Chemistry 218
Chemical Principles II

Laboratory Manual 2019-21

Athabasca University

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Printed in Canada

SLID 060618

Contents

† These labs require *formal reports;* all others require only a *short* report.

Acknowledgements

This *Chemistry 218 Laboratory Manual* has evolved over many years (since 1993), and the lead author appreciates and says thanks for all the comments and contributions of Jason Norman, Ross Witherell, Dietmar Kennepohl, Darinka Rising, Klaus Thomson, Nyron Jaleel, Jim Robinson, Rob Carmichael, and Arthur Last, and suggestions from students.

In the 2003-04 of the *Chemistry 218 Laboratory Manual*, the artistry and skill of Blaise MacMullin and Ian Grivois was added to the course team, with the dramatic improvement to all illustrations and photographs. Computer Lab simulations, based on Falcon Software's *Explore Chemistry*, were removed from the lab course in 2006. For many years the lab sim tutorial program, written by Jonathan Lociero, and the student instructions for the lab sims, written by Karen Rosa, served our student needs perfectly. In 2010, we added an Appendix section about Graphs, and corrected several step reference typos in Exp.E2 and F1 of the experiments. In this latest version of the manual (2019), we have added an alternative setup for Exp. E1, and we have made a 'procedures only' section for printing ease.

The experiments described in this laboratory manual are mainly variations of similar experiments that may be found described in the laboratory manual of other universities or in commercially produced lab texts. Each experiment has been modified and rewritten, keeping the particular needs of Athabasca University students in mind. The following sources are hereby acknowledged.

Chemistry 209 Laboratory Manual, Athabasca University. (Experiments D1, D2, D3, E2, and F1)

Chemistry 1000/1200/1001 Laboratory Manual, Sir Wilfred Grenfell College, 1982–83.

Chemistry 2420 Laboratory Manual, Sir Wilfred Grenfell College, 1983. (Experiment F1)

Over the years, many people, including the author of the present manual, contributed to the experiments described in this source, these contributors include: Drs. Geoff Rayner-Canham, Michael Webb, Robert Perkins, Mark van Roode, and Samuel Nyarku; Mr. Gary Butler; Mr. Rod Byrne; Mr. Brian Worthington; and Mrs. H. Naidu. (Experiments D4), and Robert D. Carmichael (Experiment F1).

Experiment D5 is based on materials provided by Dr. G. Rayner-Canham, and by Harris and Kratochvil, 1979, *Introduction to Chemical Analysis*, prelim. ed., *Chemistry 312 Laboratory Manual*, University of Alberta.

Special thanks to Roberta Franchuk and Elaine Goth-Birkigt for checking the experiments, and initially organizing the material for this lab.

General Information

Introduction

Welcome to the laboratory component of Athabasca University's *Chemistry 218*. Although the laboratory component of this course will involve a lot of work, we hope that you will find the experience both intellectually stimulating and enjoyable. One of the benefits of having a compulsory laboratory component in a course such as ours is that it gives students an opportunity to meet their Laboratory Coordinator, other AU students and, in some cases, their tutor. Such opportunities are rarely provided for the majority of Athabasca University students.

If you were to take a course such as *Chemistry 218* in a traditional college or university, you would probably be expected to attend a three-hour laboratory session every week for 10 to 12 weeks. During this time you would complete 10 to 12 experiments and would receive somewhere in the order of 30 hours of laboratory instruction. In our course, you will receive 16 hours of supervised laboratory time, spread over two days, and will complete 8 in-laboratory experiments. In the supervised laboratory session there is a brief introduction and safety presentation, but NO pre-lab lectures for the individual experiments. As such, the students must take the time in advance to prepare for their experimental work. Unlike traditional universities where one experiment is carried out per session, we will be running as many as eight different experiments at once.

Preparation and organization by the student before stepping into the teaching laboratory is vital!

At this time we would like to bring to your attention several points that will enhance your laboratory experience and minimize any potential problems.

1. **Hours of work.** At each day-long laboratory session, you will be working for approximately eight and one-half hours. *Your instructor will ensure that you take a proper lunch break, but we also recommend that you take both a morning and an afternoon refreshment break.* Regular breaks make it easier for you to concentrate while you are working, and will decrease the likelihood of an accident. As the level of fumes in the laboratory will increase during the day, we also recommend that you take a brief walk outside during one or more of your breaks.

2. **Feedback**. Many first year laboratory courses operate on the principle that a student submits his or her laboratory report shortly after having completed an experiment, and that the report is returned a few days later, before the student attempts the next experiment. In the Athabasca system this is clearly not possible. After completing your two days of laboratory work you will have to write up at least one report, submit it by mail to your tutor, and then wait for some feedback. We hope that the response can be provided before you submit the rest of your lab reports. *Remember, if you have difficulty in writing your laboratory report, contact your tutor.* Also remember to keep a duplicate copy of all your experimental results—we will suggest a method for doing this in the section titled "Writing Laboratory Reports."

Note: For security reasons we cannot return your reports. However, you will be given feedback by phone or mail.

3. **Preparation**. Whereas the student in a traditional institution needs to prepare only one experiment at a time, Athabasca students must prepare several at once.

   Note: Before attending the first laboratory session, you must read though each of the five experiments in Block D, making sure that you understand exactly what you will be doing, noting possible problems, and so on.

Organization

The supervised laboratory sessions of *Chemistry 218* comprises approximately 16 hours of laboratory work. Usually, this will be completed in two day-long sessions. The experiments have been grouped into three "Blocks" as in *Chemistry 217*. Please refer to the 'Contents' page at the beginning of this manual for a list of the experiments that you will be doing.

All students will complete a short quiz at the end of Block F. This quiz will cover laboratory safety, techniques and procedures, and the basic principles upon which some of the experiments are based. Your instructor will inform you whether the quiz will be written or oral or on-line.

As you can see, a total of 8 in-lab experiments are described, and others may be added as we find it necessary to modify the course. You will be required to complete five (5) short reports and three (3) formal reports for the lab experiments. Formal reports are required for Experiments D3, E2 and F1.

The *Chemistry 218* laboratory sessions may differ from other laboratory classes that you have attended in that not all of the students present will be working on the same experiment at any given time. Thus, at any given time during the first laboratory session, you may observe three students working on Experiment D3 and six working on D4, while the rest of the class is working on D5. The course is organized in such a way that most of the experiments within a given Block can be completed in any order.

Materials to Be Provided by the Student

When attending a supervised *Chemistry 218* laboratory session, each student must provide herself or himself with the following items:

- CHEM218 Lab Manual –downloaded from our website.

- a lab coat
- an electronic calculator
- a lab notebook
- a pen, a pencil and a ruler
- a supply of metric graph paper (i.e. 1 mm × 1 mm squares).

Notes:

1. Lab coats can usually be purchased at college or university bookstores, army surplus stores, or similar establishments. In case of difficulty, see "Uniforms—Retail" in the "yellow pages" of your telephone directory.

2. A lab notebook should be bound. The preferred size is approximately 24 cm × 18 cm.

Evaluation of Students' Work

All students must work individually. Pairing up and the pooling of data, solutions, etc., is not permitted unless you are specifically asked to do so by the laboratory instructor. Note that the penalties for plagiarizing laboratory reports are identical to those incurred for other types of plagiarism. You must attain an average of 60% for laboratory work in order to pass the course. The grade for laboratory work is determined as follows:

	Block D	
Experiment D1	Short Report	5%
Experiment D2	Short Report	5%
Experiment D3	Formal Report	15%
Experiment D4	Short Report	5%
Experiment D5	Short Report	5%
	Block E	
Experiment E1	Short Report	5%
Experiment E2	Formal Report	15%
	Block F	
Experiment F1	Formal Report	15%
Lab Quiz		10%
Discretionary Mark		20%
Total		100%

Writing Laboratory Reports

In *Chemistry 218* you will be expected to produce two distinctly different types of laboratory report: formal reports and short reports. Some hints designed to assist you in writing each type of report are given below. **Note:** Good laboratory report writing begins with preparing your lab note book before the experiment, taking thorough lab notes, and writing down your observations as they happen.

You will have to write a formal report for one experiment in each of Blocks D, E and F. All other experiments may be written up in the short form. Some hints designed to assist you in writing each type of report are given below.

Short Report

In a short report, we do not require that you provide a detailed description of how the experiment was carried out (see procedure instructions below), or give a detailed discussion of the results obtained. In general, the following format must be used.

1. **Title and date**

   Experiment title and date performed as well as your name, ID number (and lab partner's name(s) if you worked in pairs or in a group).

2. **Purpose of experiment**

   Clearly state what scientific principle is being tested, determined or verified. Do not rewrite what is in the lab manual. **Note:** There may be more than one major objective as well as a few minor objectives. This is a good place to write out the relevant chemical reactions/equations.

   Example: *To determine the purity of a given solution of iron (II) sulfate heptahydrate by titration with a standard solution of sodium dichromate. A minor objective is to learn how to properly clean, calibrate and operate a buret.*

3. **Procedure**

   In the short report, reference the appropriate pages in your lab manual, noting only any changes or modifications to the procedure.

   Example: *The experiment was carried out as described in Experiment X3 of the Chemistry 218 Laboratory Manual pp. xy, except that ammonium iron (II) sulfate hexahydrate was used instead of iron (II) sulfate heptahydrate.*

4. **Observations**

   Example: *When the sodium hydroxide/sodium sulfite mixture was added to the potassium permanganate solution, the solution initially turned green, and then a brown precipitate of manganese (IV) oxide was produced.*

5. Results

In general, the instructions for each experiment include a suggested format for presenting your results. The numerical results should be listed in the order they were obtained and placed into a neat, carefully-labelled table. Use more than one table if necessary so as to not to mix unrelated data sets.

6. Calculations

All calculations should be presented clearly (i.e. titled, answer underlined), and should be carried out using the appropriate number of significant figures. By clearly setting out your results and calculations you make it easier for your instructor to grade your report. Any error analysis or discussion can be included at this point.

7. Answers to questions

Don't forget that the questions pertaining to the experiments are sometimes provided separately. **Hint:** Always rewrite the question on the lab report page and provide your answer below. Show all your work because part marks are given.

8. Conclusion

You would usually include a sentence or short paragraph that summarizes your results and puts them into some kind of context to show that the results have some meaning or importance. If you've identified an unknown, make sure you clearly state it here. If you've made a product, make a final comment on its quality and quantity.

Example: *In this experiment, the solubility of potassium nitrate in water was determined at several temperatures, and a solubility curve was constructed. In common with those of many ionic compounds, the solubility of potassium nitrate was found to increase dramatically with an increase in temperature.*

Formal Report

The main difference between a formal report and the short report described above is that in the formal report we expect much more detail, particularly in the areas of the procedure used and the discussion of results. If you wish, you may think of the short report as being written for a person who is familiar with the experiment in question. In contrast, a formal report may be regarded as being written for a person who, while having an adequate background in chemistry, is not at all familiar with your experiments. A formal report should consist of the following elements:

1. **Title and date**

   Title of experiment and date performed, your name, ID number [and lab partner's name(s) if you worked in pairs or a group].

2. **Purpose of experiment**

   As for the short report.

3. **Introduction**

   Give a brief introduction to the problem to be solved and the approach to be used in the experiment. Do not copy directly from the laboratory manual. Usually, one or two paragraphs will be adequate. Remember to clearly state the aim of the experiment, and comment on the experiment's usefulness or importance.

4. **Procedure**

   Your account should be sufficiently detailed that another student could repeat the experiment based on your report. Do not simply regurgitate the laboratory manual, and keep the following points in mind.

   a. Use the third person, the passive voice and the past tense.

      Correct: *The solution was heated on a hot-plate for 30 minutes.*
      Incorrect: *I heated the solution on a hot-plate for 30 minutes.*
      Incorrect: *The solution is heated on a hot plate for 30 minutes.*

   b. Avoid the recipe format.

      Incorrect: *Heat the solution on a hot-plate for 30 minutes.*

   c. Incorporate your observations into the procedure.

      Example: *The solution was heated on a hot-plate for 30 minutes, during which time the colour of the solution changed from red to green.*

   d. Avoid unnecessary detail.

      Correct: *20 mL of hydrochloric acid was added to the solution with constant stirring.*

Incorrect: *20 mL of hydrochloric acid was poured from a graduated cylinder into a 100-mL beaker containing the solution. During this process the solution in the beaker was stirred with a 15-cm long glass rod having a diameter of 5 mm.*

5. **Results and calculations**

   As for the short report.

6. **Discussion**

   This section gives you an opportunity to discuss the significance of your results, to assess the validity of the method, to indicate possible sources of error, and so on.

7. **Questions**

   Don't forget that the questions pertaining to the experiments are sometimes provided separately. **Hint:** Always rewrite the question on the lab report page and below provide your answer. Show all your work.

8. **Conclusion**

   As for the short report.

Note that in some cases neither of the above formats is entirely appropriate. In such situations you will be advised of the most suitable form in which to submit your report.

In most laboratory courses, a student is expected to submit his or her laboratory reports in a bound notebook. With the Athabasca University system this is not practical—mailing costs would be too high, and there might be a problem with getting notebooks returned before the next scheduled laboratory session. Thus the following procedure should be adopted.

1. All your results, observations, etc. should be recorded directly in a bound laboratory notebook (preferred size 23.5 cm × 18.4 cm). This notebook is your permanent record of work carried out in the laboratory. How you choose to organize this notebook is up to you, as it will not normally be submitted to your instructor. However, in the event of some future discrepancy, you may be asked to produce the notebook for inspection.

2. Your reports should be written on loose-leaf paper (21.5 cm × 28 cm) and be submitted by mail to your instructor. Be sure to number the pages, and write your name and the number of the experiment on each page. Should your report get lost in the mail, you will still have your results recorded in your notebook and a photocopy of the submitted report. In this way the photocopy of the report can be re-submitted. Please include your address and telephone number with your reports.

Sample *Chemistry 218* Laboratory Report

Short Report Format

Title: Acid Base Titrations—The Percentage of Acetic Acid in Vinegar

By:
A. Student, #990001
dd/mm/yy
Lab Partner: M. Y. Partner

Purpose: To use a quantitative titration method to determine the percentage of acetic acid in vinegar. Also to learn the concept of neutralization, moles, dilution, and stoichiometry as it applies to titration data. This was accomplished by first determining what volume of standard hydrochloric acid (of known concentration) will neutralize a known volume of sodium hydroxide of unknown concentration, using titration with the aid of a pH indicator (see Equation 1). Once the concentration of sodium hydroxide was standardized, it was used to determine the concentration of acetic acid in a diluted unknown vinegar solution (see Equation 2).

A minor objective of the experiment was to learn how to properly clean, operate and read a burette.

Equation 1: $HCl\,(aq) + NaOH\,(aq) \rightleftharpoons NaCl\,(aq) + H_2O\,(l) + heat$

Equation 2: $CH_3COOH\,(aq) + NaOH\,(aq) \rightleftharpoons CH_3COO^-Na^+\,(aq) + H_2O\,(l) + heat$

Procedure: The experiment was carried out as outlined in Experiment R3 of the *Chemistry 218 Laboratory Manual*, pp. xx–yy. **Note:** 1.60 g of NaOH was dissolved in ~400 mL water in Part A step 1. Otherwise no changes or modification were made.

Observations: Part A. During Titration of 0.1000 M HCl with Unknown [NaOH]:

1. Cresol red pH indicator in HCl initially reddish-orange.
2. After addition of NaOH, at the endpoint, solution was pink.

Part B. During Titration of CH_3COOH with Standardized NaOH:

1. Phenolphthalein pH indicator in CH_3COOH initially was clear and colourless.
2. After addition of NaOH, at the endpoint, the solution was pink.

Results: Part A. Standardization of Sodium Hydroxide Solution

Given: Standard hydrochloric acid, [HCl] = 0.1000 M
Volume 0.1000 M HCl used = 25.00 mL
Indicator used = cresol red

Table 1. Part A. Titration Data for 0.1000 M HCl vs. Unknown [NaOH] Titrant

Burette Reading	Trial 1	Trial 2	Trial 3
Final NaOH Volume (mL)	25.00	49.98	25.02
Initial NaOH Volume (mL)	0.00	25.00	0.00
Volume NaOH Used (mL)*	25.00	24.98	25.02
Avg. Vol. NaOH Used (mL)^	25.00		

Results (cont.)**:** Sample Calculations for Part A

* Volume Used = Final Vol. – Initial Vol.

^ Average of all three trials = x

$$= \frac{\sum \text{Trials 1, 2, and 3}}{n}$$

$$= \frac{25.00\ \text{mL} + 24.98\ \text{mL} + 25.02\ \text{mL}}{3}$$

$$= 25.00\ \text{mL}$$

Amount in moles of 25.00 mL of 0.1000 M HCl present in flask:
Given: moles = M × L, therefore, 0.1000 N × 0.02500 L = 2.50×10^{-3} moles of HCl

Number of moles of NaOH reacted at titration endpoint:
Given: the stoichiometric relationship between HCl and NaOH is 1:1
(see rxn equation 1 in **Purpose**)
Thus: moles NaOH = moles HCl = 2.50×10^{-3} moles of NaOH

Concentration of Standardized NaOH Solution
Given: M = moles/L, therefore, 2.50×10^{-3} moles NaOH/0.02500 L
NaOH = **0.1000 M NaOH**

Part B. Determination of Unknown [Acetic Acid] Using Standardized NaOH Solution

Given: Standardized, [NaOH] = 0.1000 M (from Part A)
Volume diluted CH_3COOH used = 10.00 mL
Indicator used = phenolphthalein

Table 2. Part B. Titration Data for Unknown [Acetic Acid vs. Standardized NaOH]

Burette Reading	Trial 1	Trial 2	Trial 3
Final Vol. NaOH (mL)	24.30	47.76	24.16
Initial Vol. NaOH (mL)	1.02	24.35	0.83
Volume NaOH Used (mL)*	23.28	23.31	23.33
Avg. Vol. NaOH Used (mL)^	23.31		

Sample Calculations for Part B

* Volume Used = Final Vol. – Initial Vol.

^ Average of all three trials = x

$$= \frac{\sum \text{Trials 1, 2, and 3}}{n}$$

$$= \frac{23.28\ \text{mL} + 23.31\ \text{mL} + 23.33\ \text{mL}}{3}$$

$$= 23.31\ \text{mL}$$

Results (cont.)**:** Amount in moles of 0.1000 M NaOH consumed in neutralization reaction:
Given: moles = M × L, therefore, 0.1000 M × 0.02331 L = 2.331×10^{-3} moles of NaOH

Number of moles of CH_3COOH reacted at titration endpoint:
Given: the stoichiometry between CH_3COOH and NaOH is 1:1 (see equation 2 in **Purpose**)
Thus: moles NaOH = moles CH_3COOH = 2.331×10^{-3} moles of CH_3COOH

Concentration of Diluted Acetic Acid Solution
Given: M = moles/L, therefore, 2.331×10^{-3} moles of CH_3COOH/0.01000 L
CH_3COOH = 2.331×10^{-1} M CH_3COOH

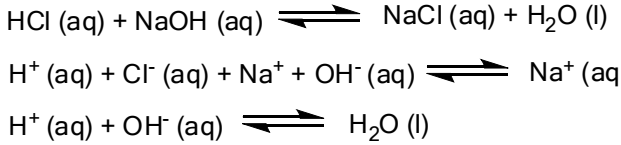
Concentration of Undiluted Acetic Acid Solution
Given: [Initial = [Diluted Unknown] × D.F., (D.F. = dilution factor = 1/dilution)
Therefore, 2.331×10^{-1} M $CH_3COOH \times 100.00$ mL/25.00 mL = 9.324×10^{-1} M CH_3COOH

Mass of CH_3COOH in 1L of Undiluted Vinegar
Given: Molecular Weight of acetic acid = 60.06 g/mol and g/L = M × Mwt.
Therefore, 9.324×10^{-1} M $CH_3COOH \times 60.06$ g/mol = 60.00 g/ L CH_3COOH

Mass Percentage of Acetic Acid in Vinegar
Given: Density of vinegar = 1.005 g/mL = 1.005 g/mL × 1000 mL/L = 1005 g/L
Therefore, 60.06 g/L CH_3COOH/1005 g/L) × 100% = 5.57% CH_3COOH in vinegar

Answers to Questions:

1. Write the net ionic equation for:
   a. HCl + NaOH

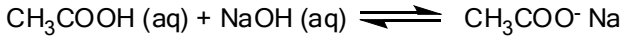


$$HCl\,(aq) + NaOH\,(aq) \rightleftharpoons NaCl\,(aq) + H_2O\,(l)$$

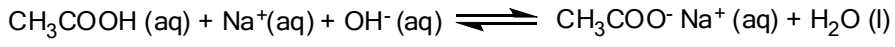
$$H^+\,(aq) + Cl^-\,(aq) + Na^+ + OH^-\,(aq) \rightleftharpoons Na^+\,(aq) + Cl^-\,(aq) + H_2O\,(l)$$

$$H^+\,(aq) + OH^-\,(aq) \rightleftharpoons H_2O\,(l)$$

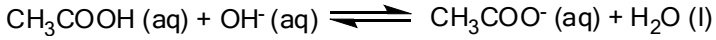
   b. Acetic acid + NaOH



$$CH_3COOH\,(aq) + NaOH\,(aq) \rightleftharpoons CH_3COO^-\,Na^+\,(aq) + H_2O\,(l)$$



$$CH_3COOH\,(aq) + Na^+(aq) + OH^-\,(aq) \rightleftharpoons CH_3COO^-\,Na^+\,(aq) + H_2O\,(l)$$



$$CH_3COOH\,(aq) + OH^-\,(aq) \rightleftharpoons CH_3COO^-\,(aq) + H_2O\,(l)$$

Conclusion: The percentage of acetic acid in vinegar was determined to be 5.57% (w/w). The concentration of the sodium hydroxide solution used to titrate the acetic acid was determined to be 0.1000 M. The titration method proved to be easy to perform and very precise in measuring concentrations of acids and bases. It is worthy of note that error was introduced into the percentage of acetic acid measurement because of the use of uncalibrated pipettes and burettes.

