

Chemistry 155
Honors General Chemistry
Laboratory Manual

University of Washington
Department of Chemistry
Winter 2004

Instructor

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LABCOATS AND GOGGLES ARE REQUIRED FOR ALL LAB WORK

COATS

Coats are a 65% polyester/ 35% cotton blend and are wash & wear.

Women's Sizes: 28 – 38 (even sizes), 42 & 44

Total Student Price: \$13.66

Men's Sizes: XS – 3XL

Total Student Price: \$12.32

GOGGLES: Must shield above and below the eye as well as the sides. Prices range from \$3.00 to \$6.00 depending on style. They can be purchased either from the University Book Store or the University Stores – South Campus.

Payment:

Cash, personal check (issued through a local bank) or Visa/MasterCard. You may try on sample coats for sizing, purchase and take yours with you that day.

Directions to South Campus Stores from Chemistry/Bagley Hall:

1. Follow path to the Sky Bridge at NE Pacific St.
2. Cross over and enter Magnuson HSC – you will be on the 4th floor, T-wing.
3. Walk through the lobby to the Information and South Campus Stores intersection – turn LEFT.
4. Follow hallway to the end – elevators will be on your RIGHT.
5. Take elevator down to the 1st floor – you will be in the basement.

6. Exit RIGHT and through hallway door.
7. Follow to the end and turn LEFT at the Dental Wing sign – you are now in B wing.

Stores is located at B-170 on the RIGHT between D and AA wing.

University Stores
B-170 HSB
1959 NE Pacific Ave
Seattle, WA 98195
(206) 543-1980
Hours: Mon. – Fri. 8:30 a.m. to 4:00 p.m.

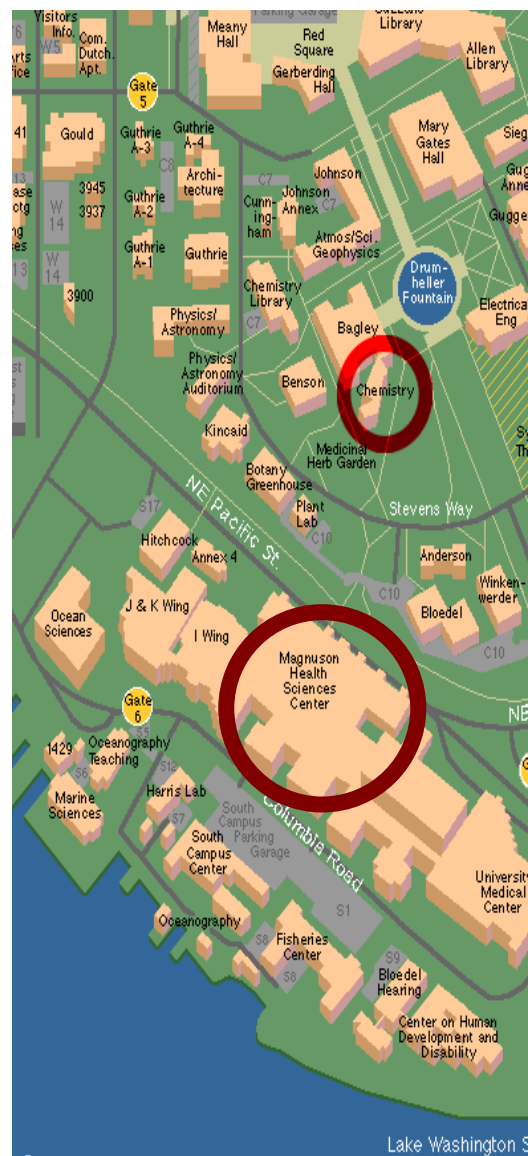


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General Information

Chemistry 145

DROP/ADD: If you need to drop, add, or change sections, you should go to the undergraduate stockroom (Bagley 271).

MATERIALS: The Chemistry 145 Laboratory Manual.
A bound notebook (available at the bookstore).
A pair of goggles (available at the bookstore).
A calculator.

You must wear your goggles in lab at all times!

CHARGE #: You will find a class list posted for your section at the laboratory entrance (Bagley 133). You have been assigned a charge number. This is your account number with the Chemistry department. You will need this number to check out items from the stockroom. If you purchase anything from the stockroom, it will be charged to this number.

EQUIPMENT: You will be assigned a drawer for the quarter that contains various items needed for the laboratory experiments. Within the first 20 minutes of the period, examine the items in the drawer against the equipment list found in your lab manual or that day's experiment. If you discover any items that are missing or broken during the first 20 minutes of lab, obtain a pink slip from your TA. On the pink slip write the name of the missing or broken items, have your TA sign the slip, then take the slip and any broken items to the stockroom for a free replacement. You will be responsible for any of the items checked-out from the stock room. If an item is broken or lost, you will have to purchase a replacement. After this 20 minute "grace" period you may charge these items using your charge number, but all accounts must be settled by the end of the quarter. You will be billed for any charged items plus an additional \$10.00 administrative fee.

