumetric pipette. Use a 1-mL volumetric pipette to add 1 mL of starch indicator to the mixture in the flask. Finally add 15 mL of potassium chloride solution from the burette.

4. Use a volumetric pipette to add 10 mL of ammonium peroxydisulfate to a 50-mL Erlenmeyer flask. From the burette, add 15 mL of ammonium sulfate solution to this flask.

5. Place the Erlenmeyer flasks from steps 3 and 4 in the constant-temperature water bath, which has been previously set to a temperature of about 50° C. Allow the flasks to remain in the bath for at least 10 minutes to equilibrate. During this time proceed to step 6.

6. Repeat steps 2 through 4. Place these two flasks in the water bath that has been set at 35° C. Allow the solutions to equilibrate for at least 10 minutes, and in the meantime proceed to step 7.

7. Repeat steps 2 through 4. Place these two flasks in a bath (e.g., a large crystallizing dish) containing ice water. Allow the solutions to equilibrate for at least 10 minutes. During this time, proceed with step 8.

8. Repeat steps 2 through 4. Place a thermometer in the reaction vessel, and quickly pour the contents of the 50-mL Erlenmeyer flask into the vessel. Start the stopwatch the instant the two solutions are mixed (see Figure D1.2, particularly if you have not yet done Experiment D1). Record both how long it takes for the permanent blue-black colour to develop, and the temperature of the reaction mixture.

9. By now, the solutions contained in the flasks that were placed in the first water bath (see step 5) should have attained a temperature of about 50° C. Place a thermometer in the reaction vessel and, keeping the reaction vessel in the water bath, quickly start the reaction as described in step 8. As before, record both the time it takes for the permanent blue-black colour to develop, and the temperature of the reaction mixture.

10. Repeat step 8 using the solutions contained in the flasks that are equilibrating at about 35° C (see step 6). **Note:** Clean the thermometer carefully between runs.

11. Repeat step 8 using the solutions contained in the flasks that are equilibrating in the ice water bath (see step 7).

WASTE DISPOSAL: The solutions used in this experiment may be washed down the drain with large amounts of water. Wash the Erlenmeyer flasks with soap and water, then rinse with distilled water followed by acetone. Waste acetone should be placed in the special container provided.

Modified Procedure for Experiments D1 and D2

In order to have an increased efficiency and to save time, students may use the following modified procedure, which combines the preparation work for Experiment D1 and D2.

Table D2.1 Volumes to be used in kinetic runs in both Exp. D1 and D2

		Volumes to be added **(mL)**						
		Reaction vessel (125-mL Erlenmeyer Flask)				**50-mL Erlenmeyer Flask**		
	Run	**KI** (0.2 M)	$Na_2S_2O_3$ (0.01 M)	Starch (3%)	KCl (0.2 M)	$(NH_4)_2S_2O_8$ (0.1 M)	$(NH_4)_2SO_4$ (0.1 M)	$CuSO_4$ (0.1M)
Exp. D1	**1**	**25.0**	5.0	1.0	0	**25.0**	0	
	2	**15.0**	5.0	1.0	10.0	25.0	0	
	3	**10.0**	5.0	1.0	15.0	25.0	0	
	4	**5.0**	5.0	1.0	20.0	25.0	0	
	5	25.0	5.0	1.0	0	**20.0**	5.0	
	6	25.0	5.0	1.0	0	**15.0**	10.0	
	7	25.0	5.0	1.0	0	**10.0**	15.0	
Catalyzed	**8**	10.0	5.0	1.0	14.0	25.0	0.0	1.0
4° C	**9**	10.0	5.0	1.0	15.0	10.0	15.0	
r. temp	**10**	10.0	5.0	1.0	15.0	10.0	15.0	
~35° C	**11**	10.0	5.0	1.0	15.0	10.0	15.0	
~50° C	**12**	10.0	5.0	1.0	15.0	10.0	15.0	

Experiment D3:
The Determination of an Equilibrium Constant Procedure
Procedure

A. Construction of a Calibration Curve

1. Using the methods learned in *Chemistry 217* (see Experiment A2), prepare 50 mL of approximately 0.20 mol · L^{-1} iron (III) nitrate solution* and 250 mL of 5.0×10^{-4} mol · L^{-1} potassium thiocyanate solution. Refer also to the flowchart on page 66.

   Note: Double check to see what hydrate of iron (III) nitrate you are using before calculating the molecular weight; it might be $Fe(NO_3)_3 \cdot 9H_2O$. [Optional: because the weigh out for the 5.0×10^{-4} M potassium thiocyanate solution is very small, you may choose to prepare a 100X stock (i.e., 5.0×10^{-2} M KSCN solution), and then dilute 1.0 mL of that 100X stock to 100 mL (or 5.0 mL of that stock to 500 mL].

   Throughout this experiment, these solutions will be referred to as having concentrations of 0.2 mol · L^{-1} and 5.0×10^{-4} mol · L^{-1}, although in practice their concentrations will differ slightly from these figures. In any calculations, be sure to use the actual concentrations, not the concentrations listed in this manual.

2. Into a 100-mL beaker, pipette 25 mL of 0.20 mol · L^{-1} iron (III) nitrate solution and 25 mL of 5.0×10^{-4} mol · L^{-1} potassium thiocyanate. Use a 25-mL volumetric pipette equipped with a pipette filler to measure out the solutions. Refer to Experiment A2 if you have forgotten how to use a volumetric pipette. Mix the two solutions thoroughly (using a magnetic stirrer) for about 15 minutes in order to allow equilibrium to be established. Use the 15-minute waiting period to finish off a previous experiment, to start another experiment, e.g., Experiment D4, Le Châtelier's Principle, or to organize yourself for step 3. Note that in this reaction mixture the $[Fe^{3+}]$ is 200 times greater than the $[SCN^-]$. This ensures that, at equilibrium, all of the thiocyanate will have reacted and the $[Fe(SCN)^{2+}]$ will be 2.5×10^{-4} mol · L^{-1} (or half the actual concentration of the potassium thiocyanate solution used).