Formal Report Format

Title: Experiment X3—The Use of a Simple Spectrophotometer

By:

A. Student, #990001

dd/mm/yy

Lab Partner: M. Y. Partner

Purpose: To learn the application and use of a simple spectrophotometer by determining the absorbance of light by a number of dilute solutions of chromium (III) nitrate solutions (see equation 1). The λ_{max} for chromium (III) ions is to be determined, then a calibration curve for several solutions of known concentration, and finally, the concentration of an unknown chromium (III) nitrate solution. A minor objective of the experiment is to learn the proper steps for the preparation of a stock solution as well as how to make dilutions.

Introduction: In this experiment, a simple spectrophotometer is used to measure the light-absorbing ability of chromium (III) nitrate solutions. A simple spectrophotometer is useful in quantitative assays because it operates on the principle of the Beer-Lambert Law, $A = \varepsilon cl$, where A = absorbance, ε = molar extinction coefficient, c = concentration, and l = path length. This law states that the absorbance is directly proportional to the concentration, i.e., the concentration of a liquid can be determined by its absorbance.

Equation 1: $Cr(NO_3)_3\,(aq) + H_2O\,(l) \rightleftharpoons Cr^{3+}\,(aq) + 3NO_3^-(aq)$

To achieve this, first we must determine the best wavelength of light to use to detect the chromium (III) ions. This is called determining the adsorption spectrum and its wavelength maximum or λ_{max}. Second we determine the absorbance of six different known concentrations of chromium (III) nitrate solutions at the optimum wavelength, and then plot a graph of the absorbance versus concentration. Once a plot is obtained, it can be used to determine the concentration of an unknown concentration solution of chromium (III) nitrate by simply measuring its absorbance.

Procedure: ref: Experiment R5 of the *Chemistry 218 Laboratory Manual*, pp. xx–yy.

Part A. Preparation of a Stock Solution of Chromium (III) Nitrate

1. A 4.0 g mass of $Cr(NO_3)_3 \cdot 9\,H_2O$, chromium (III) nitrate nonahydrate was weighed on a general balance and placed into a clean dry glass vial.
2. The mass of $Cr(NO_3)_3 \cdot 9\,H_2O$ plus vial, weighed on an analytical balance, was 12.6086 g.
3. The $Cr(NO_3)_3 \cdot 9\,H_2O$ was then transferred to a clean 100 mL volumetric flask, using a funnel. The mass of the empty vial, weighed on an analytical balance, was 9.2068 g.
4. Water was used to dissolve the solid in the 100 mL volumetric flask and bring the solution to a final volume of 100.00 mL.

Part B. Dilution of the Stock Solution

1. A 25 mL volumetric pipette was used to transfer a 25.00 mL aliquot of stock solution to a 50 mL clean dry volumetric pipette. The solution in the 50 mL volumetric flask was filled to the graduation mark with water, then sealed, and mixed thoroughly by inversions (= Solution #1).
2. . . .

Note: The rest of the procedure has been omitted here, for the sake of brevity. Of course, in your lab report, you would continue to report on the full procedure in a similar manner to the above.

Results and Calculations

Observations: Part A. Preparation of the Stock Solution

1. The chromate solution was _____ in colour.

Part B. Preparation of Dilutions of Stock Solution

1. No observations to report other than diluted solutions made were progressively lighter in colour.

. . .

Part A. Preparation of the Chromium (III) Nitrate Stock Solution

1. Mass of chromium (III) nitrate required to prepare 100.00 mL of 0.1 M solution:
   Given: Mwt. of $Cr(NO_3)_3 \cdot 9\ H_2O = 400.26$ g/mol
   Since mass (g) = Concentration (M) × Mwt. (g/mol) × Volume (L)
   mass (g) = 0.1 M × 400.26 g/mol × 0.100 (L) = 4.0 g $Cr(NO_3)_3 \cdot 9H_2O$

2. Actual mass of chromium (III) nitrate used to prepare 0.1 M stock solution:
   Mass of $Cr(NO_3)_3 \cdot 9H_2O$ + vial used = 12.6086 g
   Mass of ëmpty vialí used = 9.2068 g
   Mass of $Cr(NO_3)_3 \cdot 9H_2O$ used = **3.4018 g**

3. Actual concentration (M) of chromium (III) nitrate stock solution:
   Given: Mwt. of $Cr(NO_3)_3 \cdot 9\ H_2O = 400.26$ g/mol
   Since Mwt. = g/mole, therefore, moles = g/Mwt., and since M = moles/L,
   Therefore M = (3.4018/400.26 g/mol)/0.100 (L) = 8.499×10^{-2} M $Cr(NO_3)_3 \cdot 9\ H_2O$

Part B. Preparation of Dilutions of the Chromium (III) Nitrate Stock Solution

1. To calculate the final $[Cr(NO_3)_3]$ for each diluted solution, use the formula:
   Given: $M_i \times Vi = M_f \times V_f$, or $M_f = (M_i \times V_i)/V_f$
   e.g., Solution #1 $M_f = (8.499 \times 10^{-2} M_i \times 25.00\ mL)/50.00\ mL = 4.25 \times 10^{-2}$ M and for the calculation of the other five solutions, see Table 1 below.

Table 1. Part B. Calculation of Concentration of Six Diluted Chromium (III) Nitrate Solutions

Sol'n #	[Initial] M_i	Initial Volume (V_i)	Final Volume (V_f)	[Final] (M_f)
1	8.499×10^{-2}	25.00	50.00	4.25×10^{-2}
2	8.499×10^{-2}	10.00	25.00	3.40×10^{-2}
3	8.499×10^{-2}	25.00	100.00	2.12×10^{-2}
4	8.499×10^{-2}	5.00	25.00	1.70×10^{-2}
5	8.499×10^{-2}	5.00	50.00	8.50×10^{-3}
6	8.499×10^{-2}	5.00	100.00	4.25×10^{-3}

Part C. Determination of λ_{max} for Chromium (III) Nitrate Using a Spectronic 20

Water used as blank.

The 4.25×10^{-2} M Solution #1 was used for all readings in wavelength scan.

Table 2. Part C. Wavelength Scan* and Determination of λ_{max} for Chromium (III) Nitrate

Wavelength, λ in nm	Absorbance	Wavelength, λ in nm	Absorbance
375	0.582	575	0.740
380	0.670	580	0.731
385	0.750	585	0.720
390	0.800	590	0.700
395	0.850	595	0.682
400	0.885	600	0.650
405	0.875	605	0.620
410	0.835	610	0.589
415	0.790	615	0.544
420	0.740	620	0.505
425	0.680	625	0.468

*For the graph of the wavelength scan, please see page x of this report.

Part D. Absorbances of Diluted Chromium (III) Nitrate Solutions at λ_{max} and Graphing of Calibration Curve[1]

Water used as blank. Solutions were read at 400 nm and 575 nm wavelengths.

Table 3. Part D. Absorbance of Six Diluted Chromium (III) Nitrate Solutions

Sol'n #	$[Cr(NO_3)_3]$	Abs 400 nm	Abs 575 nm
1	4.25×10^{-2}	0.885	0.682
2	3.40×10^{-2}	0.710	0.548
3	2.12×10^{-2}	0.470	0.348
4	1.70×10^{-2}	0.355	0.277
5	8.50×10^{-3}	0.181	0.173
6	4.25×10^{-3}	0.105	0.083

[1]For the calibration or standard curves, please see page xx at the back of this report.

Part E. Determination of the Concentration of an Unknown Diluted Chromium (III) Nitrate Solution

Water used as blank. Solutions were read at 400 nm and 575 nm wavelengths.

Sol'n #	$[Cr(NO_3)_3]$	Abs 400 nm	Abs 575 nm
X	?	0.226	N/D

N/D = not determined

From the calibration graph plotted in Part D, Solution X (absorbance of 0.226 units), which corresponds with a concentration of $Cr(NO_3)_3$ equal to 1.50×10^{-2} M.

Discussion: In this experiment we learned how light can be used and measured and that all atoms and molecules absorb light of certain wavelengths. This was accomplished by testing the absorbance of chromium (III) nitrate solutions using a spectrophotometer. The adsorption spectrum of a 8.499×10^{-3} M $Cr(NO_3)_3$solution was found to have two λ_{max} at 400 nm and 575 nm as seen in graph 1 (page x). The series of diluted stock solutions were found to have a linear relationship between absorbance and concentration as seen in graph 2 (page y). Since the maximal value of absorbance occurs at the 400 nm λ_{max}, this wavelength was chosen to measure the absorbance of the unknown solution. Reading from the graph, we found that its concentration was 1.50×10^{-2} M. The major source of error in the experiment was obtaining an accurate reading for the higher absorbance levels (0.6–1.0). At the higher levels the meter had a narrowly spread

scale with intervals that were not easily seen (as to be expected on a logarithmic scale). Other sources of error would include flaws in the glass cuvette, the manual graphing process, and the use of uncalibrated pipettes and volumetric flasks. Also only one set of dilution series was made and only single readings were done in the spectrophotometer. It would have been better to have done all dilution series and readings in triplicate in order to achieve a greater degree of precision and accuracy in the determination of the concentration, 1.50×10^{-2} M, of the unknown chromium (III) nitrate solution.

Answers to Questions:

1. What coloured light is associated with electromagnetic radiation at λ 400 nm and 575 nm?

   λ 400 nm = yellow transmitted, violet absorbed
   λ 575 nm = purple transmitted, green absorbed

   Thus the transmitted light is a mixture of the yellow and purple radiation, which gives the chromium (III) ion solution a greenish/blue colour.

Conclusion: Two λ_{max} for chromium (III) nitrate were found at 400 nm and 575 nm. There was a linear relationship between absorbance and concentration as shown in the calibration curves, thus proving that the absorbance of a solution is directly proportional to concentration of the absorbing species, therefore quantitative analysis of coloured solutions could take place. By learning to use a Spectronic 20 spectrophotometer, we were then able to determine with a reasonable degree of accuracy that the concentration of an unknown chromium (III) nitrate solution to be 1.50×10^{-2} M.

Laboratory Academic Conduct

Acknowledging Others' Work (see also in Moodle)

In the definitions, most short-answer questions, and the examination for this course, you are expected to summarize or paraphrase the material that you have learned in your own words. You are not expected to provide formal references to the textbook **or Lab Manual**. However, for some short-answer questions, you may wish to quote from the textbook, following the quoted material with an in-text citation; for example, "(Smith, 1996, p. x)." **If you use more than three consecutive words from the textbook** or any other source, you must use quotation marks and provide a citation.

If you use any other source (e.g., another textbook, a dictionary, encyclopedia, journal article, or Internet source) for any of your TMA **or Lab Report** answers, you must acknowledge the source following the paraphrase or quote. Appendix B of the Study Guide provides examples of a suitable bibliographic style. Note that for Internet sources, you must also indicate the authors (even if you must use "Anonymous"), the date on which the item was posted to the Internet (if given), the title, the URL (**http://www**, etc.), and the date on which you retrieved the material. See also Chapter 10 of A Handbook of Biological Investigation . Quotations should amount to less than 10% of any answer.

Remember that using old assignments **or lab reports**, your own or those of other students, and plagiarism (presenting others' work as your own) are forms of intellectual dishonesty. Such behaviour will not be tolerated at Athabasca University. In this course, students who engage in such actions will receive a grade of zero for an entire lab report or the whole course. Cheaters will get no "second chances"; plagiarism in an assignment will result in a grade of zero, and no supplemental will be allowed. Review the sections of the Student Manual and the Athabasca University Calendar that deal with intellectual indebtedness, plagiarism, and academic misconduct. The policies that govern students at Athabasca University are presented under the "Student Services" tab of your my AU portal.

The following are the regulations as quoted from Section 10 of our Athabasca University Student Academic Misconduct Policy (**SAMP**). Please note the bolded sections.
http://calendar.athabascau.ca/undergrad/page11_02_new.php#plagiarism

10.1.2.2 Plagiarism

Plagiarism involves submitting or presenting work in a course as if that work were the student's own, when, in fact, it was not. Often plagiarism exists when:

1. the work submitted was done in whole or in part, by an individual other than the person submitting the work
2. the whole or parts of a work are taken from another source without reference to the original author, publication, journal or Internet source
3. the whole or parts of the coursework submitted lacks citations even though a list of sources is provided
4. the coursework has been copied in whole or in part from an individual, a textbook, a solution manual, the Internet or any other source
5. when paid or professional editors are used inappropriately.

Students are encouraged to contact the individual to whom their coursework is being submitted to discuss their plan on the use of an editor prior to submission of their coursework.

Anyone found guilty of plagiarism under this policy may be subject to Section 5 Penalties within this policy.

10.1.2.3 Cheating

Cheating includes:

1. submitting a proposed invigilator for approval under false pretences. This includes, but is not limited to:
   • naming one's friend, relative, fellow student or co-worker for approval
   • submitting false credentials, names, occupations, and addresses
   • the misrepresentation of other information related to a proposed invigilator
2. writing an invigilated examination or any part of an invigilated examination outside of an approved invigilation centre
3. removing, by any means, an examination or any part of an examination from an approved invigilation centre
4. communicating substantive content of any examination to course mates or others
5. in the course of writing an examination, obtaining or attempting to obtain information from another student or other unauthorized source, or giving or attempting to give information to another student, or knowingly possessing, using, or attempting to use any unauthorized material and/or electronic devices
6. leaving answer papers exposed to view, or attempting to read other students' examination papers
7. representing or attempting to represent oneself as another or having or attempting to have oneself represented by another in the taking of an examination, preparation of coursework, or other similar activity
8. submitting in any course or program of study without prior approval, all or a substantial portion of any coursework for which credit has been received or is being submitted in another course or program at AU or elsewhere

9. submitting in any course or program of study (including those courses in a clinical or laboratory setting) any coursework (including laboratory results) containing a false statement(s) intended to be perceived as fact(s), or a reference that has been fabricated
10. accessing course materials or notes pertaining to the subject matter of the course or accessing internet sites during a scheduled examination when the exam prohibits access to such materials

Anyone found guilty of cheating under this policy may be subject to Section 5 Penalties within this policy.

10.1.2.4 Collusion
Collusion involves two or more persons who, by agreement between them, prepare and submit the substantially same or identical piece of coursework, claiming that it is the work of only the person submitting it, without the prior permission of the person to whom the coursework is being submitted. Anyone found guilty of collusion under this policy may be subject to Section 5 Penalties within this policy.

10.1.2.5 Unauthorized Use of AU Materials
It is an offence to knowingly procure, sell, distribute, duplicate, transpose or receive any course material such as examinations, tests, quizzes, assignments, or laboratory results from any source without the proper written consent of Athabasca University except where licensing agreements permit otherwise.
Anyone found guilty of unauthorized use of Athabasca University materials under this policy may be subject to Section 5 Penalties within this policy.

AU Policy Regarding Laboratory Academic Conduct

All laboratory reports (both present and past) are unauthorized aids and making use of them in any way constitutes an academic offense (ref: SAMP Section 10.1.2.2.1 and 10.1.2.2.4, 10.1.2.3.7 and 10.1.2.3.10, 10.1.2.4 and 10.1.2.5)."

Undergraduate students are allowed and encouraged to discuss experimental data with one another, but students must be ever cognizant of the AU SAMP policy and realize the fact that every student is required to write an individual report. NO CONSULTATION OR COLLABORATION BETWEEN STUDENTS IS ALLOWED IN THE WRITING OF LAB REPORTS. This policy also applies to any required pre-laboratory preparation.

A mark of zero for the entire lab component of the course will be the penalty for any student found to have committed and academic offense as set out in the SAMP, if the offense was pertaining to plagiarism.

For more information please consult the following website:
http://calendar.athabascau.ca/undergrad/page11_02_new.php#plagiarism

Refer any questions concerning the Laboratory Academic Conduct policy to your laboratory instructor."

Safety

General

In 1975, a survey carried out by Her Majesty's Inspectors of Schools showed that of the 70,000 accidents reported in British schools, only two per cent occurred in a science laboratory. Although AU students are not attending laboratory sessions in Britain, and are more mature than most schoolchildren, this statistic is relevant to the laboratory component of *Chemistry 218*. The figures suggest that, although a laboratory is a potentially dangerous place to work, the chances of an injury-causing accident are relatively low. This situation exists because of the strict safety rules that are applied to students working in laboratories, and because of a willingness of both students and instructors to look out for unsafe practices and possible hazards at all times.

Some people will approach the laboratory component of their AU chemistry course with a certain amount of trepidation. In a sense, this is a good thing—no one can afford to adopt a complacent attitude towards laboratory safety. However, you should realize that you could face a greater chance of being killed or injured as you drive to the laboratory session than while you are working in the laboratory. Most of the hazards that you are likely to face while performing the experiments in this laboratory are relatively minor and easily avoided. These include the following.

minor cuts—most cuts can be avoided by never using broken or cracked glassware, and is particularly careful when carrying out potentially dangerous operations, such as inserting glass tubing into a rubber stopper.

burns—burns usually occur when a student forgets that something that has just been heated on a hot-plate or in a heating mantle may be very hot.

chemical spills—spills can usually be avoided if students pay particular attention to the technique used when pouring chemicals from a container, and injury caused by spills can be minimized if students wear the appropriate protective clothing: safety glasses, gloves, and lab coat or apron.

Another possible danger is the presence of hazardous gases (at undesirable toxic concentrations) or unpleasant vapours in the air. In this course we have attempted to keep the use (or production) of such materials to a minimum. Where this is not practical, you will be advised to work in a fume hood.

When designing the laboratory component of this course, we found it necessary to strike a balance between minimizing possible hazards and exposing you to a full range of techniques. By its very nature, chemistry often necessitates the handling of dangerous substances; if chemistry students are never exposed to such situations, we would never have any fully trained chemists. Having said this, perhaps we should reassure you that, provided you follow the safety rules that follow, we do not anticipate that any problems will arise.

Safety Rules

1. **Safety glasses must be worn in the laboratory at all times.** Wearers of prescription glasses may wear their own, but should be aware of the possibility that chemicals or flying glass could enter the eye through the gap between the temple and the frames of the glasses. Thus, in potentially hazardous situations, wearers of spectacles are advised to wear safety goggles or a safety mask over their prescription glasses. Contact lenses should not be worn in the laboratory.

   Note 1.

   Safety glasses will be provided by Athabasca University and must be worn at all times—even when you are not actively using chemicals and glassware. Remember that injury could result through carelessness on the part of one of your fellow students.

   Note 2.

   Contact lenses are not permitted for two reasons:

   a. If a chemical is splashed into the eye of a person wearing contact lenses, neither the normal tearing mechanism nor external irrigation (with water) is effective in removing chemicals from under the contact. The contact must first be removed for tearing and irrigation to be effective; however, the contact may be difficult to remove because of the tight squeezing shut of the eye that occurs in response to the chemical. Since time is of the essence with a chemical burn, a delay caused by removing a contact lens could have serious consequences.

   b. **Soft contact lenses present an additional hazard**. Any chemical (including vapours) that comes into contact with such a lens can diffuse into the interior of the lens, which then acts as a reservoir that can create additional exposure, even if the lens is removed and rinsed.

   Note 3.

   The correct emergency treatment for chemicals that enter the eye is to wash the injured eye thoroughly with plain water for 15 minutes. In addition, the Lab Instructor should be notified, and medical attention should be sought for all eye injuries. An eye-wash fountain should be available in the laboratory; make sure that you are aware of its location.

2. **A lab coat should be worn at all times.** You must purchase a lab coat to participate in the laboratory component of this course. A lab coat will not only make you look and feel like a chemist, but will also protect you and your clothes in the event that you inadvertently spill a chemical.

   While we are on the subject of clothes, dress sensibly. It can become very hot in the laboratory and you will not be comfortable working all day with a three-piece suit underneath your lab coat. Similarly, clothes worn in the laboratory tend to acquire a "chemical odour" and it may be advisable to leave your more expensive shirts and sweaters at home.

3. **Protect your feet by wearing sensible shoes.** Bare feet, open-toed sandals, etc., are not permitted. Spilling concentrated sulfuric acid on your big toe, or cutting your foot on a piece of broken glass would result in a trip to the hospital. Avoid high-heeled shoes; remember that you will be on your feet for up to eight and one-half hours on any given lab day.

4. **Tie back long hair.** Long hair can be a fire hazard. Also, when you bend over to inspect the contents of a beaker containing a chemical, long hair can easily fall into that chemical. Not only could this damage your hair, but it could also ruin your experiment!

5. **Never run in the laboratory, and never be tempted to become involved in practical jokes or other horseplay.**

6. **On no account attempt an unauthorized experiment.**

7. **Never work in the laboratory when the supervisor is not in attendance.** Our regulations require that at least one qualified supervisor be present in the laboratory whenever a student is working there.

8. **Eating, drinking and smoking are not permitted in the laboratory.** Food and drink may become contaminated by toxic substances. Smoking is a fire hazard. When you leave the laboratory, wash your hands, particularly before eating.

9. **In the event of fire**:
   a. Do not panic; many small fires can be extinguished without the use of a fire extinguisher, simply by cutting off the air supply. For example, when a flammable liquid catches fire in a beaker, the fire can quickly be put out by placing an asbestos pad or watch-glass over the beaker.

   b. If the use of a fire extinguisher is necessary, leave this to the supervisor and concentrate on getting yourself to the nearest exit.

   c. In the event that your instructor is incapacitated, e.g., through injury, be prepared to extinguish a fire, especially if human life is in danger. In order to do this you must know the location of the nearest fire extinguisher and how to use it. Most of the extinguishers that you will encounter are of the **ABC type**, which means they are effective on fires involving trash, wood or paper (Class A), liquids and grease (Class B), and electrical equipment (Class C). These extinguishers are not effective on Class D fires, i.e., those involving active metals such as sodium and potassium. Fires involving the latter substances are unlikely to occur during the course of *Chemistry 218*, but you should be aware of the special problems that these materials can cause. When using a fire extinguisher, aim at the base of the fire and use a sweeping motion. Note that you should never attempt to extinguish a laboratory fire using water. (A possible exception might be to extinguish a burning paper towel by placing it in a sink and turning on the tap.)

d. If your clothing catches fire, wrap yourself in a fire blanket (or a coat if no fire blanket is available) and roll on the ground.