Please leave the glassware clean. Another student will be using the equipment in a later lab period and will be unnecessarily delayed if he/she finds the equipment dirty. If the next student finds the glassware unusable because it was not clean, you will be charged a \$2.00 washing fee.

The Laboratory Notebook and Lab Reports

In all chemical work it is essential that good records be kept—otherwise work may be misinterpreted, lost, or unnecessarily repeated. Whether in an industrial or academic laboratory, the investigator is expected to keep understandable records written in the notebook while the work is in progress. Loose scraps of paper are unacceptable as places to record results. In many industrial laboratories, each day's work is signed by the worker and dated. Frequently the signature of the investigator is witnessed by a colleague. One reason for keeping good records is to have the information available for later use.

The notes of the students in this course are to be kept in a similar way. A bound notebook with pre-recorded page numbers must be used. A spiral notebook is not acceptable. There must be a table of contents. Each exercise is to be recorded as a unit in the notebook. Each exercise should start on an unused page in the notebook. At the start of each day's work, the date should be recorded. Records are always kept in ink. In the event that an error is made in recording an observation or a data point, the erroneous words or numbers should be crossed out and the correct information written nearby. Laboratory data is never erased.

The Laboratory Report is the means whereby you convince the instructor that you conducted the experiment thoughtfully and learned something in the process. Below are the elements of a typical Laboratory Report:

1. **Header**, containing Date and Time on left side, title of experiment in center, your name, lab partner's name. TA's name, and section on right hand side.
2. **Title** of experiment.
3. **Procedure**: A brief statement of the procedures used.
4. **Data**: A record of observations and data. Whenever possible, data for an experiment should be presented in an organized table. All observations and data should be recorded in the notebook while the work is in progress. Scraps of paper or this manual should not be used to record data.
5. **Calculations** from your data used to obtain your results. These should be presented in a readable manner. In most cases, the spreadsheet template will make the organization of your calculations obvious. Where appropriate, give an algebraic representation of the formula you used to arrive at your result.
6. **Results**: Clearly indicated so the instructor can find them. Use a table if appropriate.
7. **Answers to Questions**: Be sure to show your work, if applicable.

Your laboratory report will be due one week from the date of completion.

Laboratory Safety

State-approved safety goggles must be worn in the laboratory at all times. This is required by state health regulation. Failure to observe this requirement will result in your removal from the laboratory. Standard laboratory goggles that meet all state regulations may be purchased from the bookstore. The cost is approximately \$4.00 (and trivial in comparison to your eyesight). Safety glasses, etc. are not acceptable. If you already have goggles, they must first be approved by the stockroom personnel before you can begin working. Because of health regulations, goggles cannot be borrowed from the stockroom. For each lab section there is a drawer available for goggle storage. We strongly suggest labeling your goggles and leaving them in this desk drawer. If you take them home and forget to bring them the following week, you will not be allowed in the laboratory and, consequently, will miss the experiment. The use of contact lenses in the laboratory is **absolutely** prohibited. In the case of a splash or other emergency, they may interfere with the flushing of the eye, you may not be in a position to remove them, and those administering first aid may not know that you are wearing them or might not be able to remove them easily.

You must dress appropriately for the laboratory. Lab coats are required to be worn. Bare feet, sandals, or other open-toed shoes are not permitted in the laboratory. Shorts and short skirts are likewise not permitted; legs must be covered to below the knees. *Headphones are not allowed in the laboratory.* Failure to observe these requirements will result in your removal from the laboratory. Cotton clothing (including denim) is particularly susceptible to being eaten by acid solution. The laboratory is not a good place to wear your favorite clothes. Long hair should be tied back.

Learn the location and operation of the safety showers, emergency eye washes and fire extinguishers in the laboratory. In the case of spill onto a person or clothing, the immediate action should be to flush with water and lots of it. Do not hesitate to yell for help. Use the safety showers and/or eye washes and don't worry about the resulting mess. However, don't use the safety showers for non-emergencies since they are designed to deliver about 50 gallons of water before shutting off. Report accidents to your instructor. He/she has been certified to administer first aid. If you are not familiar with the operation of the fire extinguishers, ask your instructor to explain them to you. The fire extinguishers should only be used for real emergencies since the chemicals they contain can cause considerable damage. In any emergency that requires the assistance of the fire department, aid car, or police, send someone to the stockroom for assistance. Should clothing catch on fire, remain as calm as possible. Walk (do not run) to the safety shower and pull the ring to douse yourself with water. Alternatively, you may drop to the floor and roll to extinguish the flames.