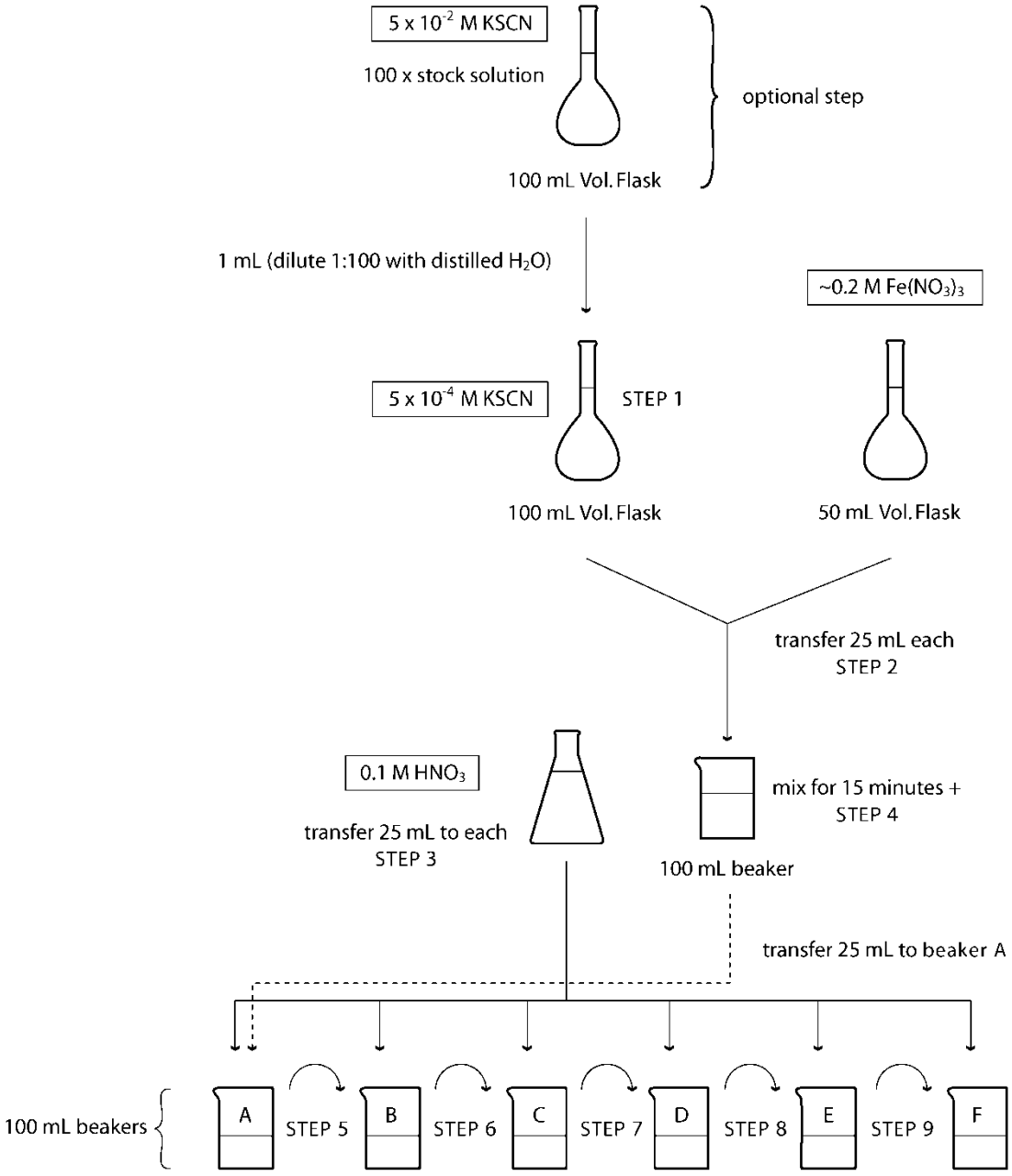
3. Obtain six clean, dry 100-mL beakers. Label the beakers A to F. Into each beaker pipette 25 mL of 0.1 mol · L^{-1} nitric acid using a 25-mL volumetric pipette.

4. When the reaction mixture prepared in step 2 has reached equilibrium, use a 25 mL volumetric pipette to transfer 25-mL of the mixture to the first beaker (beaker A) containing nitric acid. Allow the solution to mix well, stirring with a magnetic stirrer or a glass stirring rod.

5. Using a clean 25-mL volumetric pipette, transfer 25 mL of the solution from beaker A (step 4) into the second beaker (beaker B) containing nitric acid. Mix well.
6. Using the basic procedure described in step 5, transfer 25 mL of the solution from beaker B (step 5) to beaker C.
7. Transfer 25 mL of the solution from beaker C (step 6) to beaker D.
8. Transfer 25 mL of the solution from beaker D (step 7) to beaker E.
9. Transfer 25 mL of the solution from beaker E (step 8) to beaker F.

   You now have six beakers containing solutions of thiocyanatoiron (III) ions with concentrations ranging from 1.25×10^{-4} mol · L^{-1} (beaker A) to 3.9×10^{-6} mol · L^{-1} (beaker F). You will need to calculate the precise concentration of each solution later in the experiment.
10. If you have not already done so, switch on the Spectronic 20 spectrophotometer. Allow the instrument to warm up, set the wavelength to 445 nm, and set the 0% and 100% transmittance, as shown by your instructor. Use 0.10 mol · L^{-1} nitric acid in the "blank." Do not allow anyone to change the wavelength until you have completed the experiment.
11. Measure and record the absorbance of each of the six standard solutions prepared in steps 4 through 9. See your instructor for details of how to do this. As these results will be used to establish a calibration curve, each measurement should be done in duplicate. Use the same cuvette throughout the experiment, and always insert it in the sample compartment so that the orientation line on the cuvette is facing towards you.

Figure D3.1 Sample Flowchart for Part A.



NOTE: use a clean 25 mL vol. pipette for each transfer

Read all solutions in Spec20 @ A_{445nm}, steps 10 and 11.

B. Determination of the Equilibrium Constant

In this part of the experiment you will prepare five mixtures of iron (III) nitrate and potassium thiocyanate. By measuring the absorbance of the equilibrium mixtures, the equilibrium concentration of the thiocyanatoiron (III) ion will be determined and the equilibrium constant can then be calculated. (See flowchart on next page.)

1. Use a 5-mL volumetric pipette to transfer 5 mL of the 0.20 mol · L^{-1} iron (III) nitrate solution prepared in step 1 of Part A of the experiment to a 250-mL volumetric flask. Add 0.10 mol · L^{-1} nitric acid to the flask until the level of the solution in the flask reaches the graduation mark. Mix well. The concentration of the iron (III) ions in this solution is now approximately 4.0×10^{-3} mol · L^{-1}.

2. Obtain four clean, dry 50-mL volumetric flasks. Use a clean 25-mL volumetric pipette to transfer 25 mL of the solution prepared in step 1 to the first of these four flasks. Add 0.10 mol · L^{-1} nitric acid to bring the level of the solution in the flask up to the graduation mark. Mix thoroughly.

3. Use a clean 25-mL volumetric pipette to transfer 25 mL of the solution from the first (step 2) to the second volumetric flask. Again, bring the level of the solution up to the mark using 0.10 mol · L^{-1} nitric acid.

4. Repeat the procedure described in step 3 to dilute 25 mL of the solution from 3 to 50 mL.

5. Repeat the procedure described in step 3 to dilute 25 mL of the solution from 4 to 50 mL. The solutions prepared in steps 2 through 5 have concentrations ranging from (approximately) 2.0×10^{-3} mol · L^{-1} to 2.5×10^{-4} mol · L^{-1}.

6. Obtain five clean, dry 50-mL beakers. Label the beakers A to E. Use a 10-mL volumetric pipette to add 10-mL of the 5.0×10^{-4} mol · L^{-1} potassium thiocyanate solution prepared in step 1 of Part A of the experiment to each beaker.

7. Prepare five reaction mixtures in the five 50-mL beakers already containing 10 mL of 5.0×10^{-4} mol · L^{-1} potassium thiocyanate solution (i.e., beakers A to E) by using a 10-mL volumetric pipette to add the five iron (III) nitrate solutions prepared in steps 1 through 5 as follows:

To beaker	Add 10 mL of the solution prepared in step
A	1
B	2
C	3
D	4
E	5

8. Mix each solution thoroughly, and allow the mixtures to stand for at least 15 minutes in order for equilibrium to be established.