10. **Report all accidents.** All accidents, however minor, must be reported to your supervisor and the details entered in the accident book. If you are involved in an accident, do not resume work until you have received the appropriate first aid or medical attention. Never work with open cuts on your hands, cover all small cuts and scratches with band aids.

11. **Always dispose of chemical wastes in the correct manner.** In general, you would never dispose of chemicals, particularly organic solvents, by pouring them down the drain. Throughout the *Chemistry 218* laboratory manual you will find that you are told repeatedly to "pour excess reagents into the waste container provided." Ensure that waste chemicals are placed in the correct container—putting the wrong material into a container is potentially dangerous. Never attempt to return used chemicals to their original containers. Note that certain substances, such as dilute acids, solutions of harmless compounds (e.g., sodium chloride), etc., may be washed down the drain with copious amounts of water. When in doubt, check with your instructor. Be particularly careful to place any chlorinated hydrocarbons in the waste container designated for such substances. Same goes for heavy metal waste solutions.

12. **Never pour concentrated acid or base into a bottle marked 'Organic Waste only'.** Violent exothermic reactions can occur between potential reagents, causing a splatter of toxic and corrosive material.

13. **Never over fill a waste bottle.** Keep an eye on the volume level in the waste bottle and let the instructor know when it is ¾ full.

Some General Advice Regarding Laboratory Work

1. People with clean and tidy benches are less likely to be involved in accidents. Communal areas, such as balance rooms and fume hoods, should also be kept tidy. Clean up all spills. Any glassware containing chemicals that is left in a communal area should be clearly labelled with the owner's name and details of the contents (e.g., L. Worker, concentrated nitric acid).

2. Do not rummage through a cupboard or communal glassware/supply drawer or box without care and attention. Sharp object may be present. Discard sharp objects (needles, razor blades, broken glass) in the appropriate sharps discard receptacle.

3. Wear your lab coat at all times when working in the lab, and wear protective latex gloves whenever handling corrosives and solvent. Do not store sharp objects (e.g., Pasteur pipettes) in your coat pocket.

4. When assembling apparatus or glassware, always check with the instructor before proceeding with the experiment.

5. Handle all organic solvents (e.g., acetone, dichloromethane) with care. Most are flammable, and many have a long-term, cumulative effect on the body.

6. If a fire starts, or the fire alarm sounds, unplug any electrical apparatus and vacate the laboratory in an orderly manner.

7. When diluting a concentrated acid, always **add the acid to the water**. Do so slowly, with stirring.

8. If you get acid on your clothing, neutralize it with **dilute** ammonia solution (1 mol $\cdot$ L^{-1}) and wash well with water.

9. If you get alkali on your clothing, wash it off with large quantities of water.

10. If you get any corrosive chemical on your skin, wash it off immediately with water and consult your instructor. Pay special attention to the safety notes given in bold type in the "Procedure" sections of the lab manual. These notes will inform you of any special precautions that you might need to take, and will also inform you if the "wash well with water" maxim does not apply.

11. If you spill a large quantity of acid on the bench or floor, use crude sodium bicarbonate (available from the instructor) to neutralize the acid and then wash well with water.

12. Mercury from broken thermometers presents a special kind of hazard. The vapour from the spilled mercury represents a long-term hazard and so the liquid mercury should be cleaned up very carefully. If you break

the thermometer, ask your instructor for assistance in cleaning up the mercury. Do not touch the mercury globules with your bare hands.

13. Always check for any possible hazards associated with using a given chemical. The quickest way of doing so is to make certain that you read the label on the container from which the chemical is removed. Some chemical manufacturers use symbols or codes on the labels of their chemical containers to indicate possible hazards. When in doubt, consult your instructor.

14. In the event of a real emergency, it could be important for medical personnel to know certain facts about you, facts that they could not obtain if you were unconscious or in a severe state of shock. On page 24 is a copy of a Medical Information Form that you should have received either with this laboratory manual, or separately in the mail. We advise you to fill out the form that you received, and paste it inside the front cover of your lab notebook. You might regard some of this information as being rather personal. However, keep in mind that normally we do not expect you to show us your lab notebook (see "Writing Laboratory Reports") so confidentiality of your medical history should be maintained. If you still have doubts, keep in mind that, in the event of an accident, your instructor has been asked to put your lab notebook on your stretcher as they carry you off to the hospital.

15. As mentioned in the safety rules, all accidents that result in injury must be reported and recorded in the accident book. In addition, an "Accident Report Form" must be completed and returned to the course coordinator. A sample form is shown on the page after next.

Note: The *Medical Information Form* on the next page is adapted from one suggested by Ben Ruekberg and David W. Ball, *Journal of Chemical Education*, 63, **A247** (1986).

Ref: http://science.athabascau.ca/Labs/safety/

Medical Information Form
Chemistry 218

Name: A. Student

Social Insurance Number: 123 456 789

Address: 4812, 43rd Street, Small Town, Alberta

Phone: 675-6111

Alberta Health Care Number: 987.65.432.123

Age: 35

Sex: M

Height: 173 cm

Weight: 68 kg

Chronic Medical Problems: Epilepsy

Current Medical Problems: None

Do you normally wear contact lenses? No

Physical Disabilities: Partially deaf

Allergies to Medication: Allergic to penicillin

Current Medication being used: None

Personal Physician: Dr. V. Rich

In Case of Emergency, please contact: Susan Student (wife) 675-6111

Special information: My religious beliefs prevent me from accepting a blood transfusion.

Chemistry Laboratory Accident Form
(Student Labs)

Name of injured student: Alan Student

Date of incident: April 1, 1987

Time of incident: 2:06 p.m.

Course: *Chemistry 218*

Instructor: A. Tutor

Nature of injury: Glass tubing penetrated palm of right hand.

How injury incurred: Student was attempting to insert glass tubing into rubber stopper without using recommended lubricant.

First aid rendered: Wound was washed thoroughly, a piece of glass appeared to be embedded in the hand. Pressure applied around the wound using a ring pad. Covered with built-up dressing.

First aid rendered by: A. Tutor (instructor), G. Help (student)

Further medical treatment sought? Yes; if yes give details: Patient was driven to outpatients at the nearest hospital where the wound was examined and the embedded glass removed.

Instructor's comments: Student returned to lab at 4 p.m. to collect belongings. His wife had been contacted and she came to drive him home.

Was instructor in the room when the incident occurred? Yes

Student's signature: A. Student

Follow up (Course coordinator): Contacted student by phone (April 3), his condition is now being monitored by his family physician.

WHMIS

On October 31, 1988, the *Workplace Hazardous Materials Information System (WHMIS)* went into effect. This is a national system intended to provide laboratory personnel with uniform information on chemicals used in the workplace. There are three main features of *WHMIS*:

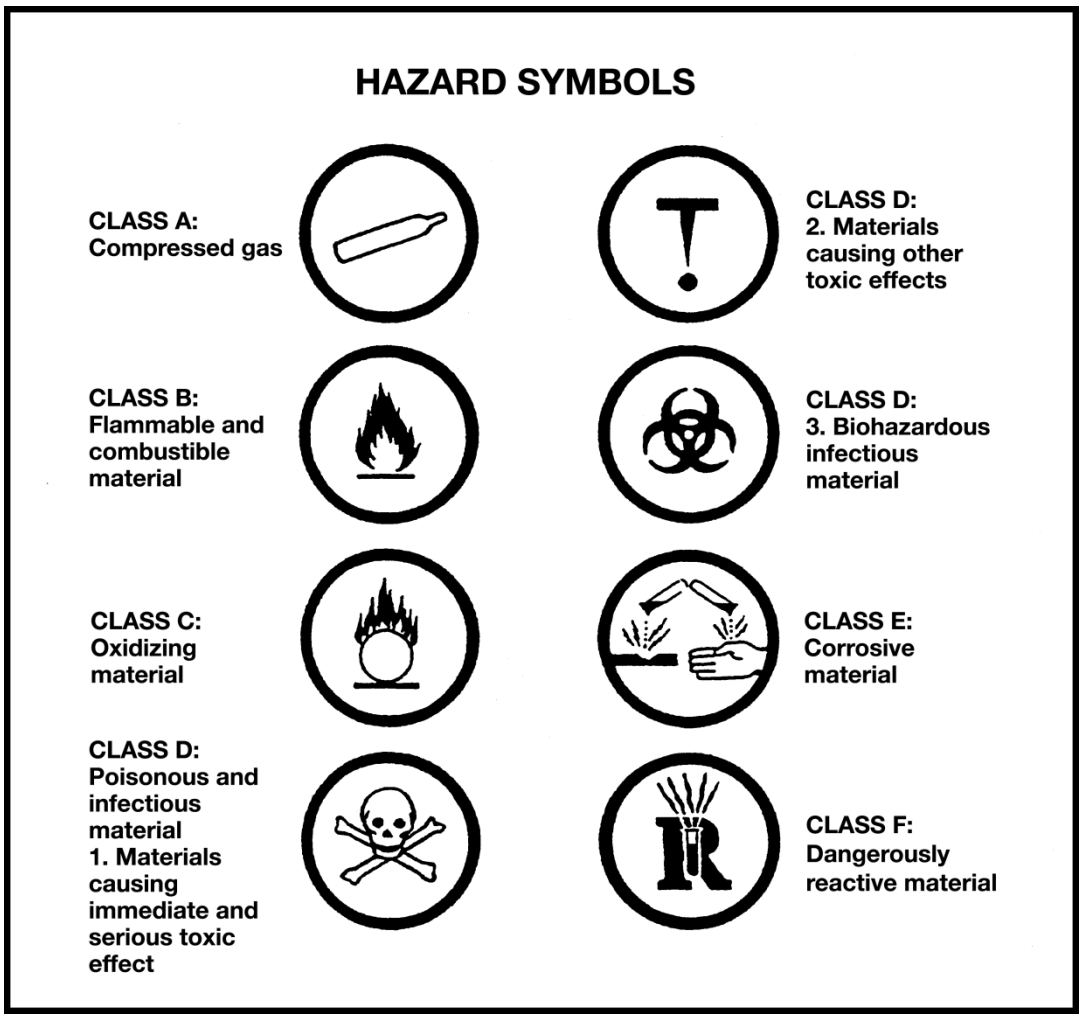
1. Chemical manufacturers are now obliged to label each container of hazardous material, giving details on the product's hazards and what action to take in an emergency.

2. The manufacturer must provide the consumer with a *Material Safety Data Sheet (MSDS)* for each hazardous product. These sheets give complete details on the possible health effects that exposure to the product can produce, preventative measures that should be taken, etc.

3. Employers must provide an appropriate education program for all workers whose work may bring them into contact with hazardous products.

The *WHMIS* regulations do not affect you as a student, although if you are involved in a chemistry-related job you should be familiar with them. Most of the chemicals that you will handle in this course are no longer in their original containers. Under the *WHMIS* regulations, such chemicals do not require detailed labels. However, you should read all labels carefully and pay special attention to the hazard warnings that appear throughout the laboratory manual. The hazard symbols that you may observe on certain chemical containers are reproduced on the following page. A file containing up-to-date MSDSs for all the chemicals used in *Chemistry 218* is maintained at each of the locations where laboratory sessions for these courses are held. Additional information on *WHMIS* may be obtained from Alberta Community and Occupational Health, Occupational Health and Safety Division.

Hazard Symbols



Safety Exercise

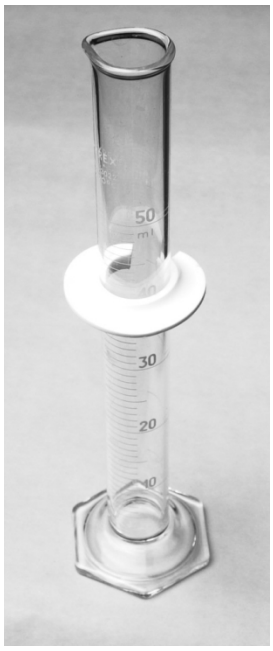
At your first laboratory session, the instructor will give a short talk regarding specific safety concerns and about the way in which the laboratory at that particular location is organized (e.g., where chemicals are located, arrangements for using balances, etc.) You may also be shown a video tape on laboratory safety. At the end of the presentation you should draw a plan of the laboratory, indicating the location of each of the following features on the plan:

1. your work bench
2. exits
3. eye-wash fountain(s)
4. safety shower(s)
5. fire extinguisher(s)
6. fire blanket(s)
7. first aid kit(s).

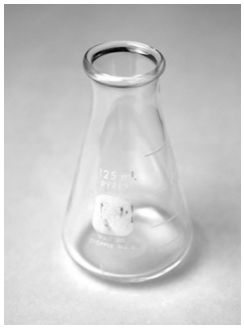
Common Apparatus

On the following pages are shown sketches of some common pieces of equipment that are found in almost all chemistry laboratories. Familiarize yourself with the name of each piece of equipment before you attend your first laboratory session.

Graduated cylinder
(Measuring cylinder)



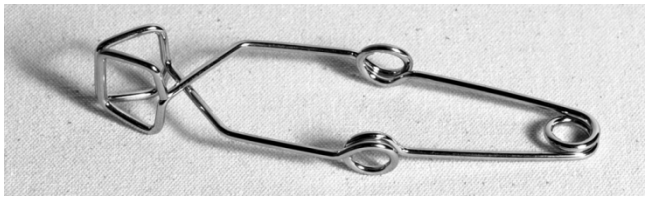
Erlenmeyer flask
(Conical flask)



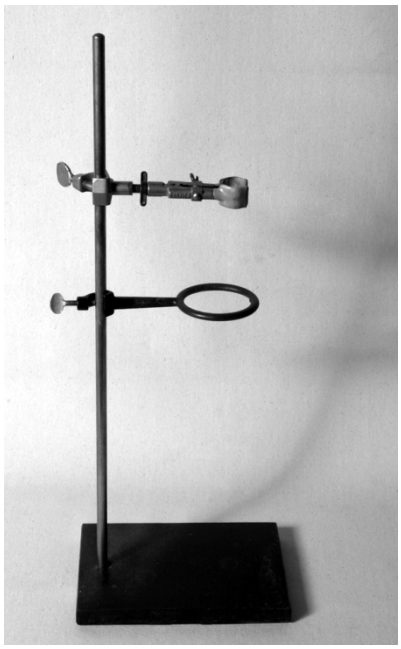
Volumetric flasks

Büchner flask
(Filter flask)
Büchner shown with
funnel and universal
rubber filter adapter

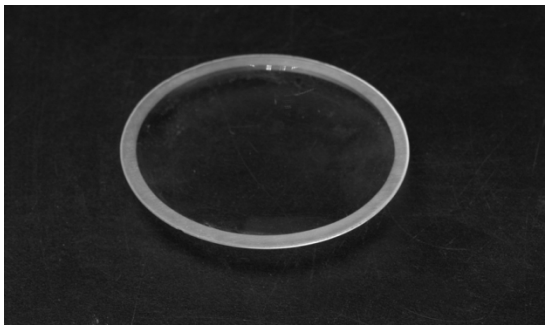
Test tube holder



Ring stand

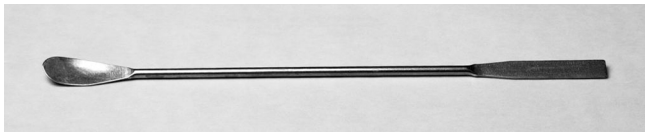


Watch glass

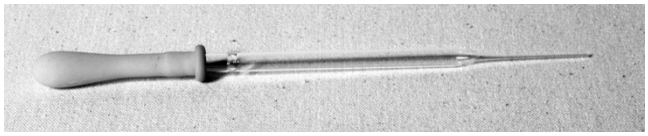


(Filter) Funnel

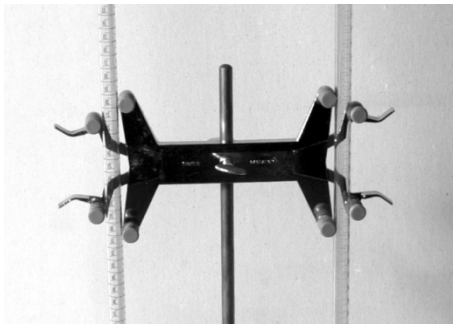
Spatula



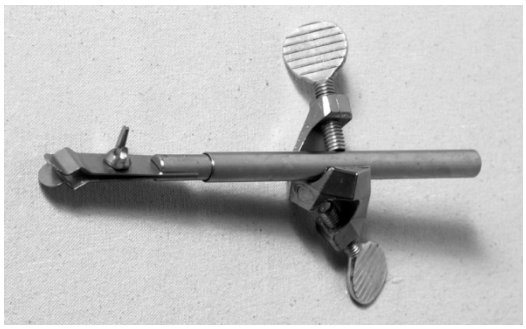
Pasteur pipette
(with rubber bulb)



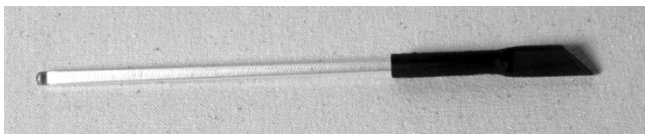
Burette clamp



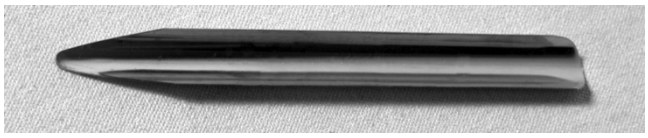
Thermometer clamp



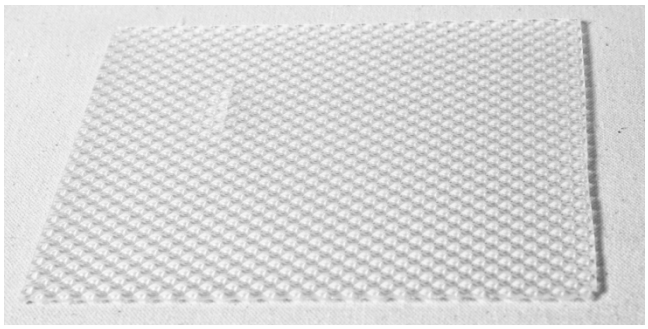
Policeman



Spoonula



Tile (white)



Checklist of Equipment Contained in Each Student Kit

Each student will be provided with a drawer, box or plastic tray containing the equipment listed below. Please inform your instructor if any of this apparatus is missing. Keep in mind that another student will be using the equipment during other lab sessions, so make sure that everything is clean and dry when you return it at the end of the day. Similarly, please let your instructor know if you find that the glassware has been left dirty by another student.

- ❑ (6) 50 mL beaker
- ❑ (6) 100 mL beaker
- ❑ (2) 150 mL beaker
- ❑ (4) 250 mL beaker
- ❑ (2) 400 mL beaker
- ❑ (1) 600 mL beaker
- ❑ (1) test tube brush (large)
- ❑ (1) test tube brush (small)
- ❑ (1) burette clamp
- ❑ (1) iron ring clamp
- ❑ (2) thermometer clamp
- ❑ (2) utility clamp
- ❑ (1) 150 × 75 mm flat bottom dish
- ❑ (7) 50 mL Erlenmeyer flask
- ❑ (7) 125 mL Erlenmeyer flask
- ❑ (6) 250 mL Erlenmeyer flask
- ❑ (1) 500 mL Erlenmeyer flask
- ❑ (1) 250 mL filter flask
- ❑ (1) 25 mL volumetric flask
- ❑ (4) 50 mL volumetric flask
- ❑ (2) 100 mL volumetric flask
- ❑ (2) 200 mL volumetric flask
- ❑ (1) 250 mL volumetric flask
- ❑ (1) burette funnel
- ❑ (1) small plastic funnel
- ❑ (1) 5.5 cm Buchner funnel
- ❑ (1) short stemmed glass funnel
- ❑ (1) long stem glass funnel
- ❑ (1) glass rod
- ❑ (1) 10 mL graduated cylinder
- ❑ (1) 50 mL graduated cylinder
- ❑ (1) 100 mL graduated cylinder
- ❑ (1) meniscus reader
- ❑ (1) policeman
- ❑ (1) safety glasses
- ❑ (assorted) rubber stoppers
- ❑ (1) spatula
- ❑ (1) spoonula
- ❑ (5) test tubes
- ❑ (1) tile (white)

- ❑ (1) thermometer (10–100° C)
- ❑ (1) crucible tongs
- ❑ (3) pieces rubber tubing
- ❑ (1) large tweezers
- ❑ (2) vials
- ❑ (1) 500 ml wash bottle
- ❑ (1) watch glass

Note: The contents of the Student Kit may be changed from time to time and vary from location to location. Your instructor will advise you if any additional items should be included or if any items should be deleted from the list. Each student is responsible for the maintenance of the glassware assigned to them. Handle with care. Clean all items before returning them to the box.

Experiments

Block D Experiments

"When it has once been given a man to do some sensible things, afterwards his life is a little different." A. Einstein

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

> "As a beginning chemist, make a habit of weighing carefully, of pouring from one vessel to another without spilling, and without missing the last drop, and of observing the small details which if overlooked often spoil several weeks of careful work." J. J. Berzelius

Prerequisite Skills

In order to undertake this experiment, you must have completed the laboratory component of Athabasca University's *Chemistry 217* or its equivalent.

Objectives

When you have completed this experiment you will have:

1. learned one method of studying the kinetics of a reaction in which iodine is a product.
2. determined the order and rate constant of a reaction.
3. observed the effect of a catalyst on the rate of a reaction.

The experiment illustrates the following topics from your textbook:

1. reaction rate,
2. identifying the order of a reaction,
3. dependence of reaction rate on concentrations,
4. second-order reactions, and
5. homogeneous catalysis.