Become familiar with all of the exits from the laboratory. A repeating siren and flashing of the FIRE indicator is the building evacuation signal. If this alarm goes off while you are in the lab, turn off any open flames, grab your valuables, and leave the building as quickly as possible.

Never attempt any unauthorized or unassigned experiments. Follow the experimental procedures explicitly, checking and double checking the identity of all reagents before you use them. There are potentially hazardous combinations of chemicals present in the laboratory. If you have an idea for further investigation, discuss it with your instructor.

Clean up spills immediately. The next person to come along has no way of knowing if the clear liquid or white powder on the lab bench is innocuous or hazardous. Neutralize acid spills with sodium bicarbonate (baking soda) before cleaning them up. Spills of sulfuric acid solutions are particularly hazardous since only the water will evaporate, thereby making the solution more concentrated upon standing.

Never return unused reagents to their storage container. If you take more than you need, dispose of the excess in the appropriate manner. Use the reagents sparingly—they are expensive and time-consuming to prepare. When taking reagents, transfer the amount you need to a clean beaker or other suitable container for taking the material back to your desk. Never insert a pipet or any other object into a liquid reagent container. Finally, check and double check the identity of all materials before using them.

Do not pick up hot objects. Be sure your apparatus is cool before picking it up.

Do not point the open end of a test tube or other vessel containing a reaction mixture toward yourself or anyone else. If the procedure calls for you to observe the odor of the contents of a vessel, hold it upright in front of you, gently fan some of the vapors toward your nose and sniff cautiously. Most chemical vapors are at least irritating, and many are quite toxic. Please do not taste any chemicals.

Do not eat, drink or smoke in the laboratory. Playing of radios, tapes, CDs is not permitted. This includes small portable devices used with earphones or headsets.

Keep coats, backpacks and other non-essential materials away from areas where people are working. Lockers are available in the hallway.

Dispose of all broken glassware and other sharp objects in the cardboard glass disposal boxes. Custodial personnel will stop collecting trash after they find broken glass in the trash cans. Chipped glassware and glass apparatus from your drawer may be traded for undamaged items at the stockroom.

Wash hands often when working in lab, and always wash thoroughly before leaving.

Use the hood for evaporation of anything other than water. The vapors from your procedure alone may not present a problem but those from all the students in the lab could combine to create a hazard.

Do not leave a Bunsen burner or other heated apparatus unattended. The person working next to you may not know what is involved with your setup and may be working with a flammable material. Turn off open flames if you must leave your area. Make sure the gas taps are completely off whenever the Bunsen burner is not lit.

Waste Disposal

Dispose of chemical reagents and other materials properly. The proper disposal of chemical wastes is essential to the health and safety of University faculty, staff, students and the surrounding community. Chemical wastes must be managed and discarded in the most responsible and environmentally sound method available. The University and Metro expect your cooperation in taking care of the environment. Your laboratory manual will specify how to dispose of chemicals used during the laboratory period. Do not put chemicals into glass boxes or wastebaskets. Only specified non-hazardous water soluble materials can be rinsed down the drain. Waste containers for other materials will be provided. If you are unsure of how to dispose of a particular material, ask your instructor.

Metro requires that any solutions going down the drain be between pH 5.5 and 12. Therefore, neutralize any excess acid and base solution before rinsing it down the drain. This can be easily accomplished by adding thymol blue indicator to the waste solution and neutralizing it appropriately with acid or base until the thymol blue is yellow.

Hazard Identification. As part of the UW Laboratory Safety Manual, each laboratory has a Chemical Hygiene Plan (CHP). This is available to all students in the lab at all times. As part of the CHP, Material Safety Data Sheets (MSDS) must be readily accessible to all students. MSDS are available through the campus computer network on the Lab Safety System (LSS). The closest computer link to LSS is located in Bagley 271 (undergraduate stockroom) in the northernmost window. This computer is accessible to students at all hours that laboratories are in session for review of MSDS only.

Material Safety Data Sheets. Material Safety Data Sheets (MSDS) are provided by the manufacturer or vendor of a chemical. They contain information about physical properties of the chemical and identify any hazards associated with the chemical. They also identify any special handling precautions and protective equipment needed when working with the chemical. You should be familiar with the MSDS before working with any chemical.

Miscellaneous Policies and Procedures

Homework and Lab Report Due Dates. Lab reports are due one week from the date of performance, at the beginning of the lab period. Only a verifiable illness (Doctor's note) or prior permission of the instructor count as excused absences. Unexcused lab reports will receive a grade of zero.

Lab Partners. For those experiments where students are to work in pairs, lab partners will be assigned randomly as announced by the instructor at the beginning of the lab period. You may not exchange lab partners. Both lab partners must be present for the entire experiment.