9. Record the absorbance at 445 nm of each of the five reaction mixtures.

Figure D3.2
Sample Flowchart for Part B

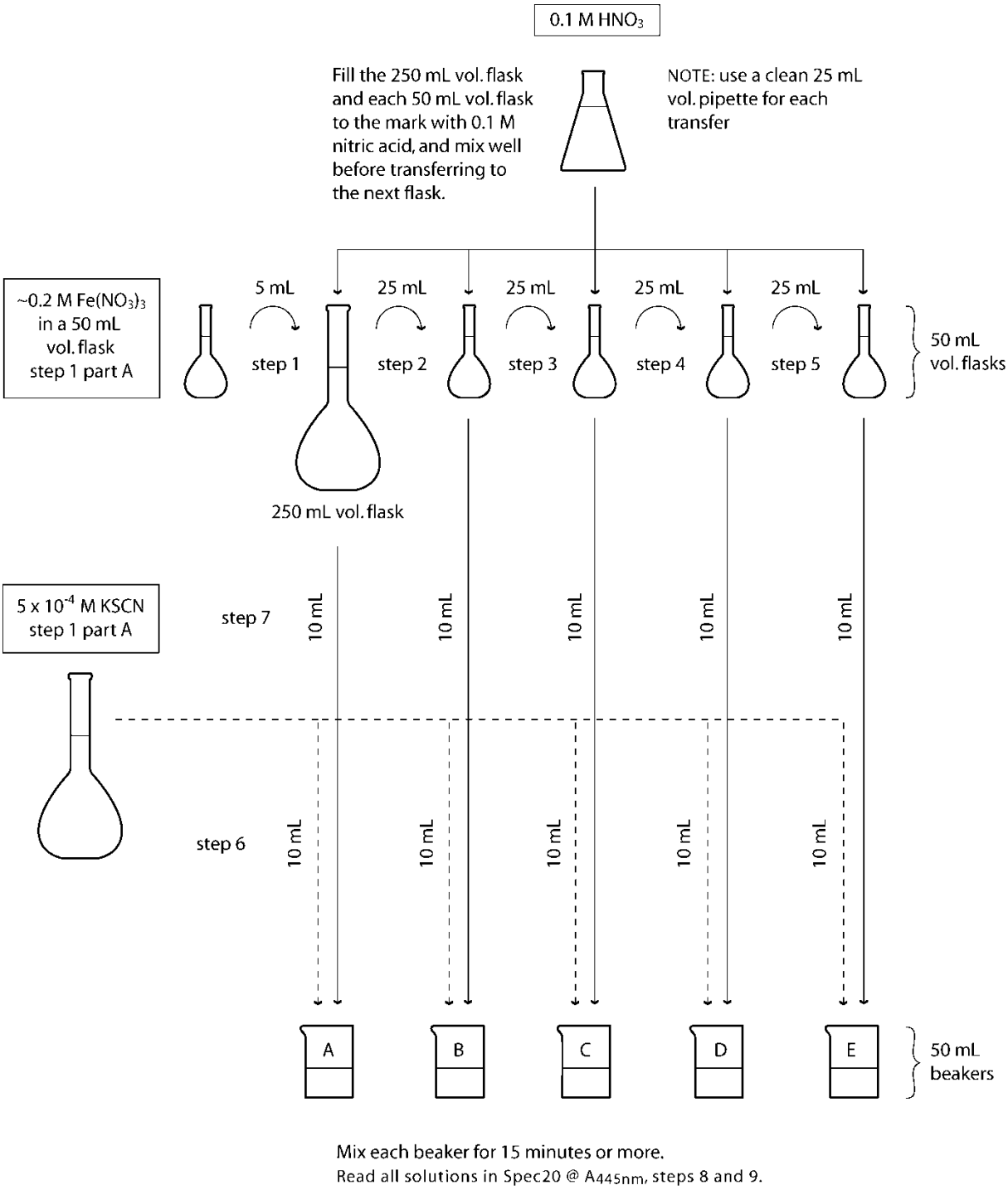


Figure D3.3 Operation of the Spectrophotometer (Spectronic 20)

1. Turn ON. Allow unit to warm up for 15 minutes.
2. Set ELECTRONIC ZERO using the 0% T Dial.
3. Set wavelength using the Wavelength Selector Dial (e.g., λ = 445 nm)
4. Insert BLANK cuvette into the sample compartment. Close lid.
5. Set Full Scale using the 100% T Dial.
6. Insert UNKNOWN cuvette into the sample compartment. Close lid.
7. Read %Transmittance (upper scale) or Absorbance (lower scale).
8. Reread BLANK cuvette to ensure it is still reading 100% T.

Note: When inserting the BLANK and UNKNOWN cuvettes into the spectrophotometer, be sure that the outside of the cuvette is clean and dry by polishing the glass with a tissue. Also place the cuvettes in the sample compartment in the same orientation each time.

WASTE DISPOSAL: The waste generated in this experiment may be disposed of by washing it down the drain with a large amount of water.

Note: When you have finished with the cuvettes, please return them to their box on the equipment bench. Do not mix these cuvettes with "regular" test tubes.

Experiment D4: Le Châtelier's Principle Procedure

When any of the three halogens, chlorine, bromine or iodine, is dissolved in water, the following equilibrium is established:

$$X_2\,(aq) + H_2O\,(l) \rightleftharpoons HOX\,(aq) + X^-(aq) + H^+(aq)$$

where X = Cl, Br or I.

1. **WARNING**: Bromine is toxic. Use disposable gloves, and do this part of the experiment in a fume hood.

   Pour 10 mL of bromine water (bromine dissolved in water) into a 50-mL beaker and place the beaker on a sheet of white paper. The yellow-brown colour of this solution is due to the presence of $Br_2(aq)$. All the other species present in this solution are colourless, thus the intensity of the yellow-brown colour gives you a rough estimate of the $[Br_2(aq)]$.

   Use a Pasteur Pipette to add sodium hydroxide ($3\ mol \cdot L^{-1}$) dropwise to the bromine water. Swirl the solution as the sodium hydroxide is added and record your observations. When there appears to be no further colour change, add sulfuric acid ($2\ mol \cdot L^{-1}$) dropwise, with swirling. Record your observations.

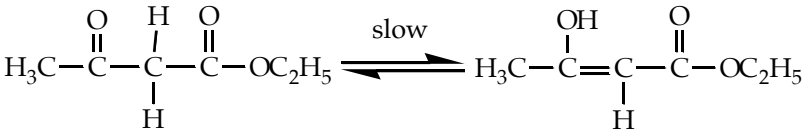
2. **WARNING:** Chromates and dichromates are suspected carcinogens. Do not permit these solutions to come into contact with your skin.

   Pour 10 mL of potassium chromate solution ($0.1\ mol \cdot L^{-1}$) into a 50-mL beaker and place the beaker on a sheet of white paper. Add several drops of sulfuric acid ($2\ mol \cdot L^{-1}$), and observe any colour change that may occur. Next add a few drops of sodium hydroxide solution ($3\ mol \cdot L^{-1}$) to the solution in the beaker, and observe any colour change. The equilibrium system that you are observing is as follows:

   $$\underset{\text{(yellow)}}{CrO_4^{2-}\,(aq) + 2H^+\,(aq)} \rightleftharpoons \underset{\text{(orange)}}{Cr_2O_7^{2-}\,(aq) + H_2O\,(aq)}$$

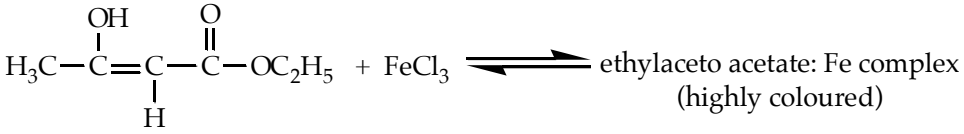
3. **WARNING:** Bromine is toxic. Use disposable gloves and carry out this part of the experiment in a fume hood.