Introduction and Theory

Both this experiment and the one that follows are concerned with the reaction between iodide ions (I^-) and peroxydisulfate ions ($S_2O_8^{2-}$). The equation for the reaction that occurs is

$$2I^-(aq) + S_2O_8^{2-} \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$$

This reaction occurs reasonably slowly at room temperature.

As you should realize, to make a quantitative study of the kinetics of this reaction, we need to be able to monitor the change in concentration of one of the reactants or products as a function of time. With the apparatus we have at our disposal, we cannot do this directly; instead, we shall use an indirect method that will allow us to determine how long it takes for a given amount of iodine to form. From the balanced equation we can see that this is equivalent to determining the time that it takes for a given amount of peroxydisulfate to react, thus we may write:

$$\text{InitialRate} = \frac{\Delta[I_2]}{\Delta t} = \frac{-\Delta[S_2O_8^{2-}]}{\Delta t} = k[S_2O_8^{2-}]_0^a[I^-]_0^b$$

where: $\Delta[I_2]$ is the change in concentration of iodine in time Δt
$\Delta[S_2O_8^{2-}]$ is the change in concentration of peroxydisulfate in time Δt
k is the rate coefficient (or rate constant)
$[S_2O_8^{2-}]_0$ is the initial concentration of peroxydisulfate
$[I^-]_0$ is the initial concentration of iodide
a is the order of reaction with respect to peroxydisulfate
and b is the order of reaction with respect to iodide

If we now write the above equation in logarithmic form (with all logs being to the base 10):

$$\log(\text{initial rate}) = \log k + a \log [S_2O_8^{2-}]_0 + b \log [I^-]_0$$

It should be apparent that by conducting a series of experiments in which $[I^-]_0$ is kept constant and $[S_2O_8^{2-}]_0$ is varied, this equation further simplifies to

$$\log(\text{initial rate}) = \text{constant} + a \log [S_2O_8^{2-}]_0$$

and a plot of log (initial rate) against log $[S_2O_8^{2-}]_0$ should yield a straight line of slope a. Similarly, if a second series of experiments is carried out in which $[S_2O_8^{2-}]_0$ is kept constant and $[I^-]_0$ is varied, a plot of log (initial rate) against log $[I^-]_0$ will yield a straight line of slope b.

Once the values of a and b have been determined, the value of k for each trial can be calculated and an average value obtained.

So far, no indication has been given of how you will determine the time it takes for a given amount of iodine to form. First you must understand that starch indicator can be used to detect very small amounts of iodine. In the presence of iodine, the starch indicator turns from colourless to blue:

$$\text{starch} + \text{iodine} \leftrightarrow \text{starch-iodine complex}$$

(colourless) (intense blue/black colour)

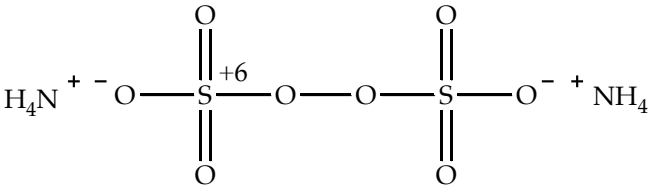
Obviously we cannot simply add starch indicator to the reaction mixture because this would result in the formation of the blue complex as soon as a small amount of iodine had been formed. Instead, as well as adding a starch indicator, we also add a known amount of sodium thiosulfate ($Na_2S_2O_3$). The thiosulfate reacts with the iodine to produce iodide ions and tetrathionate ions ($S_4O_6^{2-}$).

$$I_2\,(aq) + 2S_2O_3^{2-}\,(aq) \longrightarrow 2I^-\,(aq) + S_4O_6^{2-}\,(aq)$$

This reaction is essentially instantaneous. Thus, as soon as any iodine is formed from our principal reaction (iodide + peroxydisulfate) it immediately reacts with the thiosulfate and does not have a chance to form the blue starch-iodine complex. However, as soon as all the thiosulfate is consumed, iodine begins to accumulate and the blue complex becomes apparent. For example, suppose we added 5×10^{-5} mol of sodium thiosulfate. This is sufficient to react with 2.5×10^{-5} mol of iodine, which in turn is formed by the reaction of 5×10^{-5} mol of iodide ions with 2.5×10^{-5} mol of peroxydisulfate. Thus, if we determine the time it takes for the blue starch-iodine complex to appear, we have a measure of how long it takes for 5×10^{-5} mol of iodide ions (or 2.5×10^{-5} mol of peroxydisulfate ions) to react. From this it is a simple matter to determine the corresponding change in concentration and hence the rate of reaction.

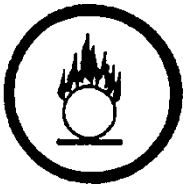
Note: As you should know, the rate of a reaction decreases with time, so the rates that you will obtain in this experiment are average rates rather than rates that correspond to a given instant. For our purposes, this small inaccuracy will be disregarded.

Safety Concerns: Handling of Chemicals



ammonium peroxydisulfate

CLASS C:
Oxidizing
material



$S_2O_8^{2-}(aq) + 2e^- \longrightarrow SO_4^{2-}(aq)\ E_0\,(v) = +2.01$

Wear gloves when weighing this reagent, and wash your hands after handling the solid. The peroxydisulfate ion is one of the strongest oxidizing agents known. Fortunately the oxidations are slow.

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.

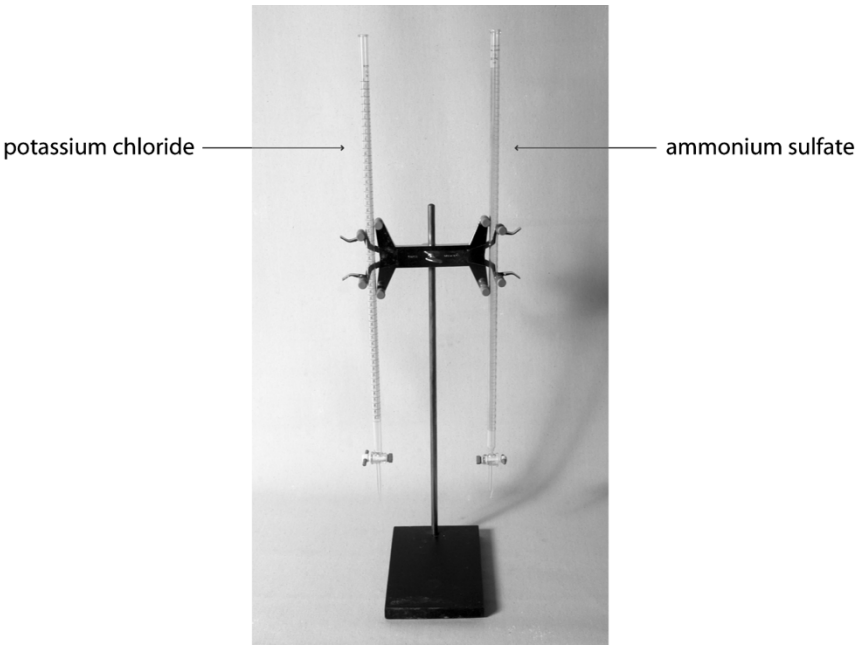


Figure D1.1: Burettes arranged to deliver potassium chloride and ammonium sulfate.

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.

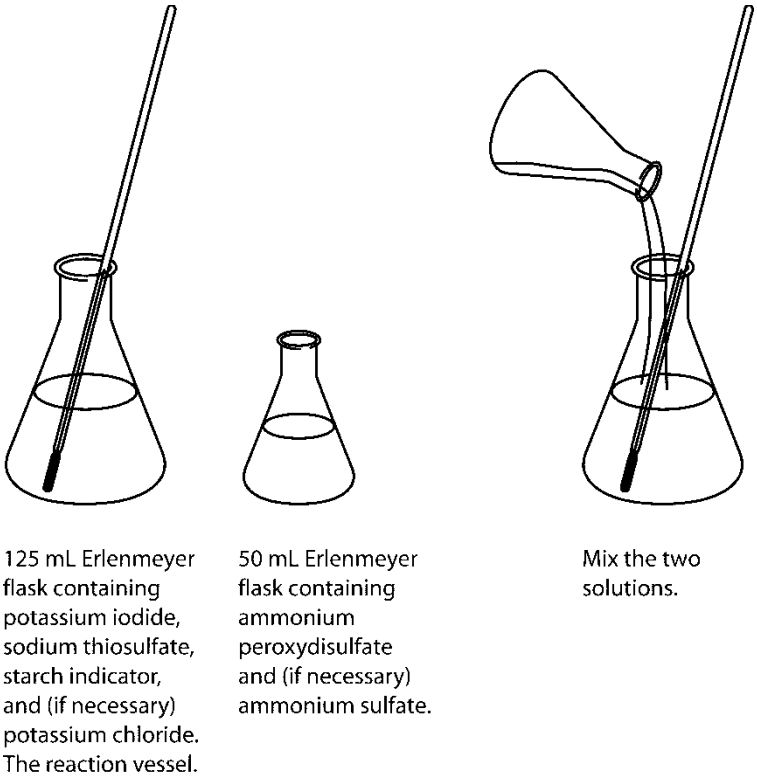


Figure D1.2
Starting the reaction

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).							

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.

Results and Calculations

Check to see if this is one of the experiments that has been assigned to you for a formal report. If it is, you may wish to review the section of this *Laboratory Manual* entitled "Writing Laboratory Reports."

A. Preliminary Investigation

The observations that you made during these tests should be recorded and interpreted. Write balanced equations for any reactions that occurred.

B. Kinetic Study

1. For each of the seven runs you should have recorded the temperature of the reaction mixture, and the time taken (Δt) for the permanent blue-black colour to appear. These results can be reported in the form of a table (see below).

2. For each of the seven runs, calculate the initial concentration of potassium iodide and ammonium peroxydisulfate. For example, in run 3 the amount of potassium iodide used was

   $$0.2 \text{ mol} \times L^{-1} \times 0.01000 \text{ L} = 2 \times 10^{-3} \text{ mol}$$

   the volume of the reaction mixture was 56.0 mL, or 0.0560 L; hence the initial concentration of KI was

   $$\frac{2 \times 10^{-3} \text{ mol}}{0.05600 \text{ L}} = 0.0357 \text{ mol} \times L^{-1} \text{ (or M)}$$

   Note: The significant figure rules have been ignored in this calculation. Of course, in your own calculations you will use the concentrations specified on the reagent bottles provided.

   Your initial concentrations should be included in a table, as illustrated on the next page.

3. Calculate the initial concentration of sodium thiosulfate. This is the same in each of the seven runs.

4. Refer back to the "Introduction and Theory" section and use the information provided to calculate the change in the concentration of the ammonium peroxydisulfate during the time it takes for the blue-black colour to form. As this is a decrease in concentration, it will have a negative sign and can be represented as $\Delta[S_2O_8^{2-}]$. This concentration change will be the same for all seven runs.

5. Calculate the rate of reaction for each run using the relationship

$$\text{Rate} = \frac{-\Delta[S_2O_8^{2-}]}{\Delta t}$$

where Δt is the time take for the blue-black colour to appear. The rate for each run should be recorded in your table of results. A suggested format for this table is shown below.

Run	$[I^-]_o$ (mol · L^{-1})	$[S_2O_8^{2-}]_o$ (mol · L^{-1})	Temp (°C)	Δt (s)	$\Delta [S_2O_8^{2-}]$ (mol · L^{-1})	Rate (mol · L^{-1} s^{-1})
1						
2						
3						
etc.						

6. For all the runs with the same initial concentration of potassium iodide, plot a graph of log (rate) (y-axis) against log $[S_2O_8^{2-}]_0$ (x-axis). As explained in the "Introduction and Theory" section, the slope of this line (rounded to the nearest whole number) gives the order of the reaction with respect to peroxydisulfate ion. For help with generating Graphs, see Appendix pp.122-126.

7. For all the runs with the same initial concentration of ammonium peroxydisulfate, plot a graph of log (rate) against log $[I^-]_0$. The slope of this line (rounded to the nearest whole number) gives us the order of the reaction with respect to the iodide ion.

8. Use the results of steps 6 and 7 to write the rate law. This will be of the form

$$\text{Rate} = k\,[S_2O_8^{2-}]^x[I^-]^y$$

Determine the rate constant, *k*, for each of the seven runs.

9. Determine the average value of the rate constant for the reaction. This rate constant applies only at the temperature at which you were working (should there not have been a great deal of variation in the temperatures at which the runs were carried out). Calculate the standard deviation of the rate constant.

C. The Effect of a Catalyst

Calculate the rate constant for the run in which copper (II) sulfate was added as a catalyst. By what factor did the presence of a catalyst increase the reaction rate over that of the uncatalysed reaction?

Questions

1. In some of the runs carried out in Part B of the experiment, potassium chloride and/or ammonium sulfate were added to the reaction mixture so that the ionic strength of the mixture was approximately the same in each run. Exactly what is meant by the term "ionic strength"?

2. The reaction system studied in this experiment is an example of a clock reaction. Explain what is meant by the term "clock reaction" and find an additional example of such a system.

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

Prerequisite Skills

In order to undertake this experiment, you must have completed the laboratory component of Athabasca University's *Chemistry 217* or its equivalent. To reduce the congestion around shared equipment, e.g., the water baths, some students may attempt this experiment before beginning Experiment D1. However, to do this, the student must have prepared his/her share of the communal solutions (see p. 41, Experiment D1) and have read the "Introduction and Theory" section of the preceding experiment.

Objectives

When you have completed this experiment you will have:

1. learned a practical method of determining activation energies.

2. gained additional experience in preparing standard solutions and in the use of a volumetric pipette.

3. seen an example of how graphs are used to extract physical quantities from experimental data.

This experiment also illustrates some of the topics discussed in your textbook:

1. activation energy,

2. reaction kinetics, and

3. effect of temperature on reaction rates

Introduction and Theory

Most chemical reactions proceed more rapidly as temperature is increased. In other words, reaction rates generally increase with an increase in temperature. We make use of this principle when we use a pressure cooker to cook our food. The pressure inside the pressure cooker raises the boiling point of the water; this in turn increases the rates of the reactions that occur as our food cooks. Conversely, when we place food in a refrigerator, the biochemical processes that take place as the food spoils are slowed down.

The effect of temperature on reaction rate can be explained using the kinetic-molecular theory. As the temperature is increased, so the average kinetic energy of the molecules is increased. In order for two molecules to react, they must collide with energy equal to, or greater than, a certain minimum energy that we call the *activation energy*. Naturally, the greater the average kinetic energy of the reactant molecules, the greater the chances of two such molecules colliding with sufficient energy for reaction to occur.

The activation energy, E_a, of a given reaction represents the difference in energy between the reactants and the transition state (or activated complex). As mentioned above, molecules must collide with at least this amount of energy to be able to react, although if the molecules do not have the correct orientation during the collision they may still not be converted into products, despite meeting the energy requirement. In 1889, Svante Arrhenius first derived the relationship that exists between the rate (or rate constant) of a given reaction and absolute temperature. This relationship is now generally called the Arrhenius equation:

$$k = Ae^{-E_a/RT}$$

where k is the rate constant, A is a probability factor, E_a is the activation energy, R is the universal gas constant, and T is the absolute temperature.

If we take logs (to the base e) of both sides of this equation, we obtain:

$$\log_e k = \log_e A - \frac{E_a}{RT}$$

Converting to the more familiar logs to the base 10, this equation becomes

$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303RT}$$

A plot of $\log_{10} k$ against $1/T$ then gives a straight line of slope $(-E_a)/(2.303R)$, which enables the value of the activation energy to be determined.

In this experiment you will determine the activation energy of the reaction that you studied in Experiment D1:

$$2I^{-}\ (aq) + S_2O_8{}^{2-} \rightarrow I_2\ (aq) + 2SO_4{}^{2-}\ (aq)$$

When determining the activation energy of a reaction, kineticists usually measure the rate constant of the reaction at four different temperatures, over a range of at least 30° C. In this experiment, you will determine the rate constant for the above reaction at room temperature, two different temperatures above room temperature, and one temperature below room temperature.

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.

Results and Calculations

Check to see if this is one of the experiments that has been assigned to you for a formal report. If it is, you may wish to review the section of the *Laboratory Manual* entitled "Writing Laboratory Reports." Note that even if you carry out this experiment before doing Experiment D1, you will not be able to complete the necessary calculations without having first completed the calculations from the earlier experiment. If, for some reason, your instructor has decided that you should omit Experiment D1, she/he will provide you with the information needed in order to complete these calculations.

1. For each of the four runs carried out in this experiment, determine the rate of reaction as described in steps 1 through 5 in the "Results and Calculations" section of Experiment D1, Part B. Use the rate law determined in step 8 of the same section to determine the value of the rate constant, *k*, in each of the four runs. If you did not do Experiment D1, obtain the rate law from your instructor.

2. Record the four rate constants in a table, as shown below.

Run	***k***	**$\log_{10} k$**	**Temperature**		**1/Temperature**
			(°C)	**(°K)**	**($°K^{-1}$)**
1					
2					
3					
4					

3. Plot a graph of $\log_{10} k$ (y-axis) against 1/temperature (x-axis). The result should be a straight-line graph, with a slope of $-E_a/2.303R$. For help with graphs in general, please consult Appendix pp.122-126.

4. Calculate the value of the activation energy, E_a.

Questions

1. A popular "rule-of-thumb" is that the rate of a chemical reaction can be expected to double each time the temperature is increased by 10° C. Do your results appear to confirm this generalization?

2. What would be the value of the activation energy for a reaction whose rate doubles when the temperature is increased from 25° C to 35° C?

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

> "The key idea is that dynamic equilibria are responsive to changes in the conditions." Jones and Atkins

Prerequisite Skills

In order to undertake this experiment, you must have completed the laboratory component of Athabasca University's *Chemistry 217* or its equivalent. In particular, you must be able to prepare a standard solution, use a volumetric pipette, carry out a dilution, and operate a Spectronic 20 spectrophotometer.

Objectives

When you have completed this experiment you will have

1. learned how an equilibrium constant can be determined spectrophotometrically.

2. received additional practice at preparing and diluting solutions of known concentration.

   As well, this experiment illustrates the following material covered in your textbook:

1. equilbria,
2. equilibrium constants, and
3. reversible reactions.

Introduction and Theory

Many chemical reactions do not go to completion; that is, no matter how long they are left, a 100% yield of product is never obtained. When a state is reached in which the concentrations of the reactants and products no longer changes with time, a reaction is said to be at equilibrium. This does not mean that the reaction has stopped; rather, it means that the rate of formation of products is equal to the rate of breakdown of the products to form reactants.

For a reaction of the type:

$$a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$$

the equilibrium constant, K_c, is given by:

$$\text{K}_\text{c} = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b}$$

where [A], [B], [C], and [D] are the equilibrium concentrations of A, B, C, and D, respectively, and *a*, *b*, *c*, and *d* are the coefficients of the balanced chemical equation. For any given reaction, the value of K_c can only be changed by a change in temperature. No matter in what proportions we might mix A, B, C, and D, they will react in such a way that the value of:

$$\frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b} \text{ is equal to } \text{K}_\text{c}.$$

In this experiment, you will determine the value of the equilibrium constant for the reaction:

$$\text{Fe}^{3+}\text{(aq)} + \text{SCN (aq)} \rightleftharpoons \text{Fe SCN}^{2+}\text{(aq)}$$

The equilibrium constant for this reaction is given by the expression:

$$\text{K}_\text{c} = \frac{[\text{FeSCN}^{2+}\text{ (aq)}]}{[\text{Fe}^{3+}\text{ (aq)}][\text{SCN}^{-}\text{ (aq)}]}$$

In solution, the thiocyanate ion, $SCN^-(aq)$, is colourless; the iron (III) ion is pale yellow, and the thiocyanatoiron (III) ion, $Fe(SCN)^{2+}(aq)$, is red. Thus, the colour of the solution provides an indication of the concentration of $Fe(SCN)^{2+}(aq)$ ions in solution. By using a spectrophotometer set at an appropriate wavelength, the concentration of $Fe(SCN)^{2+}(aq)$ ions in solution can be measured quantitatively.

Review Experiment A1, Chemistry 217, if you have forgotten the principles of spectrophotometry.

In Part A of the experiment you will prepare a number of solutions containing the thiocyanatoiron (III) ion, and you will use these solutions to plot a calibration curve of absorbance against [$Fe(SCN)^{2+}(aq)$]. The desired equilibrium constant will then be determined in Part B of the experiment by mixing together solutions of iron (III) nitrate and potassium thiocyanate of known concentration, and using the calibration curve from Part A to determine the concentration of $Fe(SCN)^{2+}(aq)$ in the resulting equilibrium mixture. At equilibrium, the concentration of iron (III) and thiocyanate will have been reduced by an amount equal to the concentration of $Fe(SCN)^{2+}(aq)$ formed. Thus the equilibrium concentration of iron (III) and thiocyanate can be calculated, and the value of K_c can be determined.

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.