Copying. All lab reports are to be your own. Lab partners are to independently produce their lab reports. It is very easy for the grader to spot identical work among two or more students. In the event of copying, all students involved will receive a grade of zero; therefore do not give a copy of your lab report to another student.

Make-Up Labs. There will be no make-up labs. Accordingly, the only excused labs (not counted on your grade) will be for a verifiable illness. A note from a Doctor is ideal, but not a note from your roommate is not ideal (and will not be accepted).

Experiment 1

Temperature Change and Equilibrium

I. Introduction.

Theory. Review Chapter 8 section 7 (pp. 253 - 258) and Chapter 9 section 7 (pp. 298 – 301) of *Principles of Modern Chemistry* by Oxtoby, Gillis and Nachtrieb 5th Ed. This section defines the change in the Gibbs free energy for a chemical reaction carried out at constant temperature as follows:

$$\Delta G = \Delta H - T\Delta S \quad (\text{Oxtoby, Eqn. 8.16})$$

where ΔH is the enthalpy change in the reaction (Oxtoby, section 7-3) and ΔS is the entropy change of the system (Section 8-3).

With reactants and products as gases at partial pressures of 1 atm, ΔG is taken as the standard Gibbs free energy (ΔG°) required for reactants to be converted to products. ΔG° is related to the equilibrium partial pressures of reactant and product gases as follows:

$$-\Delta G^\circ = RT \ln K \quad (\text{Oxtoby, Eqn. 9.4})$$

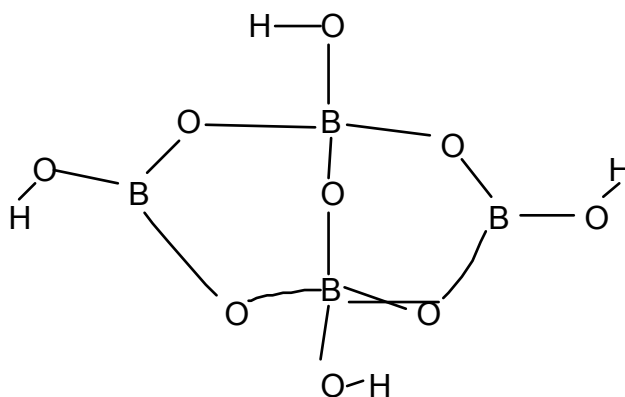
where K is the equilibrium constant as defined in Oxtoby on p. 281 Eqn. 9.9

On page 279 Oxtoby states that the Gibbs free energy change is related to concentrations of solute in dilute solutions by the equation $\Delta G = nRT \ln (c_2 / c_1)$. The Gibbs standard free energy change for solutions (ΔG°) is defined as the free energy change that occurs when reactants and products are both at a concentration of 1 mole/liter. For solutions then, equation 9-4 also applies; however, K now represents the equilibrium constant of reactants and products in solution in moles per liter instead of the partial pressure of gases. By combining equation 8.17, that uses the definition of Gibbs free energy with the equivalent of equation 9.4 for solutions, the text derives a relationship between the equilibrium constant and temperature:

$$\ln K = -\Delta G^\circ / RT = -\Delta H^\circ / RT + \Delta S^\circ / R. \quad (\text{Oxtoby, Eqn. 9.11})$$

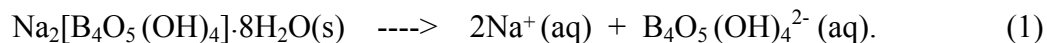
From figure 8.12 for the reaction of $3\text{NO}(\text{g}) \rightarrow \text{N}_2\text{O}(\text{g}) + \text{NO}_2$ monitored over a temperature range of 300 ° C, your text generalizes that ΔH and ΔS do not vary appreciably with temperature. We will accept that generalization for this experiment, which will be conducted over a temperature range of less than 40 ° C. As figure 9.12 of Oxtoby demonstrates, a graph of $\ln K$ vs $1/T$ is approximately a straight line with a slope of $-\Delta H^\circ / R$ and an intercept of $\Delta S^\circ / R$.

Overview of Experiment. In this experiment, you will be studying the temperature dependence of the solubility of borax, sodium tetraborate decahydrate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, in water. Borax is an example of a class of compounds named borates, which contain polyanions composed of trigonal BO_3 and/or BO_4 units linked by bridging oxygen atoms to form chain or ring structures. The tetraborate anion shown below illustrates some of these structural features and suggests that it would be more appropriate to represent borax by the formula $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$.



Borax occurs naturally in dry lake beds in the South West and California . These beds have long been important sources of this valuable mineral. An early use of borax was in soap and other cleaning products. These products continue to be used today . Borax is also used as a flux for solder, in the manufacture of glass, and as a preservative.