   In the equilibrium systems studied so far, the response of the system to the addition of a reagent appeared to be almost instantaneous. This is not always the case. Ethylaceto acetate exists as an equilibrium mixture of two forms (called tautomers):

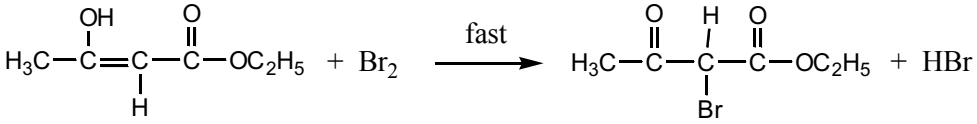


keto form enol form

If a solution of iron (III) chloride is added to ethylaceto acetate, a coloured solution is obtained due to a reaction between the enol form and the iron (III) chloride.



Note, however, that the enol form of ethyl acetoacetate will also react with bromine water:

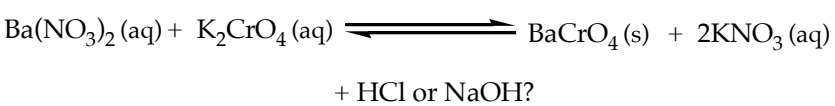


Add 5 drops of ethyl acetoacetate to 5 mL of distilled water in a large test tube. Mix the solution well and then add 3 drops of iron (III) chloride (1 mol · L^{-1}) solution. Mix well, and note the colour of the solution. Quickly add a few drops of bromine water—the colour of the solution should fade. Allow the tube to stand for a few minutes and record your observations. When you observe a colour change, repeat the process by adding a few more drops of bromine water.

4. **WARNING**: Part 4 of this experiment involves the use of chromate/dichromate solutions. These substances are suspected carcinogens. Avoid contact with your skin.

   Obtain 4 small test tubes, and a test tube rack from the supply bench.

   In the first small test tube, mix 1 mL of barium nitrate (0.1 mol · L^{-1}) with 0.5 mL of potassium chromate (0.1 mol · L^{-1}). Record your observations. Now add hydrochloric acid (3 mol · L^{-1}) drop wise to the contents of the test-tube, shaking the tube after each drop is added. Record your observations. When no solid remains in the tube, add a few drops of sodium hydroxide solution (3 mol · L^{-1}). Again, record your observations.



   In the second small test tube, mix 1 mL of barium nitrate (0.1 mol · L^{-1}) with 0.5 mL of potassium dichromate (0.1 mol · L^{-1}). Record your

observations. Acidify the contents of the tube by adding 10 drops of hydrochloric acid (3 mol · L^{-1}).

$$Ba(NO_3)_2\,(aq) + K_2Cr_2O_7\,(aq) \rightleftharpoons ? \quad + HCl?$$

In the third small test tube, place 1 mL of barium nitrate solution (0.1 mol · L^{-1}), and add 5 drops of hydrochloric acid (3 mol · L^{-1}), followed by 5 drops of potassium chromate solution (0.1 mol · L^{-1}). Record your observations.

In the fourth small test tube, place 1 mL of barium nitrate solution (0.1 mol · L^{-1}), followed by 5 drops of acetic acid (3 mol · L^{-1}), and finally add 5 drops of potassium chromate solution (0.1 mol · L^{-1}). Record your observations, and compare your results with those obtained in the previous test.

Part 4. Observations Table

Test Tube	Reagents	Observations
1	1 mL $Ba(NO_3)_2$ + 0.5 mL K_2CrO_4 + drops HCl,?, + drops NaoH ?	
2	1 mL $Ba(NO_3)_2$ + 0.5 mL $K_2Cr_2O_7$ + 10 drops HCl	
3	1 mL $Ba(NO_3)_2$ + 5 drops HCl + 5 drops K_2CrO_4	
4	1 mL $Ba(NO_3)_2$ + 5 drops CH_3CO_2H + 5 drops K_2CrO_4	

WASTE DISPOSAL: Solutions containing chromium should not be permitted to enter the environment. Place all solutions containing chromate or dichromate in the special container provided. The reaction mixture from test 3 should be placed in the special container provided. The reaction mixture from test 1 may be washed down the drain with large quantities of water.

Experiment D5: Titration Curves Procedure

A. Titration Curve for the Reaction Between a Strong Acid and a Strong Base

1. Collect about 35 mL of the standardized hydrochloric acid from the supply bench. Note the precise concentration of this solution, it should be about 0.100 mol · L^{-1}. Similarly, collect about 75 mL of the "unknown" sodium hydroxide solution from the supply bench. You will not be told the precise concentration of this sodium hydroxide solution, but it will be approximately 0.100 mol · L^{-1}.

2. Use a volumetric pipette to transfer 10.00 mL of the hydrochloric acid to a 100 mL beaker and, using a graduated cylinder, add about 20 mL of distilled water to the acid.

3. Place the beaker on a magnetic stirrer/hot-plate, place a small stirrer bar in the solution, and set the stirrer in motion—not too fast, otherwise some of the acid may splash from the beaker.

4. Fill your burette with the sodium hydroxide solution. (See Experiment A2 if you need to review the procedure for using a burette.)

5. Obtain a pH meter from the supply bench. Detailed instructions on the use of the pH meter will be provided, as the exact method of operation varies from one model to another. If you do not understand the instructions provided, please ask the lab supervisor for a demonstration. Position the pH meter so that it is close to the stirrer/hot-plate. Immerse the tip of the electrode into the hydrochloric acid and record the pH of the solution to two places past the decimal.

   Note: The pH meter electrode should always be kept moist. Thus, when the meter is not in use, the electrode tip should be kept immersed in distilled water.

6. Position your burette so that you can begin to add sodium hydroxide to the beaker of hydrochloric acid. The best way to do this may be to stand the stirrer/hot-plate on the base of the retort stand to which your burette clamp is attached. Add the sodium hydroxide approximately 0.5 mL at a time **until a total of 9.0 mL has been added.** Remember to read your burette to two places past the decimal. Record the pH of the solution after the addition of each 0.5 mL aliquot. Continue adding the sodium hydroxide, but now in approximately 0.2 mL aliquots, **until a total of 11.0 mL has been added.** As before, record the pH and total volume of sodium hydroxide after each aliquot has been added. Finally, add more sodium hydroxide in approximately 0.5 mL aliquots **until the total volume of sodium hydroxide added is 18.0 mL.** Again the pH of the solution should be recorded after each addition. The above procedure may be summarized as follows.

Volume of sodium hydroxide added:	pH measurement made:
0–9.0 mL	approximately every 0.5 mL
9.0 mL–11.0 mL	approximately every 0.2 mL
11.0 mL–18.0 mL	approximately every 0.5 mL

B. Titration Curve for the Reaction Between a Weak Acid and a Strong Base

1. Collect about 35 mL of the "unknown" solution of acetic acid from the supply bench. You will not be told the precise concentration of this acetic acid, but it will be approximately 0.100 mol · L⁻¹.
2. Use a volumetric pipette to transfer 10.00 mL of the acetic acid to a 100-mL beaker and, using a graduated cylinder, add about 20 mL of distilled water to the acid.
3. Place the beaker of acetic acid on a stirrer/hot-plate and stir the solution gently (as in step 3 of Part A).
4. Fill your burette with the sodium hydroxide solution used in Part A.
5. Repeat the procedure described in steps 5 and 6 of Part A, using the solution of acetic acid instead of hydrochloric acid and the suggested addition volumes/ranges below.

Volume of sodium hydroxide added:	pH measurement made:
0–8.5 mL	approximately every 0.5 mL
8.5 mL–11.0 mL	approximately every 0.2 mL
11.0 mL–18.0 mL	approximately every 0.5 mL

WASTE DISPOSAL: All the solutions used in this experiment may be disposed of by washing them down the sink.