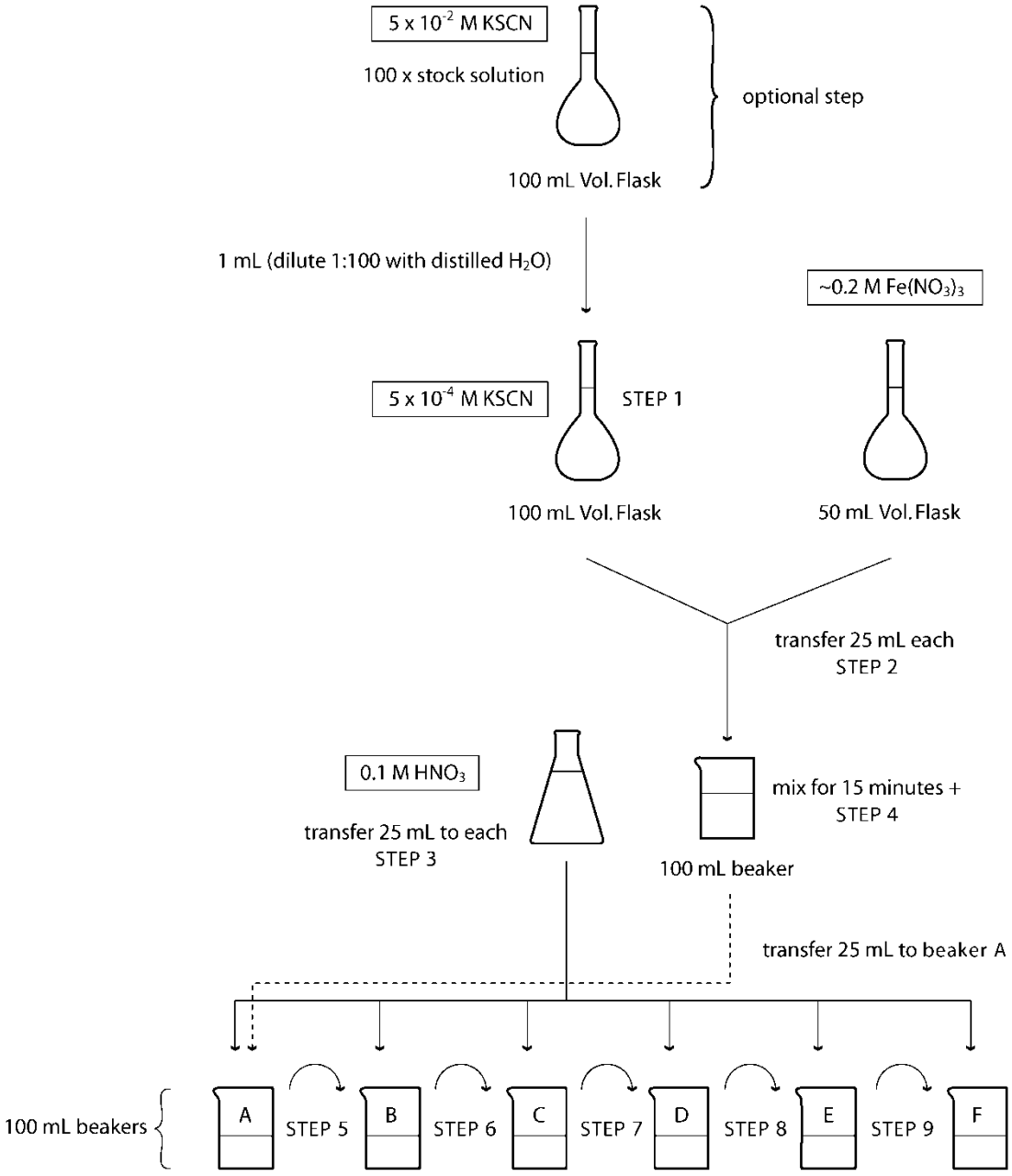
5. Using a clean 25-mL volumetric pipette, transfer 25 mL of the solution from beaker A (step 4) into the second beaker (beaker B) containing nitric acid. Mix well.

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

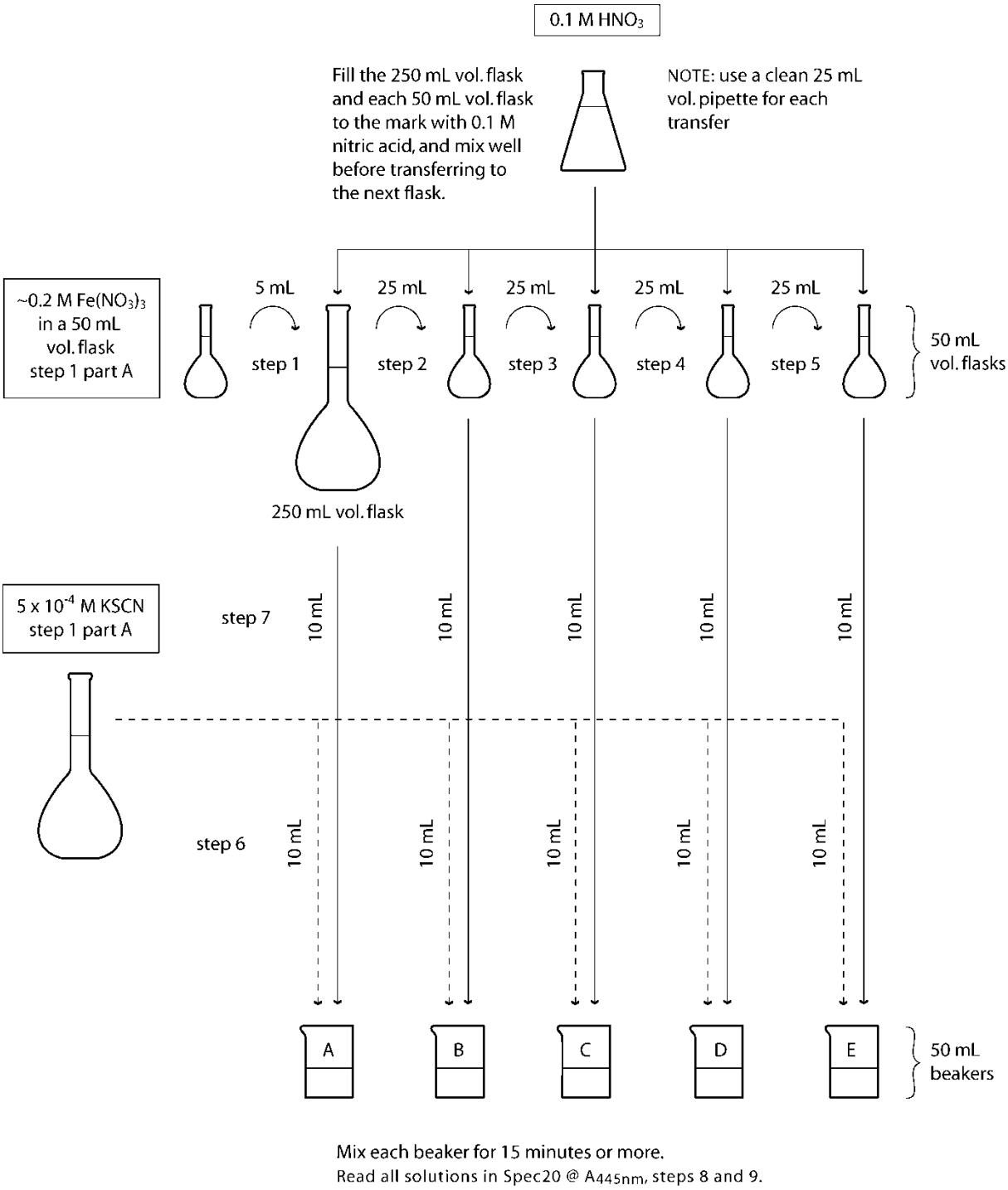
In this part of the experiment you will prepare five mixtures of iron (III) nitrate and potassium thiocyanate. By measuring the absorbance of the equilibrium mixtures, the equilibrium concentration of the thiocyanatoiron (III) ion will be determined and the equilibrium constant can then be calculated.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



Mix each beaker for 15 minutes or more.
Read all solutions in Spec20 @ A_{445nm}, steps 8 and 9.

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.

Results and Calculations

Check to see if this is one of the experiments that have been assigned to you for a formal report. If it is, you may wish to review the section of this *Laboratory Manual* entitled "Writing Laboratory Reports."

A. Construction of a Calibration Curve

The following results and calculations should be reported.

1. Preparation of a solution of iron (III) nitrate

   Mass of vial + iron (III) nitrate =
   Mass of empty vial =
   Mass of iron (III) nitrate =

   The concentration of the iron (III) nitrate solution should then be calculated.

2. Preparation of a solution of potassium thiocyanate

   Mass of vial + potassium thiocyanate =
   Mass of empty vial =
   Mass of potassium thiocyanate =

   The concentration of the potassium thiocyanate solution should then be calculated.

3. Calculate the concentration of $Fe(SCN)^{2+}$ in the solution formed from mixing 25 mL of your iron (III) nitrate solution with 25 mL of your potassium thiocyanate solution.

4. Use the result from step 3 to calculate the concentration of $Fe(SCN)^{2+}$ in each of the six solutions prepared in steps 4 through 9 in Part A of the procedure.

5. Report the results from the absorbance measurements in a table. A suitable format is suggested below.

Beaker	$[Fe(SCN)^{2+}]$ $(mol \cdot L^{-1})$	Absorbance (Trial 1)	Absorbance (Trial 2)
A	1.0×10^{-4}		
B			
etc.			

6. Plot a graph of absorbance (y-axis) against $[Fe(SCN)^{2+}]$ (x-axis). This is your calibration curve. If the Beer-Lambert Law is obeyed, the graph should be a straight line. See Appendix pp.122-126 for help with graphing.

B. Determination of the Equilibrium Constant

1. Calculate the concentration of iron (III) ions in each of the solutions prepared in steps 2 through 4 of Part B of the procedure.
2. Prepare a table as shown below. Record the measured absorbance for each of the five reaction mixtures and then use your calibration curve to determine the equilibrium concentration of thiocyanatoiron (III) ion ($Fe(SCN)^{2+}$) in each mixture.

Mixture number	Absorbance (Trial 1)	Absorbance (Trial 2)	Absorbance (mean)	$[Fe(SCN)^{2+}]$ ($mol \cdot L^{-1}$)
1				
2				
etc.				

3. For each of the five reaction mixtures, calculate
   a. the initial concentration of iron (III) ions in the mixture,
   b. the initial concentration of thiocyanate ions in the mixture,
   c. the equilibrium concentration of iron (III) ions in the mixture; this will be equal to the initial concentration of iron (III) ions *minus* the equilibrium concentration of thiocyanatoiron (III) ions, i.e., $[Fe^{3+}] = [Fe^{3+}]_0 - [Fe(SCN)^{2+}]$
   d. the equilibrium concentration of thiocyanate ions in the mixture; this will be equal to the initial concentration of thiocyanate ions minus the equilibrium concentration of thiocyanatoiron (III) ions, i.e.,

      $[SCN^-] = [SCN^-]_0 - [Fe(SCN)^{2+}]$

   e. the equilibrium constant, K_c, using the relationship:

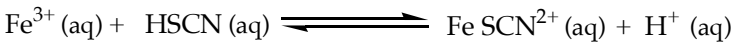
$$K_c = \frac{[FeSCN^{2+}\ (aq)]}{[Fe^{3+}\ (aq)][SCN^-\ (aq)]}$$

4. Summarize the results obtained in (3) in a table. A suitable format is outlined below.

Mixture number	Initial Concentrations		Equilibrium Concentrations			K_c
	$[Fe^{3+}]_0$ ($mol \cdot L^{-1}$)	$[SCN^-]_0$ ($mol \cdot L^{-1}$)	$[Fe^{3+}]$ ($mol \cdot L^{-1}$)	$[SCN^-]$ ($mol \cdot L^{-1}$)	$[Fe(SCN)^{2+}]$($mol \cdot L^{-1}$)	
1						
2						

Questions

1. The reaction that you studied was carried out in an acidic medium. In some textbooks the equation for this reaction is given as



   Write the equilibrium-constant expression for this reaction as written and use this expression to determine K_c for one of your reaction mixtures.

2. Under certain conditions, the product of the reaction between iron (III) ions and thiocyanate ions is the dithiocyanatoiron (III) ion, $Fe(SCN)_2^+$.

   a. Write an equation for the reaction in which dithiocyanatoiron (III) ions are produced.

   b. Write the equilibrium-constant expression for the equation written in part A.

   c. Explain how your experimentally determined values of K_c would be affected if this reaction occurred to any significant extent in your experiment.

Experiment D4:
Le Châtelier's Principle

Prerequisite Skills

In order to undertake this experiment, you must have completed the laboratory component of Athabasca University's *Chemistry 217* or its equivalent.

Objectives

When you have completed this experiment you will have observed Le Châtelier's Principle at work in a number of chemical reactions.

The experiment illustrates the following topics from your textbook:

1. applications of equilibrium constants,
2. the response of equilibria to change,
3. the difference between a weak and strong acid,
4. certain aspects of solubility equilibria,
5. complex ions and solubilities.

Introduction and Theory

You are already familiar with the fact that many chemical reactions can proceed in both the forward and reverse directions. Such reactions are said to be reversible. For example, when blue copper (II) sulfate is heated, water is driven off and white anhydrous copper (II) sulfate remains.

$$CuSO_4 \cdot 5H_2O\ (s) \rightarrow CuSO_4(s) + 5H_2O\ (g)$$

However, the addition of a few drops of water to the anhydrous salt results in the reconstitution of the pentahydrate:

$$CuSO_4(s) + 5H_2O\ (l) \rightarrow CuSO_4 \cdot 5H_2O\ (s)$$

In many reversible reactions the reaction does not lie completely to one side as it does in the above examples. Instead, we find that both the forward and reverse reactions occur concurrently. When the rates of the forward and reverse reactions are equal, the concentrations of the reactants and products do not change with time and the system is said to be at equilibrium. A classic example of an equilibrium reaction is the so-called Haber process, in which nitrogen and hydrogen combine to form ammonia:

$$N_2\ (g) + 3H\ (g) \rightleftharpoons 2NH_3\ (g)$$

No matter how long the above reaction is allowed to proceed (in a closed system), the nitrogen and hydrogen are never completely used up. That is, at any given time, there is always some nitrogen, hydrogen and ammonia present. Once equilibrium has been attained, the concentration of these three species is such that:

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

K_c is called the equilibrium constant.

If some additional hydrogen gas is added to the above system when it is at equilibrium, what would happen? As the value of K_c can only change if the temperature is changed, it should be apparent that if $[H_2]$ is increased, the only way that K_c can remain constant is if $[N_2]$ decreases and $[NH_3]$ increases. In practice this is achieved by the reaction of more nitrogen with some of the added hydrogen, and consequently the formation of additional ammonia. This is an example Le Châtelier's Principle in action. The principle states that:

"If a system at equilibrium is subjected to a change, it responds in such a way that the effect of that change is minimized."

In the above example, the effect of adding hydrogen to the system is minimized by some of that hydrogen reacting with the nitrogen already present to form more ammonia.

In this experiment you will examine a number of equilibrium systems and will use Le Châtelier's Principle to interpret the effect of adding various reagents to these systems.

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.

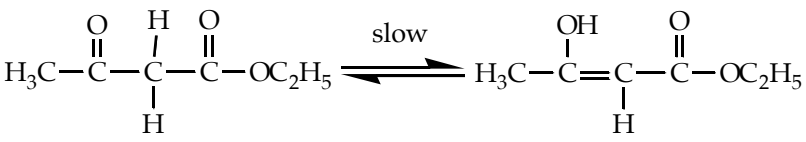
2. **WARNING:** Chromates and dichromates are suspected carcinogens. Do not permit these solutions to come into contact with your skin.

   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:

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

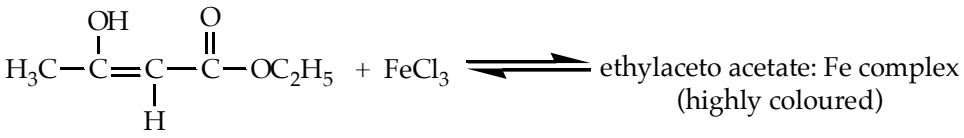
3. **WARNING:** Bromine is toxic. Use disposable gloves and carry out this part of the experiment in a fume hood.

   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):

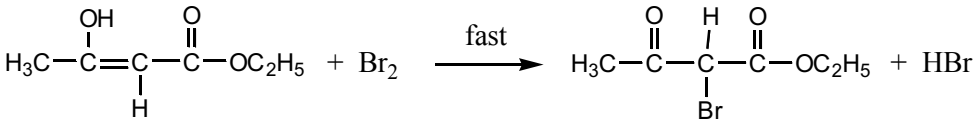


keto form enol form

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:

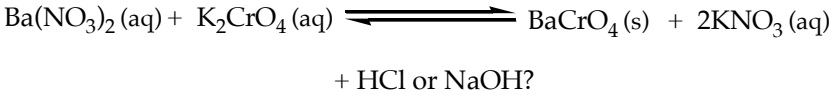


Add 5 drops of ethyl acetoacetate to 5 mL of distilled water in a large test tube. Mix the solution well and then add 3 drops of iron (III) chloride (1 mol · L^{-1}) solution. Mix well, and note the colour of the solution. Quickly add a few drops of bromine water—the colour of the solution should fade. 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.

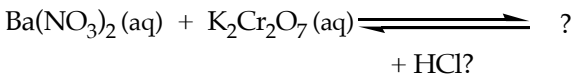
4. **WARNING**: Part 4 of this experiment involves the use of chromate/dichromate solutions. These substances are suspected carcinogens. Avoid contact with your skin.

   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}).



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.

Results and Calculations

A formal report will not be required for this experiment. However, your short report should contain details of the tests carried out and the observations that you made during each test. In addition, you must explain what happened in each test; in most cases this will involve the application of Le Châtelier's Principle.

Question

1. When a few drops of sodium fluoride solution are added to a solution containing iron (III) ions a colourless solution is obtained.

   However, when a few drops of sodium chloride are added to a solution

   $$\underset{\text{pale yellow}}{Fe^{3+}(aq) + 6F^{-}(aq)} \rightleftharpoons \underset{\text{colourless}}{FeF_6^{3-}(aq)}$$

   containing iron (III) ions a pale yellow solution is obtained, with the yellow colour deepening as more sodium chloride is added.

   $$\underset{\text{pale yellow}}{Fe^{3+}(aq) + 4Cl^{-}(aq)} \rightleftharpoons \underset{\text{intense yellow}}{FeCl_4^{-}(aq)}$$

   Predict what will occur, if a solution of sodium fluoride is added to the solution prepared from the iron (III) and sodium chloride solutions. Justify your prediction in terms of Le Châtelier's principle.

Experiment D5: Titration Curves

> "The best education is to be found in gaining the utmost information from the simplest apparatus." A. N. Whitehead

Prerequisite Skills

In order to do this experiment, you must have completed the laboratory component of Athabasca University's *Chemistry 217* or its equivalent. In particular, you must be familiar with the correct techniques for using a volumetric pipette and a burette.

Objectives

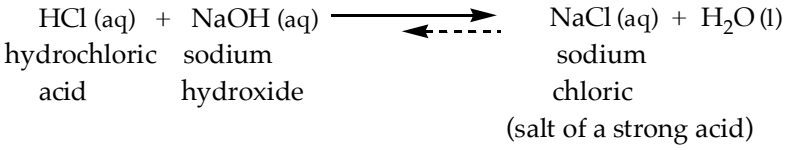
The purpose of this experiment is to determine the concentration of a given solution of acetic acid by monitoring the pH of the solution as base is added.

The experiment also illustrates how the shape of a titration curve for an acid-strong base titration depends upon the strength of the acid used, and how the pH at the equivalence point in such a titration also depends upon the strength of the acid used.

Introduction and Theory

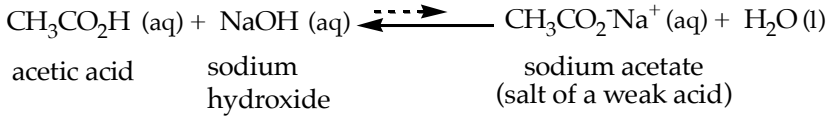
In Experiment A2 of *Chemistry 217* you performed two acid-base titrations in which the equivalence point was determined using an indicator. A more precise method of determining the equivalence point in an acid-base titration is to measure the pH of the reaction mixture as a function of added titrant. A plot of pH (y-axis) against volume of added titrant (x-axis) yields a curve whose exact shape depends on the strengths of the acid and base used.

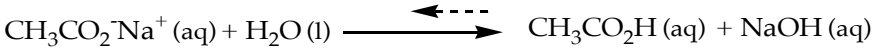
In the first part of this experiment you will titrate a strong acid (hydrochloric acid) with a strong base (sodium hydroxide). As the salt produced in this reaction, sodium chloride, is a salt of a strong acid, it does not hydrolyze, and at the equivalence point the only species present are water, sodium ions and chloride ions:



In such situations, the reaction mixture has a pH of 7.0 at the equivalence point.

In the second part of this experiment, you will titrate a weak acid (acetic acid) with a strong base (sodium hydroxide). In this case, the salt produced, sodium acetate, hydrolyzes to form hydroxide ions, thus at the equivalence point the pH of the reaction mixture will be greater than 7.0.





How a pH Meter Works—Nernst's Equation in Action

A simplified way of dealing with low H^+ ion concentrations was developed by Danish biochemist, S. P. L. Sørensen, in 1909, when he proposed the pH scale, $pH = -\log[H^+]$. pH measurements are now probably the most numerous type of quantitative chemical assay performed on this planet, and nearly all of these measurements are determined potentiometrically (electrochemically) using a pH meter, and a glass indicator and calomel reference electrode.

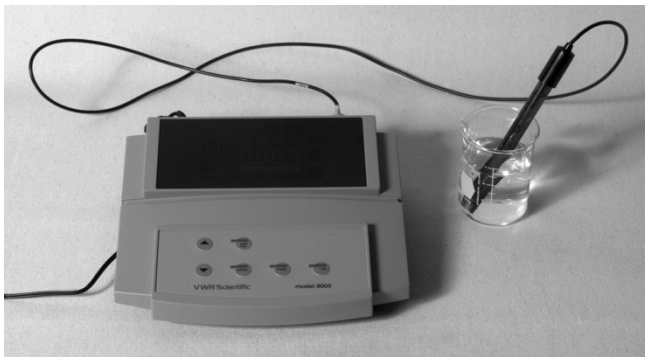


Figure D5.1 Example of a modern pH meter and combination electrode.

Thanks to nearly 50 years of research in the 20th century, scientists now have a good understanding of just how a pH meter and electrode works.

pH Meters

The meter used for pH measurements must be a highly sensitive amplifier of very small electrical signals. Amplifiers this sensitive will vary their response over time, i.e., the signal drifts during operation. To correct for this, and for variations in individual electrodes, the meter must be calibrated with known pH standard solutions before an unknown solution can be measured.

pH Electrodes

Two standard half cells (indicator/reference) are required to make a pH determination. One set of standard electrodes is the hydrogen/calomel electrode, another is the glass/calomel electrode. In this course you will use the latter, as it is much easier to operate.