Equation 1 represents the mechanism whereby borax can become dissolved in water. Essentially the borax is ionized to tetraborate ions and sodium ions in solution:



When the reaction reaches equilibrium no more $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ can go into solution unless more water is added. The solution has become saturated and if more $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}(\text{s})$ is added, it will build up as a solid mass of crystals at the bottom of the reaction vessel. The equilibrium constant for this type of reaction is known as the solubility product, K_{sp} . For the tetraborate case, the solubility product is expressed as:

$$K_{\text{sp}} = [\text{Na}^+]^2[\text{B}_4\text{O}_5(\text{OH})_4^{2-}] \quad (2)$$

$\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}(\text{s})$ does not appear in the expression because it is in the solid phase, and as long as the solution remains saturated, changes in its amount will have no effect on the concentration of the dissolved species. Water does not appear in the expression because it is present in such excess that its concentration remains essentially constant during the reaction. These points are covered in Oxtoby, sections 9.2 and 9.3.

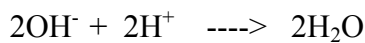
If x is used to represent the tetraborate-ion concentration, and there are two sodium ions per tetraborate ion, then $2x$ represents the sodium-ion concentration. The equilibrium expression can now be represented as:

$$K_{sp} = [\text{Na}^+]^2[\text{B}_4\text{O}_5(\text{OH})_4^{2-}] = [2x]^2[x] = 4x^3 \quad (3)$$

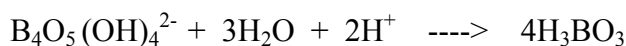
In this experiment, we desire to measure K_{sp} as a function of temperature. The determination of K_{sp} requires measurement of the amount of tetraborate ion in solution. This may be done by titration, taking advantage of the fact that the tetraborate ion is a weak base and reacts with water to release a pair of hydroxide ions. This reaction may be represented as follows:



The basic nature of the dissolved tetraborate ion allows its concentration to be determined by titration with a standard acid solution. Because products and reactants strive to maintain an equilibrium, as the acid reacts with the hydroxide ions on the right side of the above equation to consume product, more of the tetraborate ion reacts with water to form more hydroxide ions and restore the equilibrium. The effect of pH on solubility is discussed in Oxtoby, section 11.4. The reaction of an acid with the hydroxide ions is:



Combining this reaction with the reaction of the tetraborate ion with water gives a net reaction of:



Acid base reactions are generally fast, so the formation of hydroxide ions will continue as long as acid is added to the solution or until all of the tetraborate ions are consumed. The point at which the chemical amount of acid equals the chemical amount of base (tetraborate ion) originally present is known as the *equivalence point* (Oxtoby, section 10.6). Once the tetraborate ions are consumed, excess acid will accumulate and the pH of the solution will shift from basic to acidic. When a suitable pH indicator changes color, then one will know that all of the tetraborate ions have been consumed. The use of indicators is described in Oxtoby, p329.

Since the concentration of the tetraborate ion will be one half of the concentration of the acid used to titrate to the equivalence point, the above expression in terms of the acid concentration becomes:

$$K_{sp} = 4(0.5[\text{H}^+])^3 = 0.5[\text{H}^+]^3$$

The $[H^+]$ term in this expression refers to the total moles of a monoprotic acid used to reach the equivalence point divided by the volume of sample extracted from the solution at equilibrium in order to perform the titration. By taking samples at various temperatures under equilibrium conditions you can use the K_{sp} values along with temperature measurements taken for each sample to graph Equation 9-6 above. From the values of the slope, intercept and gas constant R

(8.3145 J / mole K), you are able to determine ΔH° and ΔS° . ΔG° , which is not independent of temperature (See Figure 8.12 in your text) can be calculated from equation 8.17. Once ΔG° is known for any temperature, a value for K_{sp} also can be calculated for that temperature. A spreadsheet will enable you to designate a cell for entering different temperatures, while designating another cell to automatically calculate the K_{sp} for the temperature value you select.

Materials**Items in your drawer**

2 oz plastic bottle
Plastic cap with spout
5 ml volumetric pipet
Blue pipet bulb
Wash bottle
Thermometer (-20 to 110 °C)
3 - 150 ml beakers (one for HCl, one for dissolving Borax)
30 ml beaker to obtain Borax solution at room temperature
5 - 125 ml Erlenmeyer flasks
Scripto markers to label glassware
Crucible tongs for holding onto hot beakers
250 ml beaker

Supplies in the Lab

Hot plate
Buret stand with Buret clamp and Thermometer holder
Balances
Chemwipes
Borax solution
Bromothymol Blue indicator in dropper bottles
Acetone in 500 ml wash bottles
Distilled water carboy
0.5xx M HCl in 20 L carboys for titration
Saturated Borax Solution at Room Temperature

Supplies to Check Out From the Stockroom

10 ml volumetric flask
50 ml buret

Procedure

Overview Since you will be withdrawing samples of a saturated (equilibrium) salt solution at elevated temperatures you will be constantly plagued by problems of the salt precipitating out of solution as soon as the sample you extract cools down. This precipitation can happen before you have finished collecting your sample quantitatively. Therefore a procedure has been designed to keep your sample at the proper temperature while you are collecting it, and while you are diluting it after collection. Hopefully, this will prevent premature precipitation. Once you have quantitatively collected the solution and transferred it to the titration vessel, it no longer matters if it precipitates, since the titration process will dissolve all of the precipitate.