6. .

Experiment E1:
Voltaic Cells Procedure

1. Collect a clean U-tube and fill it completely with potassium chloride solution (1.00 mol · L^{-1}). Wrap some glass wool into a smooth, very tight ball to form a plug for the end of the U-tube. Saturate the plug with potassium chloride by immersing the glass-wool ball in some potassium chloride solution. This will minimize the number of air bubbles that get trapped in the salt bridge. Insert the plug into one end of the U-tube. Form a second glass-wool plug and saturate this plug with potassium chloride as described above. Before inserting this plug into the open end of the U-tube, check that there are no air bubbles in the tube and that the side to be plugged is completely filled with potassium chloride solution. Insert the second glass-wool plug and invert the salt bridge. No solution should leak from the bridge when it is inverted.

2. Obtain two 100-mL beakers. Into the first beaker pour 50 mL of zinc sulfate solution (1.00 mol · L^{-1}), and into the second beaker pour 50 mL of lead (II) nitrate solution (1.00 mol · L^{-1}).

3. Obtain a strip of zinc metal and a digital pocket multimeter (a voltmeter). Use the alligator clip provided to connect one of the wires from the multimeter to the zinc strip. Lower the metal strip into the zinc sulfate solution so that about 2–3 cm of the metal is below the surface of the solution. Use a stand and clamp to support the insulated wire and keep the electrode in position. Similarly, connect a strip of lead to the second wire from the multimeter and immerse this metal strip into the solution of lead (II) nitrate. Again, clamp the wire so that the metal strip does not touch the side of the beaker.

4. Set the function switch on the multimeter to DCV. The reading that you observe will not make sense. No voltage is produced. Without a salt bridge the cell does not work!

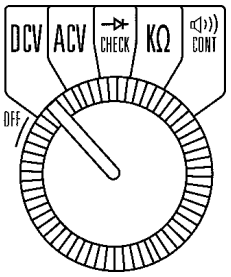


Figure E1.1:
Multimeter Switch Setting

5. Lower the salt bridge into position so that one end of the U-tube is immersed in the lead (II) nitrate solution and the other end is in the zinc sulfate (see Figure E1.1).

   Note: Ensure that the level of solution is the same in both beakers before you set the salt bridge in place, otherwise a siphon effect may occur.

   Clamp the salt bridge into position and determine the voltage produced by the cell. If the reading on the multimeter is negative, simply reverse the connections.

6. Disconnect the electrodes and remove the salt bridge from the solutions. Rinse the salt bridge by dipping the ends in distilled water. Remember to keep the salt bridge inverted at all times.

7. Pour 50 mL of copper (II) sulfate solution (1.00 mol · L⁻¹.) into a clean 100-mL beaker. Connect a strip of copper metal to one of the wires from the multimeter and immerse the bottom 2–3 cm of the copper metal in the copper (II) sulfate solution. Construct a voltaic cell using this half-cell and the zinc metal/zinc sulfate solution half-cell from step 3. Measure the voltage produced by this cell.

8. Disconnect the electrodes and again rinse the ends of the salt bridge in distilled water. Construct a third voltaic cell using the copper metal/copper (II) sulfate half-cell from step 7 and the lead metal/ lead (II) nitrate half-cell from step 3. Record the voltage produced.

Alternative Voltaic Cell Setup

1. Use only 0.1M heavy metal solutions and use 0.1M potassium nitrate for the salt bridging solution. Use filter paper strips, saturated with 0.1 M potassium nitrate, for the salt bridges.

2. Connect and then swap your voltmeter leads between any two of the cells to quickly find the voltages. See Fog.E.1.3.

WASTE DISPOSAL: The solutions of lead (II) nitrate, zinc sulfate, and copper (II) sulfate should be placed in the waste containers provided.