The potential, *E*, that develops between the glass and calomel electrodes when both are immersed in a solution can be measured by the sensitive pH meter. A typical glass indicator electrode consists of a thin, bulb-shaped glass membrane sealed onto the end of a glass tube. The inside of the glass electrode is filled with an electrolyte, usually 0.1 M HCl, to maintain a constant internal pH. The calomel reference electrode can be either external (Figure D5.2) or internal, as in a combination pH probe. The cell is diagrammed below.

$$\text{Ag} \,\big|\, \text{AgCl (sat.) 0.1 M HCl} \,\big|\, \text{glass membrane} \,\big|\, \textbf{test solution} \,\big\|\, \text{Hg}_2\text{Cl}_2\text{, KCl (sat.)} \,\big|\, \text{Hg}$$

The glass membrane has two hydrated glass layers (i.e., interfaces), one internal and one external. The rapid diffusion of H^+ ions into and out of each of these layers quickly comes to equilibrium, and potentials are established and then recorded by the pH meter. Note that no actual electron transfer occurs, and thus this is not a normal redox process.

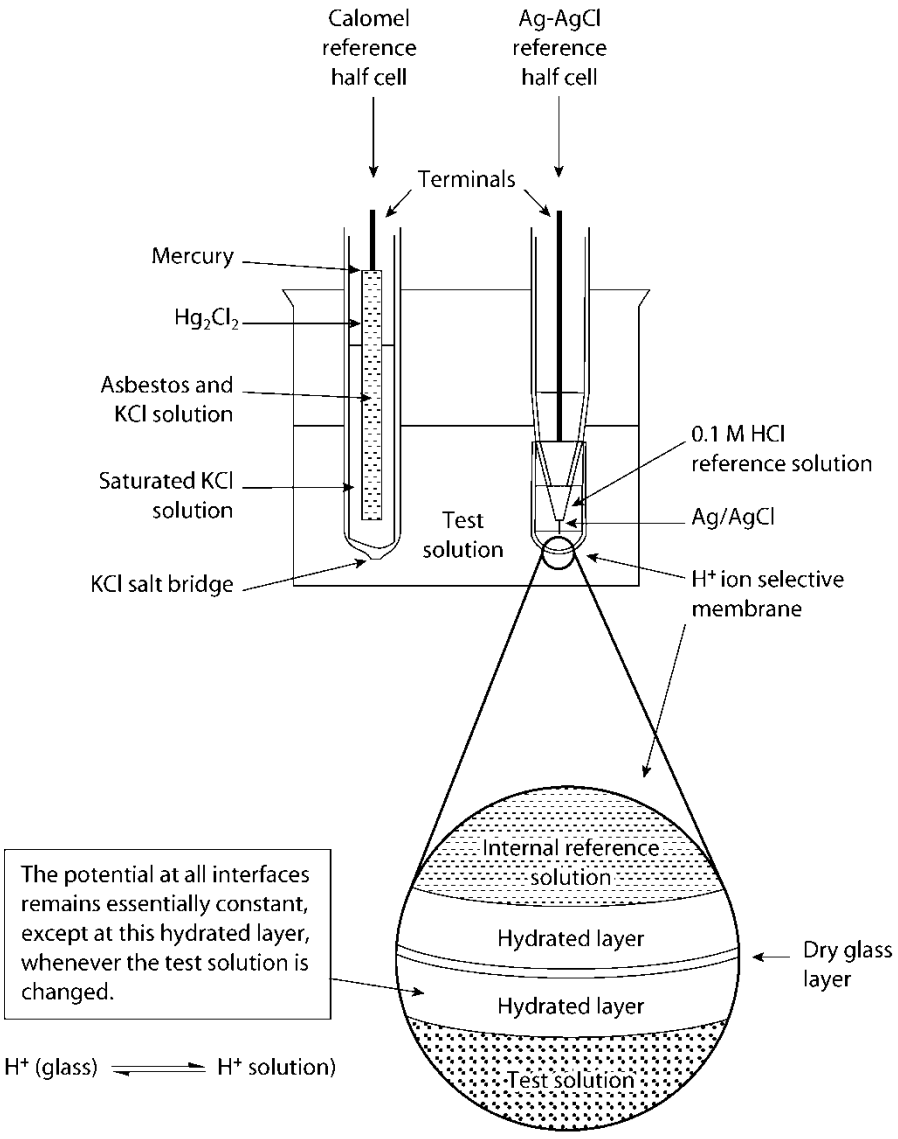


Figure D5.2 Schematic diagram of a calomel (Hg/Hg_2Cl_2) reference, and Ag/AgCl indicator electrode, with H+ ion selective glass membrane. (Adapted from Harris and Kratovchvil CHEM 312 Lab Manual)

By first calibrating the pH meter using a buffer of known pH, and then measuring the cell potential, *E*, the pH can be determined directly because $E = E' + (0.592\ \text{V}) \times \text{pH}$, an expression derived from **Nernst's Equation**. If *E* is measured first for a solution of known pH, it is not necessary to calculate *E'*, and the meter automatically converts and displays the corresponding pH reading.

Note: You do not need to know all the detailed information shown here for the lab quiz.

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.

Results and Calculations

Check to see if this experiment is one of those assigned to you for a formal report. If necessary, review the "Writing Laboratory Reports" section of this *Laboratory Manual* before you begin your write up.

Results

The data that you collected should be reported in two tables, one for each part of the experiment. A suggested format is shown below.

Total volume of NaOH added	pH meter reading
0.00	1.64
0.50	1.67
1.00	1.70
1.50	-
etc.	-

For each set of results plot a graph of pH (y-axis) against total volume of sodium hydroxide added (x-axis). For help with generating graphs, please see Appendix pp.122-126.

Calculations

1. In a titration curve, the equivalence point is at the mid-point of the steepest part of the curve. One method of determining the equivalence point is to draw a tangent to each of the upper and lower parts of the curve (note that these tangents must be parallel) and drawing a third parallel line half-way between the two tangents. The point at which this third line bisects the titration curve is the equivalence point (see Figure D5.1).
2. Determine the equivalence point for the titration between sodium hydroxide and hydrochloric acid.
3. From the volume and concentration of the hydrochloric acid used and the volume of sodium hydroxide required to reach the equivalence point, calculate the concentration of the sodium hydroxide solution.
4. Determine the equivalence point for the titration between sodium hydroxide and acetic acid.
5. From the volume of acetic acid used, the concentration of the sodium hydroxide solution (found in step 2, above), and the volume of sodium hydroxide required to reach the equivalence point, calculate the concentration of the acetic acid solution.

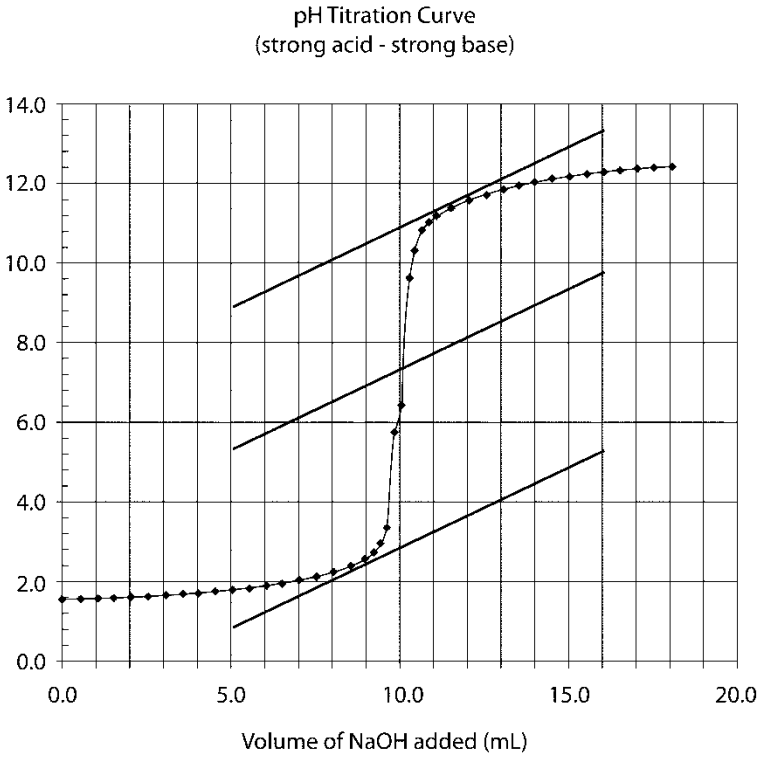


Figure D5.3: Finding the equivalence point on a titration curve.
WARNING: The grade given for this experiment depends mainly on the accuracy of your results. If you feel that the curves you obtained are not satisfactory, you should repeat the experiment before submitting your report.

Questions

1. Calculate the pH at the equivalence point in a titration between 10.00 mL of acetic acid (0.100 mol · L^{-1}) and sodium hydroxide (0.100 mol · L^{-1}). How does this value compare with the value you obtained in the experiment?

2. In the table shown in the "Results and Calculations" section of this experiment, the pH of the solution before sodium hydroxide has been added is indicated as being 1.00. This corresponds to the pH of a 0.10 mol · L–1 solution of hydrochloric acid. Your initial pH reading was probably not 1.00. Why?

3. In a potentiometric titration between weak acid and a strong base, such as the one carried out in Part B of this experiment, the pKa of the weak acid is equal to the pH of the solution, when half of the volume of sodium hydroxide required to reach the equivalence point has been added. From your results, determine the pKa of acetic acid. Compare your value with the literature value.

Block E Experiments

Note: Students must complete all of the experiments described in Block D before proceeding to Block E. The three experiments in Block E must be completed before the student proceeds to Block F.

Experiment E1:
Voltaic Cells

Prerequisite Skills

In order to begin this experiment you must have completed the laboratory component of Athabasca University's *Chemistry 217*, or its equivalent and Block D of *Chemistry 218*.

Objectives

The aim of this experiment is to provide the student with the opportunity to construct a number of voltaic cells and to measure the electromotive force (emf, denoted E_{cell}) produced by each cell. The experiment illustrates the following topics that are covered in the theory component of the course: galvanic or voltaic cells, and cell emf.

Introduction and Theory

When zinc metal is added to a solution of copper (II) sulfate, the zinc metal dissolves and metallic copper is deposited:

$$Zn\,(s) + CuSO_4\,(aq) \rightleftharpoons Cu\,(s) + ZnSO_4\,(aq)$$

zinc metal	copper (II) sulfate	copper metal	zinc sulfate

In this reaction, each atom of zinc gives up two electrons to form a zinc ion, i.e., the zinc is oxidized, and each copper (II) ion gains two electrons to form a copper atom, i.e., copper (II) ions are reduced to copper metal. We can write the following half-equations to represent these two processes:

$$Zn\,(s) \rightleftharpoons Zn^{2+}\,(aq) + 2e^-\,(aq)$$

$$Cu^{2+}\,(aq) + 2e^-\,(aq) \rightleftharpoons Cu\,(s)$$

The overall process can therefore be represented as:

$$Zn\,(s) + Cu^{2+}\,(aq) \rightleftharpoons Cu\,(s) + Zn^{2+}\,(aq)$$

In the reaction described above, the electrons are transferred directly from the zinc metal to the copper (II) ions. In a simple voltaic cell, the species providing and receiving the electrons are in separate containers (half-cells) in which the metal concerned is partially immersed in a solution of its own ions. The electrons pass along a wire in order to get from the half-cell in which oxidation occurs (the anode), to the half-cell in which reduction occurs (the cathode). As the electrons pass through this external circuit they can be made to do work, e.g., to provide the energy for a small light-bulb. In practice, in order to maintain electrical neutrality in each half-cell, a salt bridge must be provided to allow the migration of anions and cations into and out of the half-cells.

We can predict the electromotive force, or emf (voltage) produced by a voltaic cell using standard electrode potentials:

$$E^0_{cell} = E^0_{ox} + E^0_{red}$$

where E^0_{cell} represents the standard emf produced by the cell,
E^0_{ox} represents the standard oxidation potential of the reaction occurring at the anode, and
E^0_{red} represents the standard reduction potential of the reaction occurring at the cathode.

The standard potentials for the most common half-reactions may be found in your textbook. Thus for the half-reactions described above:

$$Zn\,(s) \rightleftharpoons Zn^{2+}\,(aq) + 2e^{-}\,(aq)$$

$$Cu^{2+}\,(aq) + 2e^{-}\,(aq) \rightleftharpoons Cu\,(s)$$

and $E = 0.76V + 0.34\ V = 1.10\ V.$

Note that this electromotive force (emf) will only be observed for a cell at 25°C, in which the concentration of zinc ions, and copper (II) ions are both 1.00 mol · L⁻¹.

Some 'Definitions' to Remember:

'Red Cat' = **red**uction occurs at the **cat**hode
'Oxan' = **ox**idation occurs at the **an**ode
'leo' = **l**oss of **e**lectrons is **o**xidation
'ger' = **g**ain of **e**lectrons is **r**eduction
Voltaic or Galvanic Cell: chemical reactions used to produce electrical cells.
Electrolytic Cell: electrical energy used to bring about chemical reactions.

Electrode Conventions:

	Cathode	**anode**
Ions attracted	cations	anions
Direction of electron movement	into cell	out of cell
Half reaction	reduction	oxidation
Sign		
Voltaic or Galvanic Cell	positive	negative
Electrolysis Cell	negative	positive

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!

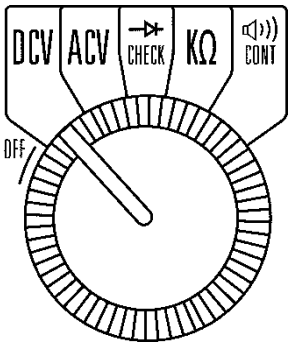


Figure E1.1:
Multimeter Switch Setting

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 Fig.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.

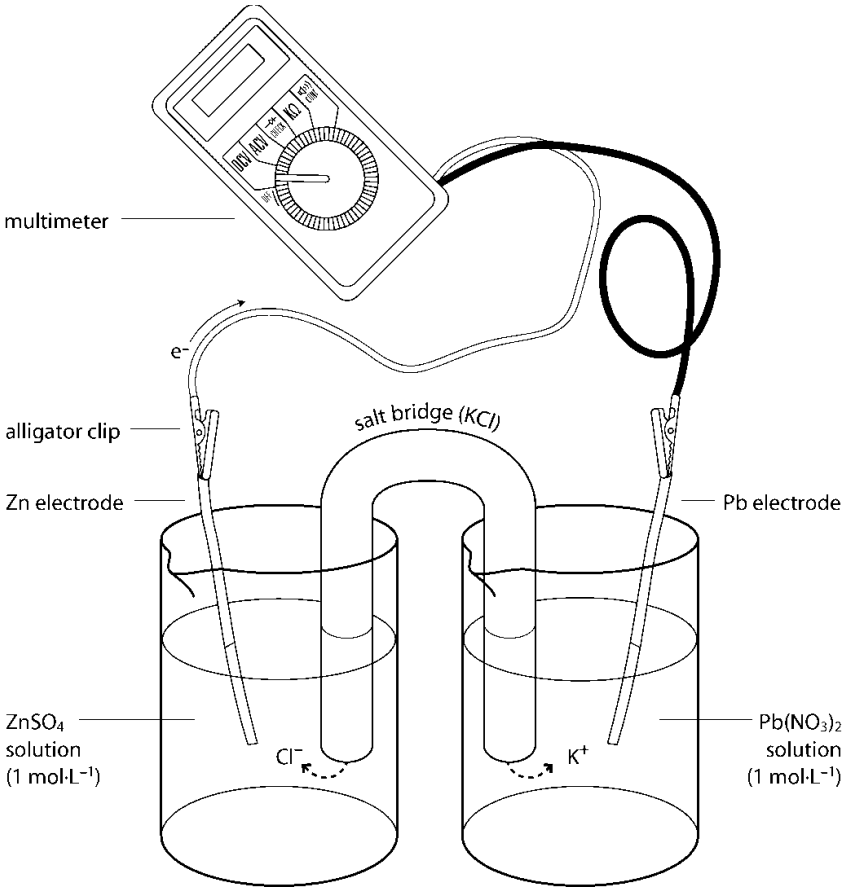


Figure E1.2:
Set up of half-cells

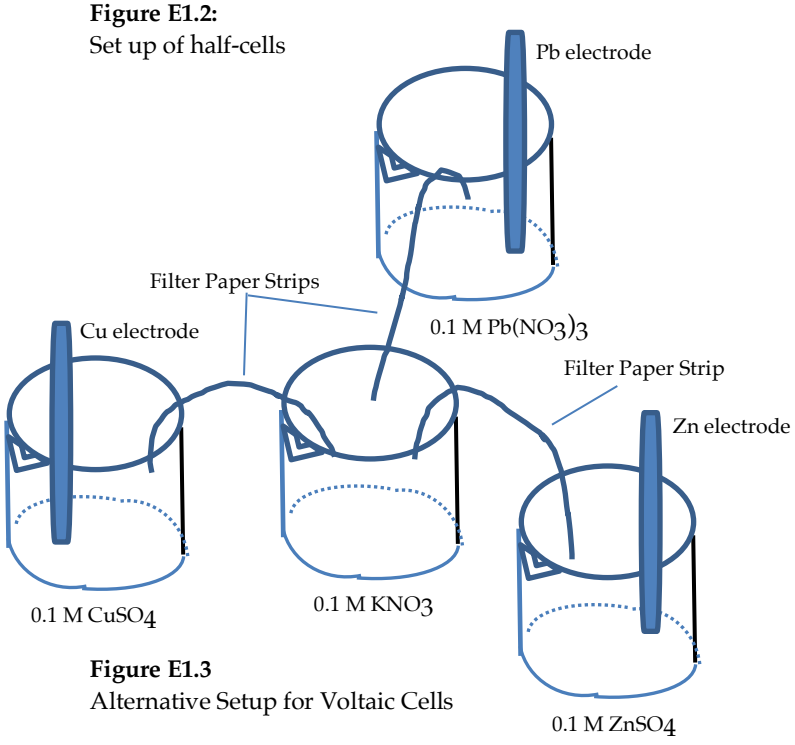
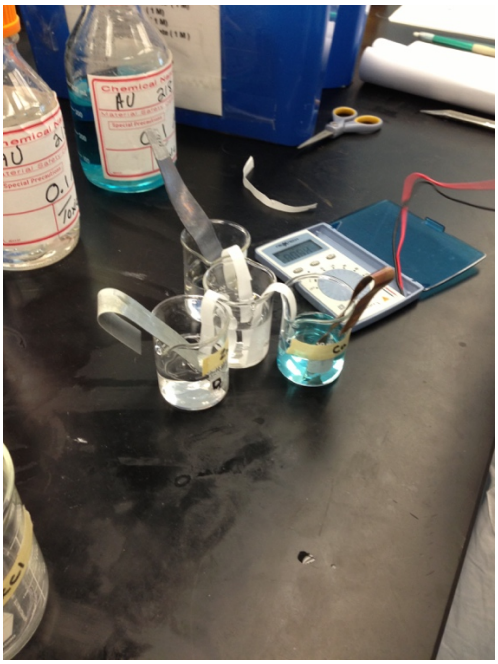


Figure E1.3
Alternative Setup for Voltaic Cells



Results, Calculations and Write-up

This experiment will not be assigned to you for a formal write-up. However, you should review the section "Writing laboratory reports—Short reports" in this *Laboratory Manual* before you begin writing your report.

Results

Voltage produced from cell using Zn/Zn^{2+} and Pb/Pb^{2+} half-cells =
Voltage produced from cell using Zn/Zn^{2+} and Cu/Cu^{2+} half-cells =
Voltage produced from cell using Cu/Cu^{2+} and Pb/Pb^{2+} half-cells =

Calculations

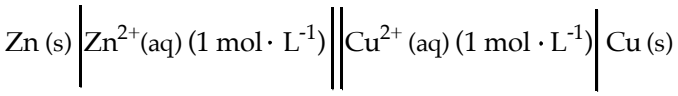
1. Use standard electrode potentials (see textbook) to calculate the voltage that you would expect to be produced for each of the three cells investigated in this experiment. Comment on any cases in which the predicted voltage does not agree with the experimentally observed value.

2. For each of the three cells studied
   d. write the overall cell reaction
   e. identify the anode and cathode

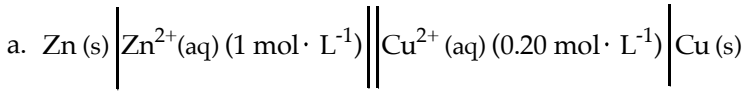
3. On the basis of your results, arrange the three metals studied in this experiment (zinc, copper, and lead) in order of decreasing ease of oxidation (i.e., list the most easily oxidized metal first). Briefly justify your answer.

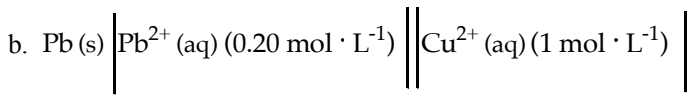
Questions

1. The cell constructed in step 7 of the experiment is often represented in the following way:



In such representations, the anode is always written first, with the single vertical lines (|) representing phase boundaries and the double vertical lines (‖) representing the salt bridge. For each of the following voltaic cells, (1) write the overall reaction and (2) determine the voltage produced:

a. 

b. 

Experiment E2: Determination of a Molar Mass by Electrolysis

Prerequisite Skills

In order to start this experiment you must have completed the laboratory component of Athabasca University's *Chemistry 217* or its equivalent and Block D of *Chemistry 218*.

Objectives

The purpose of this experiment is to illustrate a method by which an unknown metal can be identified through the determination of its molar mass in an electrolytic cell.

The experiment requires you understand:

1. the qualitative behaviour of electrolytic cells,

2. the potential needed for electrolysis,

3. and the quantitative aspects of electrolysis, i.e., Faraday's Law of Electrolysis.

In order to determine the amount of hydrogen gas produced during the electrolysis, use will be made of the Ideal Gas Law, and Dalton's Law of Partial Pressures.