To proceed, you will be collecting a hot saturated solution of borax into a 2 oz bottle. It will cool in this bottle while you monitor the temperature. As the solution cools to the desired temperatures, you will cover the opening of the bottle with a small piece of filter paper (kimwipe), then screw on a warmed cap with a spout on it. You will then squeeze out an aliquot of the liquid into a small volumetric flask already containing a premeasured aliquot of warm water. The kimwipe allows only liquid to pass so you will only collect dissolved salt, not salt crystals. The cap is warmed to prevent the solution from cooling and clogging up the spout. The premeasured water in the flask dilutes the sample to help prevent precipitation as it cools, and it also allows you to collect less sample. To know exactly how much sample you do collect, it is important that an accurately premeasured amount of water be pipetted into the flask. Once the known volume of sample is collected, it is transferred to an Erlenmeyer flask for titration with acid, and the volumetric flask is cleaned and dried in preparation for collecting another sample. If you try to pipet an aliquot directly from the solution as it cools, there is a high probability that the salt will precipitate in the pipet and clog it up.

Setting Up

1. Immediately turn on the hot plate to 2/3 of its highest setting. Fill the 250 ml beaker to about 100 ml with distilled water and set it on the hot plate. While the water is heating up, test the pipet and bulb by filling a 150 ml beaker with distilled water and drawing water out of it. Also rinse out the 10 ml volumetric flask with a **small** amount of acetone. Dump the waste acetone in the appropriate container. Holding the opening to the flask up to a small rubber tube attached to an aspirator, aspirate out any remaining acetone from the flask, using your hands to warm the flask and speed the evaporation of the acetone. Finally be sure you have plenty of Chemwipes handy. You will tear them into small squares to serve as filters later. When the water has begun to boil, turn down the hot plate without removing the beaker.

2. While waiting for your high temperature samples to reach equilibrium, rinse out a 30 mL beaker a few times with the saturated borax solution that has been sitting at room temperature over night. Then collect 15 ml of the borax solution at room temperature. Measure the temperature of the room temperature borax solution. Rinse out a 125 ml Erlenmeyer flask with distilled water. Rinse out the 5 ml volumetric pipet a few times

with small portions of the room temperature borax solution, and quantitatively pipet five ml of the solution into the 125 ml flask. Rinse the pipet two or three times with hot water from the 250 ml beaker and discard this rinsing down the drain. Titrate this solution and include this result along with all of your other measurements.

3. Take your 2 oz bottle and wash bottle to the TA to obtain your borax solution and a wash bottle of hot water. Take several paper towels with you to wrap around the hot plastic bottles to keep from burning your fingers. Place the 2 oz bottle on a few layers of paper towel at your work area to keep it from cooling too rapidly. Place the wash bottle in the hot water in the 250 mL beaker to keep it warm.

4. Rinse the thermometer with hot water from the wash bottle to warm it up, holding on to the wash bottle with a layer of paper towels. Wipe the thermometer with a kimwipe, and using the thermometer holder, position the thermometer in the 2 oz bottle so that the mercury bulb reaches half way down into the liquid in the bottle.

Taking Samples

You are to take your first hot borax sample when the thermometer reaches about 56 °C. You will take the next sample after the temperature drops another 4 °C. The temperature will probably drop about a degree centigrade, while you are taking the sample. Thus your samples will be spaced about 5 °C apart. However, you will make temperature readings for your calculations **after** taking each sample, as the sample is well mixed at this point and at a uniform temperature throughout.

1. Using the volumetric pipet, pipet 5 mL of hot water from the 250 mL beaker into the 10 mL volumetric flask. Let the pipet drain in a vertical position. Do not blow out water remaining in the tip. (Volumetric pipets are calibrated to deliver appropriate volumes by being allowed to drain naturally.)

2. Be sure the spout on the cap to the 2 oz bottle is in the open position. Remove the wash bottle from the 250 mL beaker, and put the cap to the 2 oz bottle into the hot water in the beaker to heat up.