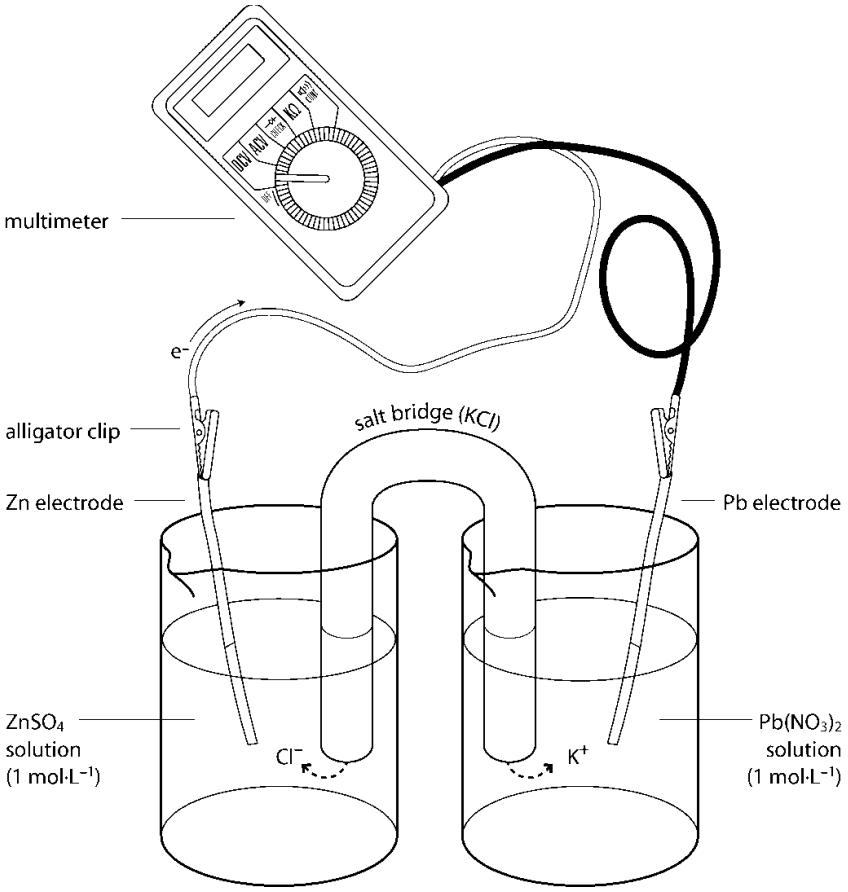


Figure E1.2:
Set up of half-cells

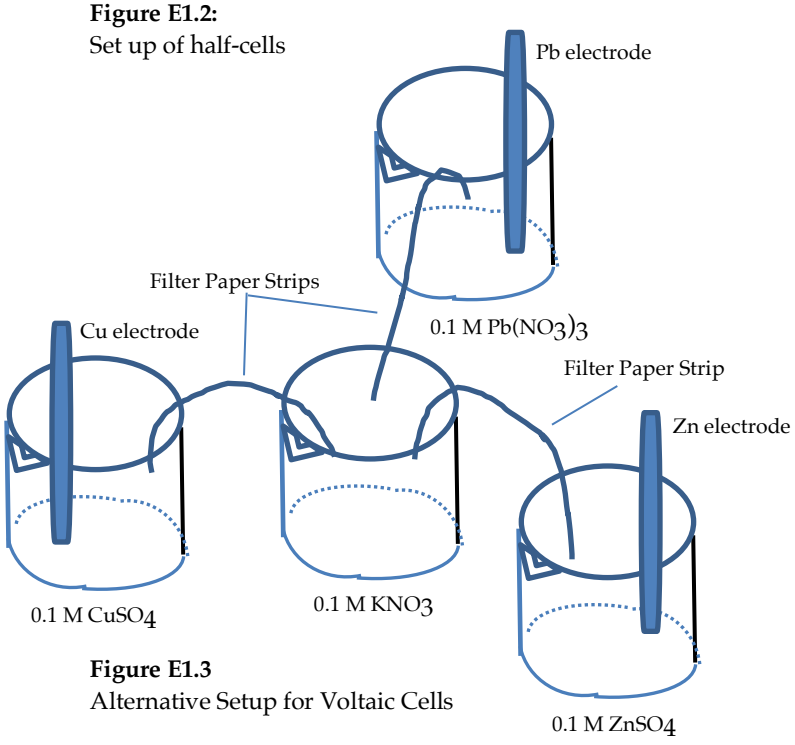
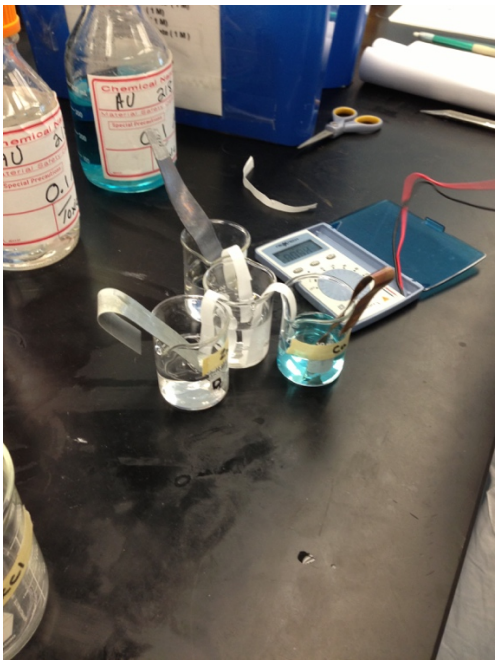


Figure E1.3
Alternative Setup for Voltaic Cells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Experiment E2: Determination of a Molar Mass by Electrolysis Procedure

A. Electrolysis Reaction Setup

1. Your instructor will provide you with an unknown metal strip. **Determine the mass of this strip using an analytical balance.**

2. Obtain two clean 250-mL beakers. Into the first beaker pour 150 mL of sulfuric acid (1.0 mol · L^{-1}) and into the second beaker pour 150 mL of potassium nitrate solution (0.5 mol · L^{-1}). Use a graduated cylinder for these measurements.

   CAUTION: Sulfuric acid (1.0 mol · L^{-1}) is corrosive. Wear disposable gloves when measuring out this substance. Be sure to wear your safety glasses throughout the experiment.

3. Use a retort stand to support an inverted burette. Insert the bare, coiled end of the heavy copper wire into the mouth of the burette, and lower the burette into the beaker containing the sulfuric acid (see Figure E2.1 on following page).

   Note: Only the coiled end of the copper wire should be bare; the rest of it should be covered with watertight insulation.

4. Attach a large rubber bulb to the tip of the burette as shown in Figure E2.1. Open the stopcock, and use the rubber bulb to draw sulfuric acid into the burette until the level of the acid is approximately at the 0-mL mark (near the top). Close the stopcock.

   Note: Do not allow the level of the sulfuric acid to go higher than the 0-mL mark.

5. Connect your strip of unknown metal to the positive terminal of the power source using the wire and alligator clips provided. Partially immerse the metal strip into the potassium nitrate solution as shown in Figure E2.1.

   CAUTION: Do not allow the alligator clip that connects the metal to the wire to come into contact with the potassium nitrate solution. Use a retort clamp to prevent this from happening.

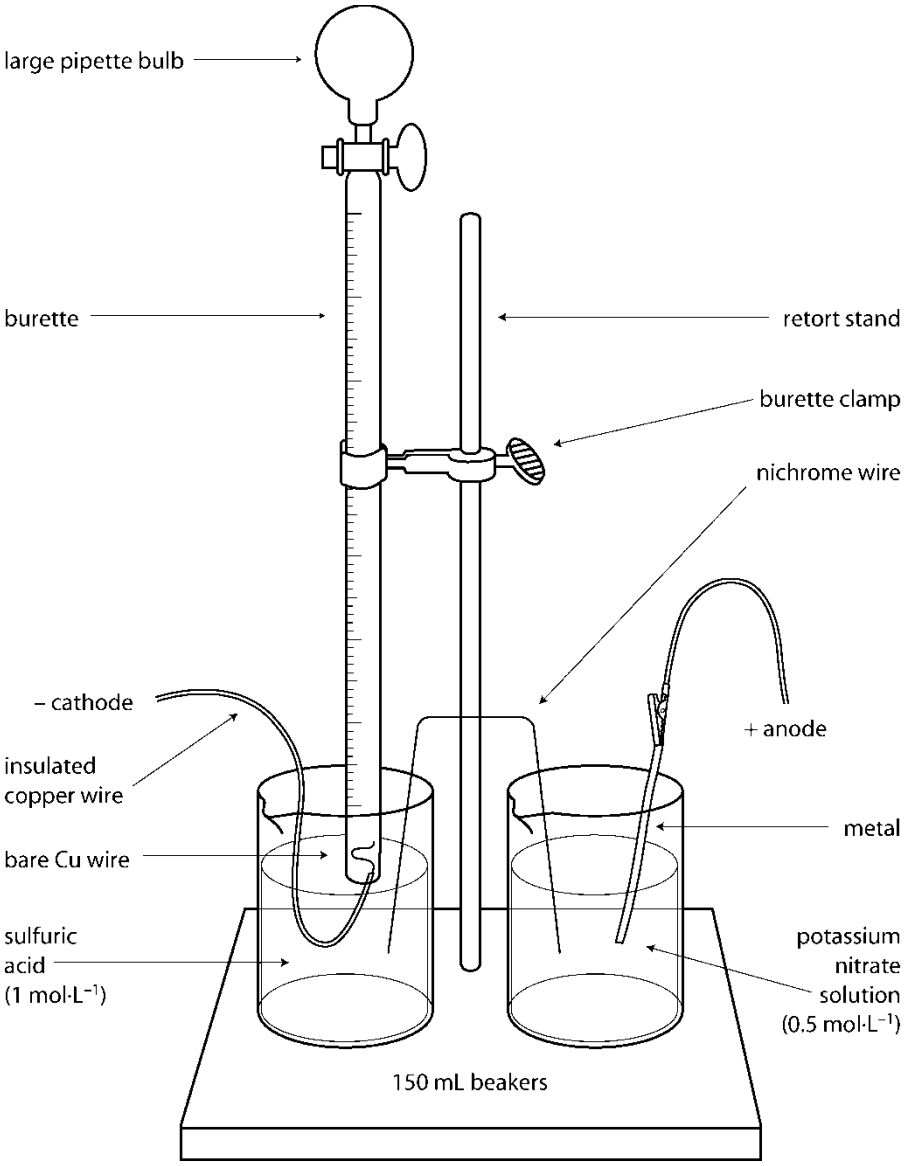


Figure E2.1:
Apparatus set up

6. Connect the two half cells by placing one end of a bent piece of nichrome wire so that each end is partially immersed in the solutions (see Figure E2.1). The wire used should be about 40 cm long.

   CAUTION: During the course of the electrolysis, some of the nichrome wire may dissolve. Check periodically to ensure that the wire has not dissolved to the extent that it is no longer in contact with both solutions. If so, re-immerse the wire in the solutions.