Introduction and Theory

In an electrolytic cell, a non-spontaneous chemical reaction is made to occur through the application of electrical energy. A typical arrangement is to immerse two inert electrodes into the solution to be electrolyzed and to connect these electrodes to a suitable source of electrical energy, e.g., a battery. During the course of the electrolysis, oxidation takes place at the anode, and reduction occurs at the cathode. For example, if an aqueous solution of zinc bromide is electrolyzed, the following half-reactions occur

at the anode:

$$\underset{\text{bromide}}{2Br^-(aq)} \longrightarrow \underset{\text{bromine}}{Br_2(aq) + 2e^-(aq)}$$

at the cathode:

$$Zn^{2+}(aq) + 2e^-(aq) \longrightarrow Zn(s)$$

The overall reaction taking place in such a cell is

$$ZnBr_2(aq) \longrightarrow Zn(s) + Br_2(aq)$$

However, if the metal used as the anode is more easily oxidized than both the water and the anion present in the solution being electrolyzed, the anode itself will be oxidized and will dissolve during the course of the electrolysis. For example, if we try to electrolyze an aqueous solution of copper (II) sulfate using a copper anode, we find that the copper anode is more easily oxidized than either water or sulfate ion. Thus, the half-reaction that occurs at the anode is

$$Cu(s) \longrightarrow Cu^{2+}(s) + 2e^-(aq)$$

In the electrolysis of sulfuric acid, hydrogen ions are reduced to hydrogen gas according to the following half-equation:

$$2H^+(aq) + 2e^-(aq) \longrightarrow H_2(g)$$

This half-equation tells us that in order to produce 1 mol of hydrogen gas, 2 mol of electrons (or 2 faradays of electricity) must be passed. Thus, if we can determine the amount (i.e., number of moles) of hydrogen gas produced during a given electrolysis, we can use this quantity to calculate the number of faradays passed.

If such an electrolysis is carried out using an unknown metal as the anode, the identity of the metal used can usually be deduced. All we have to do is

remember that the number of faradays of electricity consumed by the cathode half-reaction must equal the number of faradays produced in the anode reaction, and assume that the anode half-reaction can only be:

$$M\,(s) \longrightarrow M^{+}\,(aq) + 1e^{-}\,(aq)$$

$$M\,(s) \longrightarrow M^{2+}\,(aq) + 2e^{-}\,(aq)$$

$$M\,(s) \longrightarrow M^{3+}\,(aq) + 3e^{-}\,(aq)$$

$$M\,(s) \longrightarrow M^{4+}\,(aq) + 4e^{-}\,(aq)$$

By determining the mass of the anode before and after the electrolysis, and knowing the number of faradays passed, we can calculate four possibilities for the molar mass of the metal anode.

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.

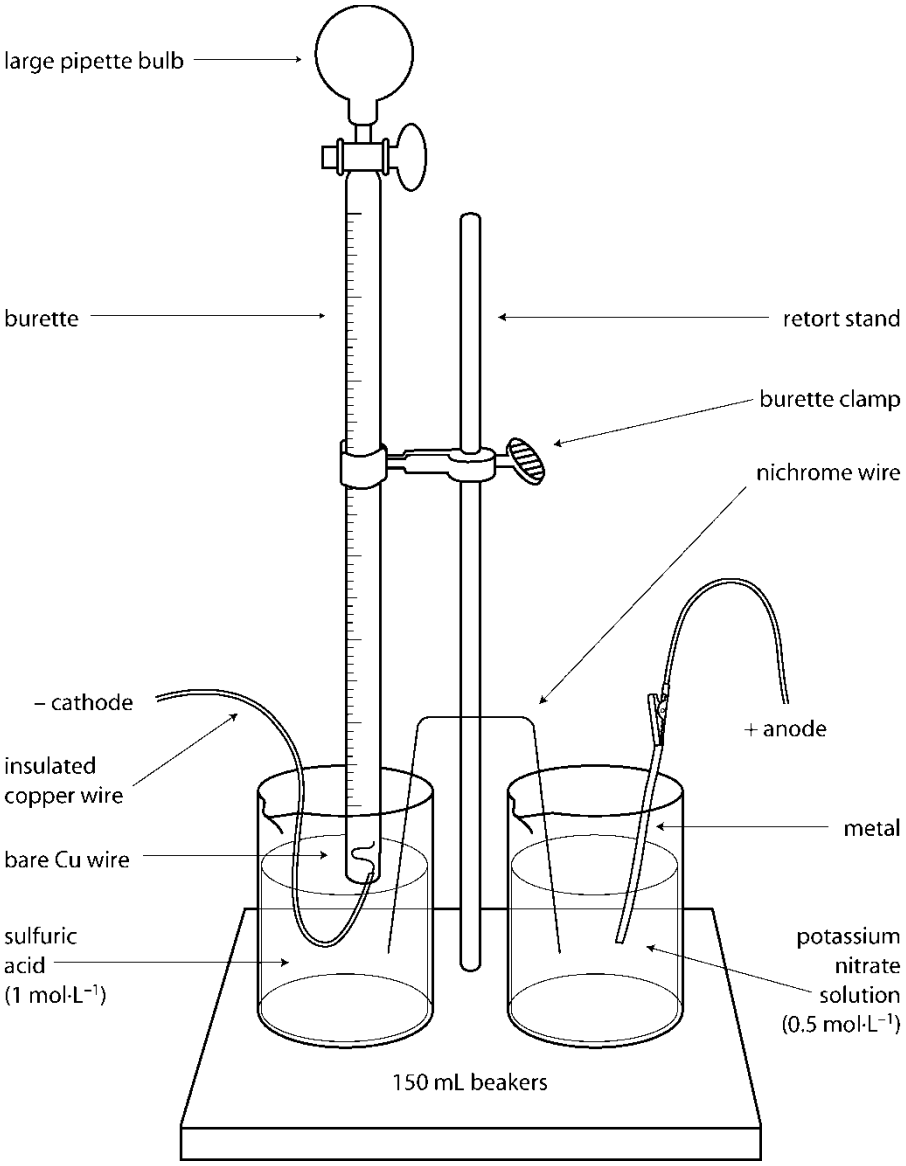


Figure E2.1:
Apparatus set up

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.

Results, Calculations and Write-Up

Find out from your instructor if this experiment has been assigned to you for a formal report or whether a short report will suffice. If necessary, review the section "Writing Laboratory Reports" in this *Laboratory Manual*.

Results

_____ = mass of metal anode before electrolysis

_____ = mass of metal anode after electrolysis

_____ = mass of metal consumed during electrolysis

_____ = initial burette reading

_____ = burette reading after first half of experiment

_____ = volume of $H_2(g)$ collected in first half of experiment

_____ = burette reading after being refilled

_____ = burette reading at end of experiment

_____ = volume of $H_2(g)$ collected in second half of experiment

_____ = total volume of $H_2(g)$ collected

_____ = air temperature

_____ = barometric pressure

_____ = vapour pressure of water at the above air temperature

Calculations

1. Use Dalton's Law of Partial Pressures to determine the pressure of the hydrogen gas collected in the burette.

2. Determine the amount (i.e., number of moles) of hydrogen gas that was collected. This may be done using the ideal gas law; however, be sure to use the correct value of *R*, the ideal gas constant. Use SI units throughout your calculation.

3. Given that the reaction occurring at the cathode is

$$2H^+(aq) + 2e^-(aq) \longrightarrow H_2(g)$$

determine the number of faradays passed during the course of the electrolysis.

4. The general form of the half-equation that represents the process occurring at the metal anode is

$$M(s) \longrightarrow M^{n+}(aq) + ne^-(aq)$$

where n is an integer. For $n = 1, 2, 3$, and 4, determine the amount of metal consumed during the electrolysis.

5. Calculate the four possibilities for the molar mass of the unknown metal. (These values correspond to the four possible values of n: 1, 2, 3 or 4.) Use your periodic table to determine the four possible identities of the metal.

6. Determine which of the four possibilities corresponds best with the metal that you used. Briefly justify your choice.

WARNING: Your grade will depend to a large extent upon the accuracy and precision of your results. You should satisfy yourself that you have completed this experiment to the best of your ability before you proceed to the next experiment.

Question

1. The chloroplatinate ion may be represented by the formula $PtCl_x^-$. When an aqueous solution containing chloroplatinate ions was electrolyzed for 2.00 hours, using a current of 0.0750 A, 0.546 g of platinum was deposited on the cathode. Determine the charge on the chloroplatinate ion.

Block F Experiments

Note: Students must complete all of the experiments described in Block D and E before proceeding to Block F.

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

> Anemic, bilious, blind, cluster, dynamite, helmet, lumbar, migraine, Monday morning, organic, reflex, spinal, tension, toxic, and vacuum are all types of headaches. Take two aspirins to alleviate any pain from just reading this. – Unknown.

Prerequisite Skills

In order to begin this experiment you must have completed the laboratory component of Athabasca University's *Chemistry 217* or its equivalent and Blocks D and E of *Chemistry 218*.

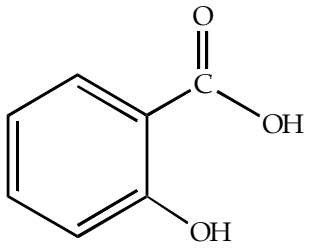
Objectives

The objective of the experiment is to prepare acetylsalicylic acid (Aspirin®) from salicylic acid and acetic anhydride. The experiment introduces a number of techniques that are commonly employed during the synthesis of organic compounds. The Aspirin® produced will be purified by recrystallization.

Introduction and Theory

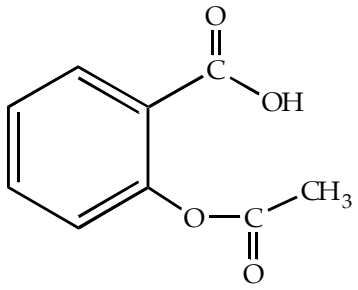
Aspirin® is one of the most-commonly used drugs available. Over 8,000,000 kg of Aspirin® is consumed every year in the United States alone.

In 1863, Edward Stone found that an extract from willow bark was useful in reducing the feverish symptoms associated with malaria. Subsequently, the active ingredient in the willow bark was identified as being salicylic acid (2-hydroxybenzoic acid).



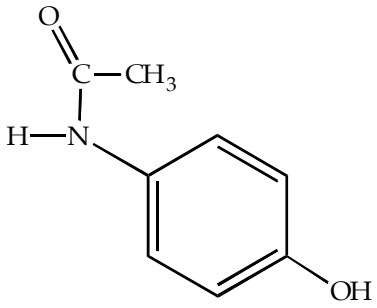
Salicylic acid
$C_7H_6O_3$
Mol. Wt.: 138.12

It was soon discovered, however, that the acidic properties of salicylic acid caused severe irritation of the mucous membranes lining the mouth, gullet and stomach. Using the sodium salt of salicylic acid only partly overcame this problem because of its objectionable taste. By 1893 it had been discovered that acetylsalicylic acid (ASA, Aspirin®) had the same medicinal properties as salicylic acid itself, but did not irritate the mucous membranes, or have an objectionable taste.

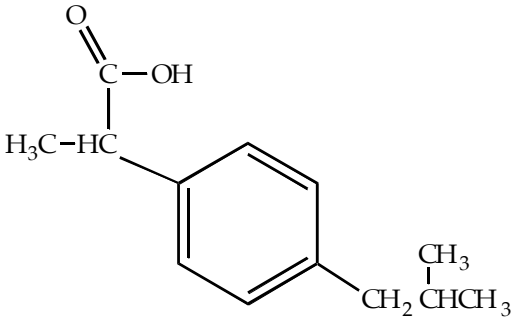


Acetylsalicylic acid
$C_9H_8O_4$
Mol. Wt.: 180.16

Acetylsalicylic acid is the major ingredient of Aspirin®, Anacin®, Bufferin®, etc. It is both safe and effective as a non-prescription pain-reliever, but it can cause undesirable side effects, such as bleeding ulcers, in a few people. For these people a common alternative is to use drugs whose active ingredient is acetaminophen (*p*-hydroxyacetanilide), or ibuprofen. Tylenol® and Advil® are examples of each drug respectively.

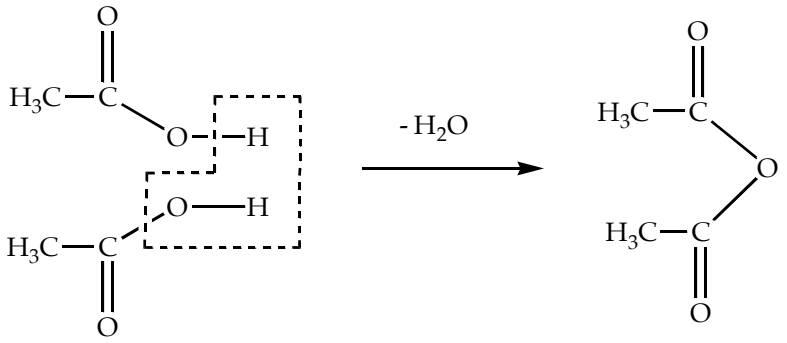


Acetaminophen
$C_8H_9NO_2$
Mol. Wt.: 151.16



Ibuprofen
$C_{10}H_{12}O_2$
Mol. Wt.: 164.20

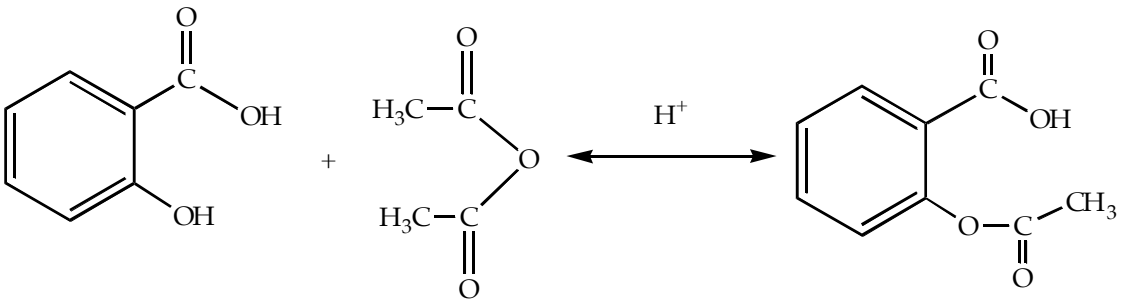
In order to produce Aspirin®, an ester must be formed between the phenolic hydroxyl group of salicylic acid and the carboxyl group of acetic acid. As the latter reaction does not give a particularly good yield, instead of using acetic acid we use acetic anhydride (IUPAC name: ethanoic anhydride). Acetic anhydride can be considered to be formed by the condensation of two molecules of acetic acid.



2 Acetic acid molecules

Acetic anhydride
$C_4H_6O_3$
Mol. Wt.: 102.09

In the presence of an acid catalyst, acetic anhydride reacts with salicylic acid to produce Aspirin®. It is this reaction that you will carry out today.



Salicylic acid
$C_7H_6O_3$
Mol. Wt.: 138.12

Acetic anhydride
$C_4H_6O_3$
Mol. Wt.: 102.09

Acetylsalicylic acid
$C_9H_8O_4$
Mol. Wt.: 180.16

When we prepare an organic compound, particularly one which may be destined for use in medicine, we obviously want that compound to be as pure as possible. Organic solids are usually purified by recrystallization. Recrystallization involves dissolving the solid in the *minimum amount of hot solvent,* rapidly filtering this hot solution to remove any insoluble impurities, and then allowing the filtrate to cool *slowly* so that the desired compound comes out of solution in the form of large crystals. After cooling slowly to room temperature, the suspension of crystals in the mother liquor is chilled in ice water in order to maximize the amount of crystals formed. The crystals are collected in a Büchner funnel by suction filtration and then dried. If desired, the filtrate can be concentrated by boiling off some of the solvent to give a second crop of crystals.

In addition to removing impurities that are less soluble than our compound (during the hot gravity filtration), and impurities that are more soluble than our compound (these remain in the filtrate during the suction filtration), we can also remove some of the impurities that can impart colour to an otherwise colourless substance. These last impurities often have a high molar mass, and they are removed by adding activated charcoal to the solution just before the hot gravity filtration. The coloured, high molar mass compounds absorb onto the surface of the insoluble activated charcoal, and are thus removed during the gravity filtration.

Table F1.1 Decision Process for Choosing Type of Filtration

Type of Filtration	Product	Impurity
Gravity	Liquid	Solid
Vacuum (or suction)	Solid	Liquid

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.

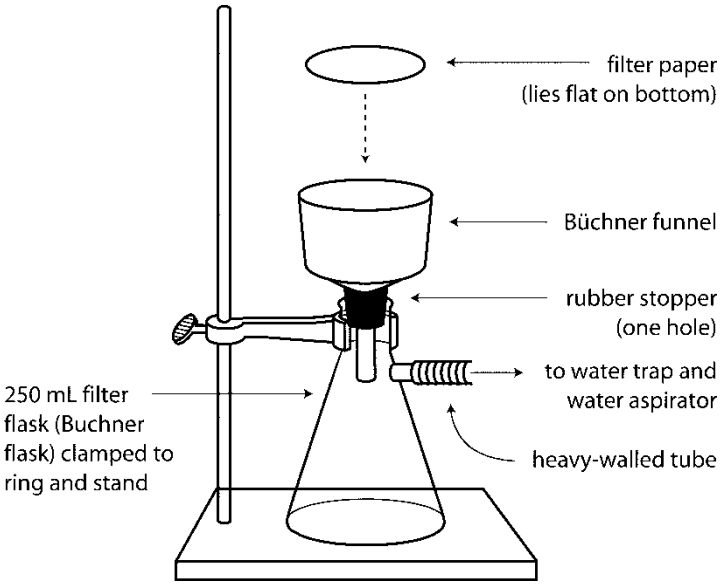


Figure F1.1:
Apparatus for suction (vacuum) filtration

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 (119ulphat. 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.)

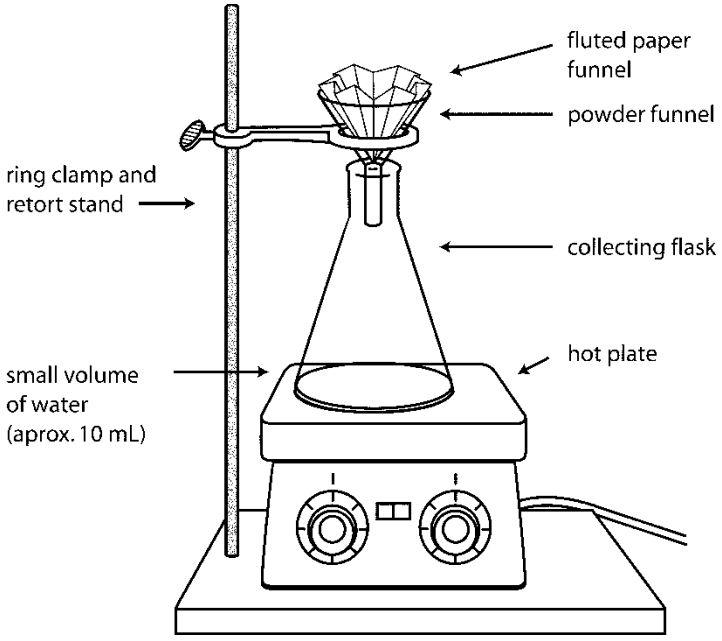


Figure F1.2:
Arrangement for hot gravity filtration

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.

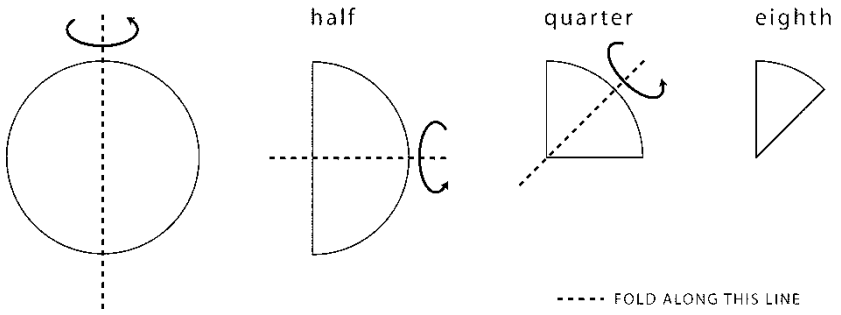
5. Transfer the recrystallized ASA to a sample bottle. Label the bottle with your name and hand it to your instructor. Your sample will be graded according to both quantity and quality.

Note:

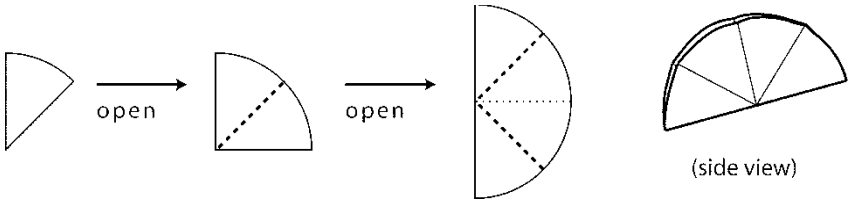
Fluted Filter Paper

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.

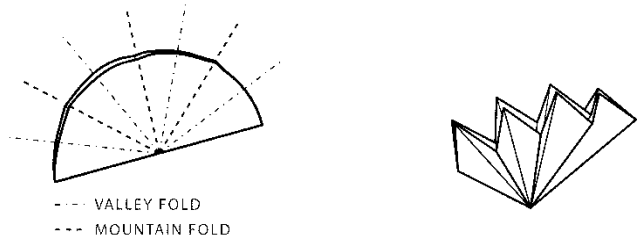
1. Fold paper in half, then in half again and then in half again in the same direction. You should have a 1/8 section cone.



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.

Results, Calculations and Write-up

Before starting your write-up of this experiment, check to see whether it has been assigned to you for a formal report.

Results:

The following data should have been recorded:

_____ = mass of salicylic acid used

_____ = volume of acetic anhydride used

_____ = mass ass of aspirin obtained

Calculations:

Calculate the percentage yield obtained. **Note:** You should look up the molar mass of salicylic acid, acetic anhydride, and acetylsalicylic acid, as well as the density of acetic anhydride in the *Handbook of Chemistry and Physics* before you leave the laboratory.