3. Raise the thermometer from the 2 oz bottle and remove the bottle from under it. Wipe it off with a damp kimwipe.

4. Tear a square off a kimwipe that is large enough to cover the opening of the 2 oz bottle and fold down to cover the threads of the bottle. Cover the mouth of the 2 oz bottle with the square piece of kimwipe. Using tongs remove the cap to the 2 oz bottle, shake it vigorously to remove any water, and touch a kimwipe to the open spout to remove any droplets of water that might be in the spout. Screw the cap onto the 2 oz bottle, right over the square of kimwipe covering the opening. The cap should lock the piece of kimwipe in place as you screw it down.

5. With the spout to the cap open, invert the 2 oz bottle and squeeze borax solution into the 10 mL volumetric flask to fill the flask until the bottom of the meniscus is just touching the etched line on the neck of the flask. You have the ability to add solution to the flask one small drop at a time, so be careful not to fill the flask above the etched line.

[The kimwipe serves as a filter to prevent solid particles of borax from getting into the flask, thus preventing error caused too high a borax concentration. The warmed cap prevents the solution from cooling when it passes the filter and prematurely crystallizing with a resultant reduction of the concentration of the borax solution entering the volumetric flask.]

6. Immediately after the volumetric flask is filled to the mark, unscrew the cap from the 2 oz bottle and remove the small square of kimwipe from its opening. Grasp the wash bottle with a layer of paper towels and rinse the thermometer with hot water. Wipe it dry with a kimwipe and lower the thermometer into the 2 oz bottle, submerging it into the borax solution without burying it in the crystals present in the bottle. Watch the thermometer to see what temperature it stabilizes at. Write this temperature on a 125 mL Erlenmeyer flask with a Sharpie marker.

7. Using the wash bottle, rinse the cap with the spout over a sink with hot water, be sure to shoot a stream of water through the open spout.

8. Empty the contents from the 10 mL volumetric flask into the labeled 125 mL Erlenmeyer flask. Rinse the volumetric flask three times with portions of hot water from the wash bottle into the labeled 125 mL Erlenmeyer. Return the wash bottle to the 250 mL beaker of hot water.

9. Rinse the 10 mL volumetric flask with acetone, and dry it with the aspirator in preparation for the next sample.

After the thermometer drops another 4 ° C from the value recorded on the 125 mL Erlenmeyer flask, repeat the procedure for **taking samples** starting at step 1.

Note: AS THE SOLUTION APPROACHES ROOM TEMPERATURE IT WILL TAKE LONGER TO COOL DOWN. AFTER COLLECTING THREE SAMPLES YOU MAY FEEL THAT YOU HAVE ENOUGH TIME BEFORE COLLECTING THE NEXT SAMPLE TO BEGIN TITRATING THE FIRST THREE. IF SO, FOLLOW THE INSTRUCTIONS BELOW.

After collecting the last sample, place the cap on a 2 oz bottle in the open position. Place the capped bottle in the 250 mL beaker on the hot plate. If necessary, add enough water to reach up to the cap on the bottle and turn up the hot plate to cause the water to boil. Allow the water in the beaker to boil for five minutes, then pour the borax solution in the 2 oz bottle into the used borax container.

Titrating the Tetraborate Ion

1. After taking five samples at approximately 5 °C intervals, wipe dry a 150 mL beaker. Fill the beaker with 0.5 M HCl from the carboy. (*Note the exact concentration of the HCl on the carboy in order to correctly calculate the concentration of the tetraborate ion.*)
2. Rinse the 50 mL buret several times with small amounts of the 0.5 M HCl, then fill it.
3. Rinse the sides of the first 125 mL Erlenmeyer flask with the wash bottle, add 3 to 4 drops of Bromothymol Blue indicator, and titrate to the green to yellow equivalence point. The indicator starts out blue in the borax, then turns green as the equivalence point is approached, then turns sharply yellow at the equivalence point. Solutions titillated just to the equivalence point can be poured down the drain.

Clean Up

1. Rinse the borax from the 2 oz bottle into the "Used Borax Beaker". Be careful not to add any excess water to the beaker. If crystals of borax remain in the bottle after you have dumped the solution into the beaker, rinse the bottle once only with a small portion of hot water, then rinse the rest of the crystals in the bottle down the drain.
2. Empty borax/HCl solutions that have been titillated just to the equivalence point down the drain.
3. Empty excess acid solutions into the acid/base waste bottle.
4. When finished, thoroughly rinse all glassware that held the borax solution with tap water only, not acetone or distilled water. Empty the buret into the acid waste bottle, and rinse the buret with water.

III. Data Analysis and Lab Report

1. Use the following "Report Form" as a guideline in performing perform your calculations.
2. For each temperature, calculate K_{sp} , $\ln K_{sp}$, T , and $1/T$. Plot $\ln K_{sp}$ versus $1/T$ as described in the Introduction. Using a linear lest-squares fit, obtain the slope and intercept values. From these, calculate ΔH° and ΔS° . Finally, calculate ΔG° for the reaction at the standard temperature, 25°C. Provide error estimates for your values of ΔH° , ΔS° , and ΔG° .