7. Record the level of the sulfuric acid in the burette. Remember to read the burette to two places past the decimal.

B. Electrolysis of Unknown Metal

1. Begin the electrolysis by connecting the copper wire to the negative terminal of the power source. Hydrogen gas should immediately begin to form at the copper cathode. Allow the electrolysis to continue until about 50 mL of gas has been collected in the burette. Stop the electrolysis by disconnecting the copper wire from the negative terminal of the power source. Record the level of the sulfuric acid in the burette.

2. Use the rubber bulb to again draw sulfuric acid up the burette as described in step A4.

3. Repeat the electrolysis by again performing steps B1 and B2.

4. After the second electrolysis has been completed and the copper wire has been disconnected from the power source, remove the metal anode from the electrolysis cell and rinse it carefully with dilute ($0.1\ mol \cdot L^{-1}$) acetic acid. If the metal is covered by a flaky substance, remove the latter by gently scraping the electrode and rinsing it once again with the dilute acetic acid. Finally, dip the electrode in acetone, allow the acetone to evaporate, and then determine the mass of the electrode using an analytical balance.

5. Record the air temperature and the barometric pressure. Use the *Handbook of Chemistry and Physics* to determine the vapour pressure of water at the prevailing room temperature.

Note: During the course of the electrolysis, some cloudiness and discolouration may appear in the two solutions. This is the result of various side-reactions that occur and does not affect the results of the experiment.

WASTE DISPOSAL: The solutions used in the electrolysis should be placed in the waste containers provided.

Experiment F1:
The Preparation of Acetylsalicylic Acid (Aspirin®)Procedure

A. The Preparation of Crude Acetylsalicylic Acid

1. Use a general-purpose balance to measure out about 3.1 g of salicylic `acid. Transfer the salicylic acid to a 125-mL Erlenmeyer flask. **Carry out Steps 2 through 4 in the fume hood.**

2. Carefully add 10 mL of acetic anhydride and 2 mL of concentrated phosphoric acid to the flask containing the salicylic acid. Swirl the flask gently to dissolve any salicylic acid crystals that may adhere to the walls of the flask.

   CAUTION: Wear gloves when measuring out acetic anhydride and phosphoric acid. Acetic anhydride has an irritating odour. Phosphoric acid (85%) is a strong acid. Both substances can cause severe chemical burns.

3. Obtain about 200 mL of hot water in a large, flat-bottom dish and heat the water to a temperature of about 75° C on a hot plate. Clamp the 125-mL Erlenmeyer flask so that it is partially immersed in the dish of water. In this way, heat the contents of the flask for about 15 minutes, swirling the flask occasionally. (If available, a magnetic stirrer may be used to keep the solution stirred.)

4. Cool the flask, but while it is still warm, add about 1 mL of distilled water one drop at a time in order to decompose any excess acetic anhydride. After any reaction has subsided, add 20 mL of cold water and cool the Erlenmeyer flask in an ice water mixture (an "ice bath"). Crystals should begin to appear. Allow the crystals to form for at least 30 minutes.

B. The Recovery of Crude Aspirin

1. Set up the apparatus for suction filtration (see Figure F1.1) and filter off the crude aspirin. Use small portions of **ice-cold** distilled water to rinse the flask and wash the crystals.

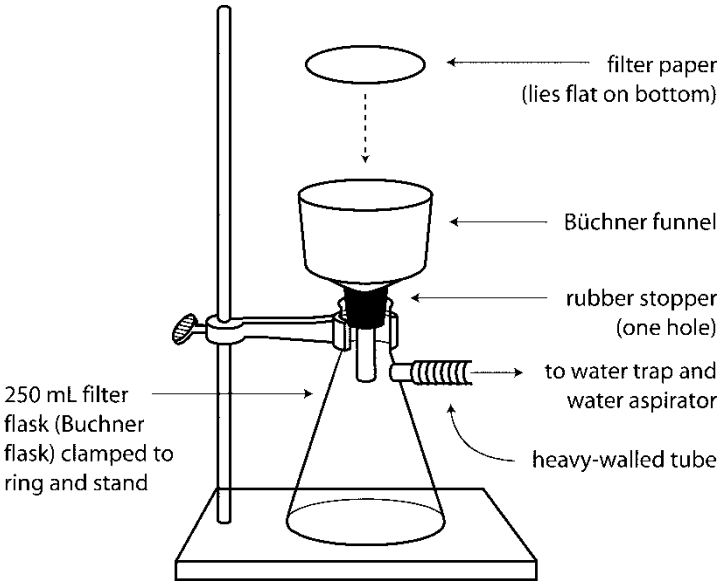


Figure F1.1:
Apparatus for suction (vacuum) filtration

C. The Purification of ASA–Removal of High Molar Mass Byproduct

1. Dismantle the vacuum filtration apparatus. Pour the filtrate down the drain and rinse the vacuum flask with water. Remove the crude ASA from the Buchner funnel and dissolve it in 40 mL of saturated sodium hydrogen carbonate solution in a 250-mL beaker. Stir the solution until all signs of reaction have ceased. Then gravity filter the dissolved aspirin solution through a cone filter. Wash any solid that remains on the filter paper with a few millilitres of ice-cold water from your wash bottle.

2. Prepare a solution of dilute hydrochloric acid by adding 6 mL of concentrated hydrochloric acid to 15 mL of water in a 150-mL beaker. **Alternatively**, your lab instructor might supply you with 6 M HCl, in which case you would add 12 mL of 6M acid to 9 mL of water. Carefully (i.e., a few millilitres at a time), and with constant stirring, pour the gravity filtrate from step C1 into this hydrochloric acid solution. Acetylsalicylic acid will precipitate.

   CAUTION: Wear gloves when using concentrated hydrochloric acid. Remember to ADD ACID TO WATER, NOT VICE VERSA.

3. Cool the mixture in an ice bath and filter off the solid by suction filtration (as per step B1). Wash the product with a **small** quantity of **ice-cold** water.

D. The Purification of Aspirin–Recrystallization

Recrystallize the acetylsalicylic acid as follows:

Recrystallization from isopropanol (no colored impurities present therefore no need to add charcoal, and therefore no hot gravity filtration).

1. Transfer the solid from the Buchner funnel to a clean 50 or 125 mL Erlenmeyer flask and add approximately 10 mL of isopropanol. You may wish to use some of this isopropanol to help transfer the last of the solid.

2. Add a stirring bar and stir the mixture on a stirring hot plate. If a stir bar is not available, add a few boiling stones instead. Heat the mixture at a medium setting until the acetylsalicylic acid has dissolved. If the solution boils before the solid is fully dissolved, continue heating gently and add small amounts of isopropanol until it dissolves.

3. Once the solid has dissolved, remove the flask from the heat and allow it to cool on your bench. While you are waiting, Place an additional 10 mL of isopropanol in another small flask and cool it in an ice bath.

4. Once crystals begin to form in the flask containing the dissolved acetylsalicylic acid, transfer the flask to an ice bath. If crystals do not form, transfer the flask to an ice bath once it cools to room temperature. If crystals still do not form, ask your instructor for assistance.

5. After at least 10 minutes in the ice bath, recover the recrystallized product by vacuum filtration. Wash the crystals with the cold isopropanol from step 3. You may also use the cold isopropanol to help transfer the solid from the flask to the Buchner funnel.

6. Allow the product to dry under vacuum, then collect and weigh it to determine the yield.

Alternative recrystallization from water (insoluble and or colored impurities present).