Questions

1. The goal of a recrystallization is to obtain the maximum amount of pure product. Why would this goal be adversely affected if

    a. the hot filtration step is omitted?

    b. an excessive volume of solvent is used when the compound is initially dissolved?

2. Write equations for each of the following reactions.

    a. the reaction of salicylic acid with methanol (the product, methyl salicylate, is known as "oil of wintergreen")

    b. the reaction between acetylsalicylic acid and sodium hydrogen carbonate (step 6 of the experiment)

    c. the reaction between the product from reaction (2) and hydrochloric acid (step 7 in the experiment).

Appendix

Graphs

In both the practical and theoretical components of this course you will be required to plot and interpret a number of graphs. Experience has shown that this is one area in which many students are unaware of the standards required for university-level work. Thus, these notes have been included in this manual in order to alert you to some of the criteria, which your laboratory instructor will use when marking a graph that is submitted as part of a laboratory report.

In order to draw a graph you will require 1) some data, 2) a pencil, pen and ruler, and 3) some graph paper.

3. Data

   When plotting a graph as part of a laboratory report, you will normally have obtained the data during the experiment. It is essential that you organize your data in such a way that your instructor can check your experimental results in the event that you are unable to obtain a satisfactory graph. Usually, the best way to present your data is in the form of a table.

4. **Pencil, Pen and Ruler**

   To many of you reading this manual, this section may seem to be superfluous. However, you would be amazed to see some of the work that has been submitted to us in the past.

   A pen should be used for writing the title of the graph across the top of the page, for labelling the axes, for marking the scales on the axes, and for writing your name on the paper. A pencil is used to mark the data points and to draw the actual graph. A ruler is used to assist you in drawing the best straight line through the data points; that is, if the points look as if they lie on a straight line rather than a curve. The ruler should also be used for drawing your axes.

5. **Paper**

   With regard to paper, most chemistry instructors have seen an incredible variety of paper used by students to prepare graphs: blank paper on which students have drawn their own lines, regular lined writing paper with vertical lines added by hand, and so-called "graph paper" on which the squares are so large that the paper would more appropriately be used as a surface on which to play chess or checkers. The only graph paper accepted for use in this course is the type, which is popularly known as "metric graph paper" (i.e., 1 mm × 1 mm squares). The use of this particular type of paper will enable you to plot very precise graphs, and will give your graphs a suitably professional appearance. Graphs submitted on any other type of paper will be returned to the student, unmarked.

6. **Computer-generated Graphs**

   Although we encourage students to use a personal computer to produce easily read laboratory reports, we wish to caution you in regard to including computer-generated graphs in your reports. Such graphs rarely meet the requirements of a scientific report and should not be used. Students who feel that their software is capable of generating graphs of the required standard should discuss the matter with their laboratory instructor before investing any time in such an endeavour.

Getting Started

Let us imagine that you have some data and you are ready to begin plotting your graph. By convention, the independent variable (that is, the controlled factor) is marked off along the horizontal (x) axis, and the dependent variable (the varying factor) is marked off along the vertical (y) axis.

Thus, if we were to plot a graph of the concentration of a solution against time, time would be the independent variable and would be placed on the horizontal (x) axis. Similarly, in a plot of volume of gas against temperature, temperature would be regarded as the independent variable. In each case you must decide for yourself whether the short side of your paper is to be the x axis, or whether the paper should be turned around so that the longer side forms the bottom of the page and represents the x axis.

An important consideration when plotting a graph is the choice of a suitable scale. All too frequently a poor choice of scale makes a graph difficult to interpret, hides an important trend or deviation, or is simply inappropriate. A useful guideline is to select the scale in such a way that the graph fills as much of the available space as possible. It is possible to choose your scale so that the data appear to be "better" than they really are. This is a ruse which has been used by generations of chemistry students (and their instructors), and is also used by governments and private business in their publicity materials.

Let us consider an example to illustrate exactly what we mean by choosing an appropriate scale. Suppose that you have measured some physical property of a reaction mixture (e.g., concentration of a particular species) as a function of time. As indicated above, time is the independent variable and should be placed on the horizontal (x) axis. Whether you choose the short or long side of the paper to be your x axis will depend how convenient it is to choose scales that will enable you to make your graph as large as possible. Suppose that you have taken readings of the concentration of a certain species approximately every 10 minutes for two hours (i.e., 120 minutes). Notice that the short side of the graph paper is marked off into eighteen 1-cm blocks, with each block sub-divided into ten 1-mm blocks. (This type of graph paper is often designated as 10 mm/cm.) If you chose to let 1 cm represent 10 minutes—which might be particularly convenient as 1 mm would then represent 1 minute—by choosing the short side of the paper as your x-axis, only two thirds (i.e., 12/18) of the axis will be used. Notice that

if we allow the long side of the paper to be our x axis, we can use a scale of 1 cm = 5 minutes (or 2 mm = 1 minute) and 96% (i.e., 24/25) of the axis is used.

Two matters remain to be mentioned regarding the choice of scale. First, if you refer to the example just described, you should note that your final decision regarding which side of the paper should represent the x-axis cannot be made without considering the choice of scale for the y axis. Although the long side of the paper appears to be the best choice for the x-axis at the moment, this may have to be reviewed after the range of concentrations to be plotted has been considered. Second, do not become over-obsessed with the idea of using the largest possible scale. For example, when plotting the above data with the x-axis on the long side of the paper, you should resist the temptation of allowing 1 cm to represent 4.8 minutes just so the whole of the axis is used. By choosing this scale, 1 minute = 2.08 mm, and it becomes very difficult to plot data points that may have been taken at 11 minutes, 32 minutes, 53 minutes, etc.

Once you have decided on how your axes and scales are to be organized, the next step is to plot the data points. In courses at this level it is generally sufficient for you to mark the point with a dot and to place a small circle around the dot so that can be readily identified as a data point by your instructor.

Straight-line Graphs

By far the most useful graphs to chemists are those that result in a straight line. Such graphs are particularly useful in verifying or deriving laws. You may recall that the general form of a relationship that will give rise to a straight-line graph is

$$y = mx + c$$

where, m is the slope of the graph, and c is a constant which corresponds to the value of y when x is equal to zero. Of course, if the value of the constant itself is zero, the relationship simplifies to

$$y = mx$$

and the straight line which relates y and x passes through the origin.

You will encounter many such relationships in your general chemistry course(s). Frequently, the value of y increases as the value of x increases, but sometimes the value of y decreases as x increases. Graphs pertaining to the former type of relationship are said to have positive slopes, whereas graphs in which y decreases as x increases have negative slopes (see Figure App.1).

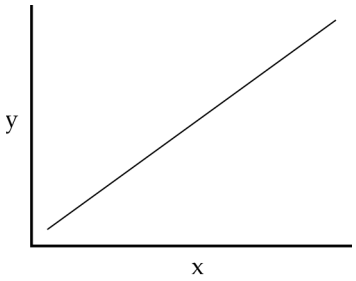


Figure App.1a
Graph with a positive slope

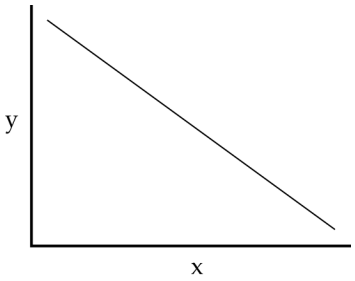


Figure App.1b
Graph with a negative slope

The slope of graph is sometimes defined as "rise over run," i.e.,

$$\text{slope} = \frac{\text{rise}}{\text{run}}$$

and may be determined as follows:

Select two points that lie on the graph (these points should generally be as far apart as possible and should not be actual data points). Determine the values of x and y for each of these two points; in general terms these values may be expressed as x_1, y_1 for point 1, and x_2, y_2 for point 2. The slope of the graph may then be calculated as follows:

$$\text{slope} = \frac{(y2 - y1)}{(x2 - x1)}$$

The calculation of the slope of the graph and any other relevant calculations can be carried out at a convenient location on your sheet of graph paper. By doing this you will avoid the situation in which your tutor must flip through several sheets of paper in order to determine to which graph a given calculation belongs.

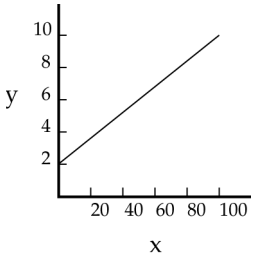


Figure App.2a
Graph with a positive slope
and a positive (+2) intercept

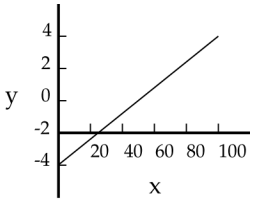


Figure App.2b
Graph with a positive slope
and a negative (–2) intercept

In the foregoing discussion we have focussed on the calculation of the slope of a straight-line graph. In addition, it is sometimes necessary to determine the intercept, i.e., the value of c in the equation y = mx + c. The

value of c can be found directly from the graph (see Figure App.2), or through calculation once the value of the slope (m) is known.

From the graphs shown in Figure App.2, it should be apparent that the value of the intercept, c, is equal to the value of y when x = 0.

We have now reviewed the process for obtaining the slope and/or intercept from a straight-line graph. However, some students experience difficulty in drawing the straight line once the data points have been plotted. Remember that when you are dealing with experimentally determined data points, the points themselves are unlikely to fall exactly along a straight line. When you draw the line through the points, draw the best straight line through all the points. For example, if you have five data points, three of which appear to lie "exactly" on the line with the other two points just above or below the line, you are not justified in neglecting the latter points. Instead, you should draw a line that passes as close as possible to all the points (see Figure App.3).

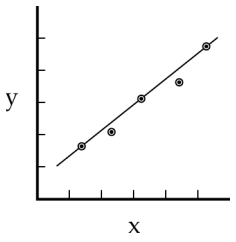


Figure App.3a
Incorrectly drawn straight-line graph

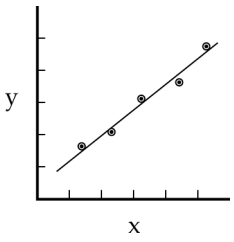


Figure App.3b
Correctly drawn straight-line graph

Occasionally, one data point may be so far away from what would appear to be the "best straight line" that it should be discarded (see Figure App.4). Sometimes the experimenter makes a genuine error (e.g., misreading a burette, or not mixing a solution adequately) and the resulting data point is not valid. If you feel that there is a good reason for rejecting one of your data points, by all means do so, but include your rationale for doing so within the body of your laboratory report.

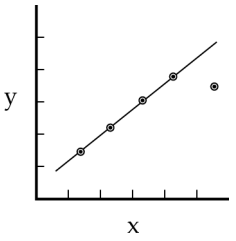


Figure App.4
Example of a straight-line graph with an obviously erroneous data point

Table of Reagents

Compound Name	Chemical Formula	Exp. #	Solid (S) or Liquid (L)	Formula Weight	MP or BP (°C)	Density (g/mL)	Hazardous Properties*
acetic acid, 0.1 M	CH_3CO_2H	D5, E2	L	60.05			Mildly corrosive
acetic acid, 3.0 M	CH_3CO_2H	D4	L	60.05			Corrosive, hygroscopic
acetic acid, glacial (17.4 M)	CH_3CO_2H	D4-5, E2	L	60.05	118.1	1.049	Corrosive, hygroscopic
acetic anhydride	$(CH_3CO)_2O$	F1	L	102.09	140	1.082	Corrosive, lachrymator
acetone	CH_3COCH_3	all	L	58.08	56.5	0.818	Flammable, irritant
acetylsalicylic acid (aspirin)	$CH_3CO_2C_6H_4CO_2H$	F1	S	180.16	138-140		Irritant, toxic
ammonia, 3% solution	NH_4OH	B1, B4	L	35.05		0.90	Corrosive, lachrymator
ammonium peroxydisulfate	$(NH_4)_2S_2O_8$	D1, D2	S	228.18	d120	1.982	Oxidizer, corrosive
ammonium sulfate	$(NH_4)_2SO_4$	D1, D2	S	132.14	d235	1.769	Irritant
aspirin	$CH_3CO_2C_6H_4CO_2H$	F1	S	(see also salicylic acid, acetate ester, or acetylsalicylic acid)			
barium nitrate	$Ba(NO_3)_2$	D4	S	261.35	592	3.240	Oxidizer, toxic
barium nitrate, 0.1 M	$Ba(NO_3)_2$	D4	L	261.35			Toxic
boiling stones		F1					
bromine water	Br_2 in H_2O	D4	L	159.82			Toxic, oxidizer
copper, metal	Cu	E1, E2	S	63.546	1063	8.92	
copper (II) 131ulphate pentahydrate	$CuSO_4 \cdot 5H_2O$	D1, E1	S	249.68	110	2.284	Toxic, irritant
copper (II) 131ulphate, 0.1 M	$CuSO_4$	D1	L	249.68			Toxic, irritant
copper (II) 131ulphate, 1.0 M	$CuSO_4$	E1	L	249.68			Toxic, irritant
distilled water	H_2O	all	L	18.02	100	1.000	See water
ethylacetoacetate	$C_6H_{10}O_3$	D4	L	130.15	180.4	1.0282	Irritant
hydrochloric acid, 0.1 M	HCl	D5	L	36.46			Corrosive, highly toxic
hydrochloric acid, 3.0 M	HCl	D4	L	36.46			Corrosive, highly toxic
hydrochloric acid, conc. 12 M	HCl	F1	L	36.46		1.20	Corrosive, highly toxic
iodine	I_2	D1, D2	S	253.81	113	4.930	Toxic, corrosive
iron (III) chloride, 1% sol'n	$FeCl_3$	F1	L	270.30			
iron (III) chloride, 1.0 M	$FeCl_3$	D4	L	270.30			Corrosive

* Ref: CRC *Handbook of Chemistry and Physics,* 65th ed., 1984, and *Aldrich Handbook Catalog of Fine Chemicals,* 1994; d = decompose

Compound Name	Chemical Formula	Exp. #	Solid (S) or Liquid (L)	Formula Weight	MP or BP (°C)	Density (g/mL)	Hazardous Properties*
iron (III) nitrate	$Fe(NO_3)_3 \cdot 9H_2O$	D3	S	404.00	47	1.680	Oxidizer, irritant
lead, metal	Pb	E1, E2	S	207.19	327.5	11.344	Toxic
lead (II) nitrate	$Pb(NO_3)_2$	E1	S	331.2	d470	4.53	Oxidizer, toxic, irritant
lead (II) nitrate, 1.0 M	$Pb(NO_3)_2$	E1	L	331.2			Toxic, irritant
methanol, anhydrous	CH_3OH	F1	L	32.04	64.5	0.791	Highly toxic, flammable
nichrome wire	Ni/Cr	E2					Toxic
nickel, metal	Ni	E2	S	58.69	1455	8.90	Toxic
pH Buffer 7.0		D5				1.003	Irritant
pH Buffer 4.0		D5				1.005	Irritant
phosphoric acid (85%, 14.7 M)	H_3PO_4	F1	L	98.00		1.685	Corrosive
potassium chloride	KCl	D1, D2	S	74.56	770	1.984	Irritant
potassium chloride, 1.0 M	KCl	E1	L	74.56			Irritant
potassium chromate	K_2CrO_4	D4	S	194.20	968	2.732	Canc.susp.agent, oxidizer
potassium chromate, 0.1 M	K_2CrO_4	D4	L	194.20			Canc.susp.agent, oxidizer
potassium dichromate	$K_2Cr_2O_7$	D4	S	294.19	398		Highly toxic, canc.susp.agent
potassium dichromate, 0.1M	$K_2Cr_2O_7$	D4	L	294.19			Highly toxic, canc.susp.agent
potassium iodide	KI	D1/D2	S	166.01	681	3.130	irritant
potassium nitrate	KNO_3	E2	S	101.11	334	2.109	Oxidizer, irritant
potassium nitrate, 0.5 M	KNO_3	E2	L	101.11			Oxidizer, irritant
potassium thiocyanate	KSCN	D3	S	97.18	173.2	1.886	toxic
propanol, 2- or iso	$CH_3CH(OH)CH_3$	F1	L	60.11	82.4	0.7855	Flammable
salicylic acid	$HOC_6H_4CO_2H$	F1	S	138.12	158-160		Toxic, irritant
salicylic acid, acetate ester	$CH_3CO_2C_6H_4CO_2H$	F1	S	180.16	138-140		Irritant, toxic
sodium bicarbonate	$NaHCO_3$	F1	S	84.01		2.159	
sodium hydrogen carbonate	$NaHCO_3$	F1	S	84.01	270	2.159	
sodium hydroxide, 0.1 M	NaOH	D5	L	40.00			Mildly corrosive, toxic
sodium hydroxide, 3.0 M	NaOH	D4	L	40.00			Corrosive, toxic
sodium thiosulfate	$Na_2S_2O_3$	D1/D2	S	158.11		1.667	Irritant, hygroscopic

Compound Name	Chemical Formula	Exp. #	Solid (S) or Liquid (L)	Formula Weight	MP or BP (°C)	Density (g/mL)	Hazardous Properties*
sodium thiosulfate penthydrate	$Na_2S_2O_3\ 5H_2O$	D1/D2	S	248.18	40-45	1.729	Irritant, hygroscopic
starch indicator	$(C_6H_{10}O_5)_n$	D1/D2	L				Highly toxic, irritant
sulfuric acid (conc. 18 M)	H_2SO_4	D4,E2	L	98.08		1.840	Corrosive, oxidizer
sulfuric acid, 1M	H_2SO_4	E2	L	98.08			Corrosive, oxidizer
sulfuric acid, 2 M	H_2SO_4	D4	L	98.08			Corrosive, oxidizer
water, distilled	H_2O	all	L	18.02	100	1.00	Will burn skin when hot
zinc metal	Zn	E1, E2	S	65.37	419.5	7.14	Flammable
zinc sulfate heptahydrate	$ZnSO_4 7H_2O$	E1	S	287.54	100	1.957	Irritant, hygroscopic
zinc sulfate, 1.0 M	$ZnSO_4$	E1	L	287.54			Irritant

Table of Concentrated Acids and Bases

Acid or Base	Molecular Weight	Density (g/mL)	Weight Percentage	Molarity
HCOOH (formic acid)	46.03	1.16	70	17.6
CH_3COOH (acetic acid)	60.05	1.05	99.5	17.4
CCl_3COOH (trichloroacetic acid)	163.38	1.28	50	3.9
H_2SO_4 (sulfuric acid)	98.07	1.83	94	17.6
H_2SO_4 (sulfuric acid)	98.07	1.84	*96*	18.0
HF (hydrofluoric acid)	20.01	1.14	45	25.7
HCl (hydrochloric acid)	36.46	1.18	36	11.6
HCl (hydrochloric acid)	36.46	1.19	*38*	12.4
HBr (hydrobromic acid)	80.91	1.52	48	9.0
HNO_3 (nitric acid)	63.01	1.41	69	15.4
$HClO_4$ (perchloric acid)	100.46	1.67	70	11.6
H_3PO_4 (phosphoric acid)	98.00	1.69	85	14.7
NaOH (sodium hydroxide)	40.00	1.43	40	14.29
NaOH (sodium hydroxide)	40.00	1.53	*50*	19.1
NH_3 (ammonia) and	17.03	0.90	28	14.8
NH_4OH (ammonium hydroxide)	35.05	0.90	58	14.8
KOH (potassium hydroxide)	56.11	1.39	40	9.89
KOH (potassium hydroxide)	56.11	1.50	50	13.4
$NaHCO_3$ (sodium bicarbonate)	84.01	1.04	6	0.743

Common Acid/Base Dilutions:

Nitric acid from concentrated
HNO_3 (70%, 15.6M) diluted to:

0.1M	6.4 mL in 1L dH_2O
1.0M	64 mL in 1L dH_2O
3.0M	192 mL in 1L dH_2O

Acetic acid from glacial
CH_3COOH (99%, 17.4M) diluted to:

0.1M	5.7 mL in 1L dH_2O
1.0M	57 mL in 1L dH_2O
3.0M	171 mL in 1L dH_2O

Hydrochloric acid from concentrated:
HCl (37%, 12.0M) diluted to:

0.1M	8.33 mL in 1L dH_2O
1.0M	83.33 mL in 1L dH_2O
3.0M	250.00 mL in 1L dH_2O

Sodium Hydroxide from solid:
NaOH (40.00 g/mol) dissolved to:

0.05M	1 g in 500 mL dH_2O
0.1M	2 g in 500 mL dH_2O
1.0M	20 g in 500 mL dH_2O
3.0M	60 g in 500 mL dH_2O

Sulfuric acid from concentrated:
H_2SO_4 (96%, 18.0M) diluted to:

1M	56 mL in 1 L dH_2O
2M	111 mL in 1 L dH_2O
3M	167 mL in 1 L dH_2O
6M	333 mL in 1 L dH_2O

Sulfuric acid from 6M:
H_2SO_4 (6.0M) diluted to:

1M	167 mL in 1 L dH_2O
2M	333 mL in 1 L dH_2O
3M	500 mL in 1 L dH_2O

Phosphoric acid from concentrated:
H_3PO_4 (85%, 14.7M) diluted to:

1M	6.80 mL in 1 L dH_2O
2M	68.03 mL in 1 L dH_2O
3M	204.08 mL in 1 L dH_2O

Potassium Hydroxide from solid:
KOH (56.11 g/mol) dissolved to:

0.1M	2.81 g in 500 mL dH_2O
1.0M	28.05 g in 500 mL dH_2O
3.0M	84.15 g in 500 mL dH_2O
20%	100.00 g in 500 mL dH_2O (3.56M)

pH of Common Items

Solution	pH
Battery Acid	0
	1
Stomach acid	2
lemon juice	3
	4
Black coffee	5
	6
Pure water	7

Solution	pH
Pure water	7
Sea water	8
Baking soda	9
Toilet soap	10
	11
	12
Household ammonia	13
Drain cleaner	14

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