1. Transfer the aspirin to a clean 125-mL Erlenmeyer flask, add a few boiling stones, and then add boiling distilled water to the flask until all the acetylsalicylic acid (ASA) has just dissolved (33ulphat. 40–50 mL). During this addition, the contents of the Erlenmeyer flask should be kept on the boil by heating the flask on a hot-plate. Obtain a short-stemmed funnel from the supply bench and place it, along with a clean, dry 125-mL Erlenmeyer flask, in the oven to warm (> 100° C). Remove the flask containing the ASA solution from the hot-plate and allow it to cool slightly while you prepare a fluted filter paper. To the hot (but not boiling) solution add a pinch of activated charcoal. Place the flask back onto the hot-plate and once more bring the contents to the boil.

2. Filter the contents of the flask through the fluted filter paper set in the pre-heated, short-stemmed funnel supported by a ring clamp so that the filtrate drips into the pre-heated 125-mL Erlenmeyer flask (see Figure F1.2). Should premature crystallization occur and clog the filter paper, transfer the crystals and the filter paper to the original Erlenmeyer, add an appropriate amount of boiling water to redissolve the ASA, and filter as before with a new fluted filter paper. (See note below for instructions on how to fold the filter paper.)

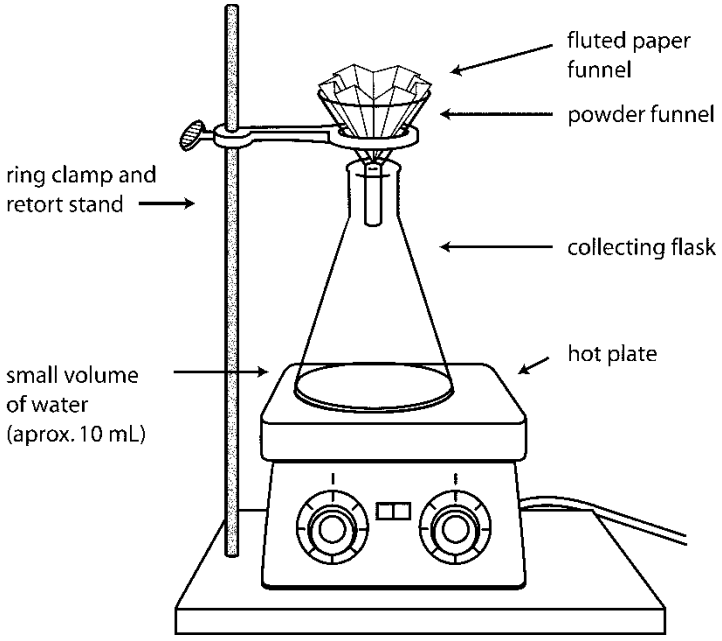


Figure F1.2:
Arrangement for hot gravity filtration

3. Place a cork or rubber stopper in the mouth of the Erlenmeyer flask and allow the filtrate to cool slowly. Crystals should begin to appear after a few minutes. **Note:** If the crystals appear too quickly, for example, if solid appears as soon as the filtrate runs into the receiving Erlenmeyer flask, this is a sign that not enough solvent (water) has been used. In such situations, a small amount of water should be added to the flask, and its contents warmed on the hot-plate until the solid disappears.

4. After the flask has air cooled for about 30 minutes it should be chilled thoroughly in an ice bath for a further 15–20 minutes. The crystals should then be separated from the mother liquor by suction filtration (see Figure F1.1). Use small portions (2 × 10 mL) of ice-cold distilled water to rinse/wash your crystals in the Büchner funnel. Allow the crystals to dry partially by leaving them in the Büchner funnel for at least 30 minutes, then remove the crystals and filter paper from the funnel, and gently scrape the crystals onto a large, pre-weighed watch-glass. Allow the crystals to air dry for the rest of the day, and just before you leave, determine the mass of recrystallized ASA obtained by weighing the watch-glass and the recrystallized ASA.

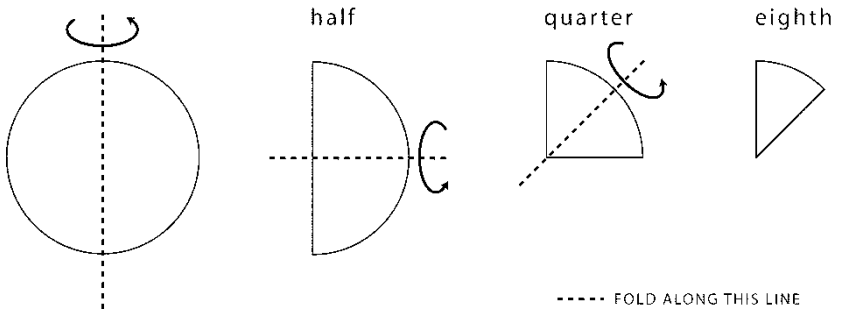
5. Transfer the recrystallized ASA to a sample bottle. Label the bottle with your name and hand it to your instructor. Your sample will be graded according to both quantity and quality.

Note:

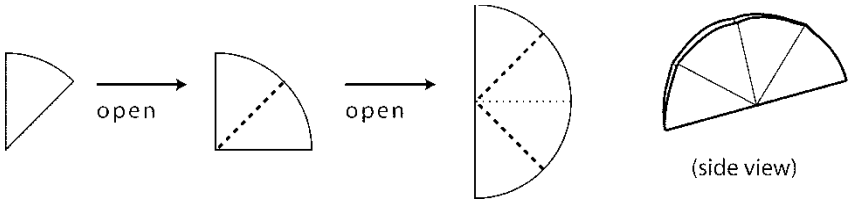
Fluted Filter Paper

You will need to fold your filter paper in a "fluted" manner to increase the surface area that is in contact with your filtrate in this experiment. The following instructions will show you how to flute your filter paper. It is essentially basic Origami for chemists.

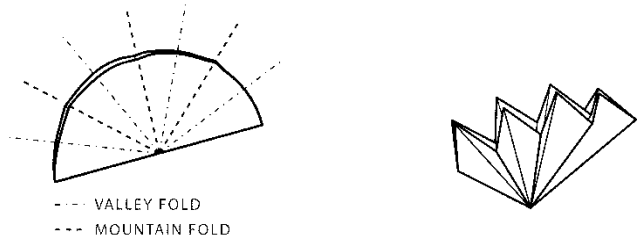
1. Fold paper in half, then in half again and then in half again in the same direction. You should have a 1/8 section cone.



2. Unfold this cone twice so it looks like a semicircle.



3. Now try a "fan fold." Alternately fold up and down every eighth section of the semicircle.



4. Open the fan until you get a fluted filter cone.

5. As a final touch, try to find the two opposing sections that are not folded correctly. Fold them inward to complete your perfect fan-folded filter paper.

Note: To make all creases, fold and press the paper. Do **not** run your finger or thumbnail along the folds. It may weaken the paper enough to introduce unwanted holes during filtration.

Optional Recrystallization Method

ASA tends to decompose when recrystallized from boiling water. Therefore one may use a two solvent recrystallization method instead. Dissolve the crude ASA in a minimum amount of hot methanol, and then pour in 2× volumes of distilled water at 45° C. If a solid or oil appears heat gently until it all redissolves. Finally cool the flask slowly to allow the pure ASA crystals to form.

Test for Salicylic Acid (if you dare!):

Place 100 mg of your "pure" recrystallized ASA into a test tube. Add 1–2 drops of 1% $FeCl_3$ solution. If the solution remains clear, your product is pure. If the product turns a deep red colour, the product contains salicylic acid (from unreacted starting reagent or from decomposed ASA), and therefore should be recrystallize a second time.

You can set up positive and negative controls for this test by asking the instructor for authentic standards of salicylic acid and acetylsalicylic acid.

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