Questions

1. Comment on the significance of each of the possible sources of error listed.
 - (a) The saturated borax solutions may not show ideal behavior.
 - (b) ΔH° and ΔS° may not be independent of temperature.
 - (c) Obtaining the intercept requires significant extrapolation.

Report Form

Actual concentration of 0.5 M HCl solution: _____

Beaker label	50°C	45°C	40°C	35°C	30°C
Temperature reading, °C	_____	_____	_____	_____	_____
Kelvin temperature, K	_____	_____	_____	_____	_____
1/T, K	_____	_____	_____	_____	_____
Buret final volume, mL	_____	_____	_____	_____	_____
Buret initial volume, mL	_____	_____	_____	_____	_____
Volume of HCl used, mL	_____	_____	_____	_____	_____
Moles of H ⁺	_____	_____	_____	_____	_____
Moles of B ₄ O ₅ (OH) ₄ ⁻²	_____	_____	_____	_____	_____
M, B ₄ O ₅ (OH) ₄ ⁻²	_____	_____	_____	_____	_____
K _{sp}	_____	_____	_____	_____	_____
ln K _{sp}	_____	_____	_____	_____	_____

Experiment 2

Titration of a Diprotic Acid: Identifying an Unknown

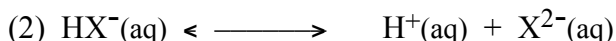
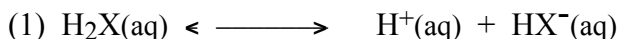
Introduction

There are three goals in this experiment:

1. Identify an unknown diprotic acid by finding its molecular mass.
2. Determine the acid dissociation constants, K_{a1} and K_{a2} , of the diprotic acid.
3. Compare two methods of data analysis: (a) the classical method which estimates the unknown parameters from specific points on the graph of pH vs. volume of added base, and (b) the modern method which compares the overall data with a simulation model in which the unknown parameters are varied to achieve the best fit according to the least squares criterion.

Theory

A diprotic acid is an acid that yields two H^+ ions per acid molecule. Examples of diprotic acids are sulfuric acid, H_2SO_4 , and carbonic acid, H_2CO_3 . A diprotic acid dissociates in water in two stages:

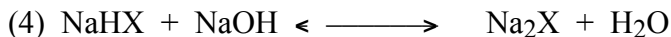


Because of the successive dissociations, titration curves of diprotic acids have two equivalence points. Figure 10.17 in Oxtoby et. al. fifth edition shows two equivalence points for phosphoric acid (the third proton dissociates at the same pH as the water proton and its equivalence point cannot be clearly seen). The equations for the acid-base reactions occurring between a diprotic acid, H_2X , and sodium hydroxide base, NaOH, are:

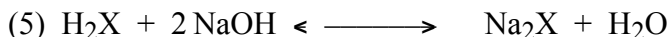
From the beginning to the first equivalence point:



From the first to the second equivalence point:



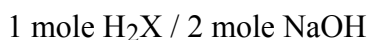
From the beginning through the second equivalence point (net reaction):



At the first equivalence point, all H^+ ions from the first dissociation have reacted with NaOH base. At the second equivalence point, all H^+ ions from both reactions have reacted (twice as many as at the first equivalence point). Therefore, the volume of NaOH added at the second equivalence point is exactly twice that of the first equivalence point (see Equations 3 and 5).

One purpose of this experiment is to identify an unknown diprotic acid by finding its molecular mass. A diprotic acid is titrated with NaOH solution of known concentration. Molecular mass (or molar mass) is found in g/mole of the diprotic acid. Weighing the original sample of acid will tell you its mass in grams. Moles can be determined from the volume of NaOH titrant needed to reach the first equivalence point. The volume and the concentration of NaOH titrant are used to calculate moles of NaOH. Moles of unknown acid equal moles of NaOH at the first equivalence point (see Equation 3). Once grams and moles of the diprotic acid are known, molecular mass can be calculated, in g/mole. Molecular mass determination is a common way of identifying an unknown substance in chemistry.

You may use either the first or second equivalence point to calculate molecular weight. The first is somewhat easier, because moles of NaOH are equal to moles of H_2X (see Equation 3). If the second equivalence point is more clearly defined on the titration curve, however, simply divide its NaOH volume by 2 to confirm the first equivalence point; or from Equation 5, use the ratio:



The second purpose of this experiment is to determine the acid dissociation constants, K_{a1} and K_{a2} , for the two dissociations of the diprotic in this experiment. The K_a expressions for the first and second dissociations, from Equations 1 and 2, are:

$$K_{a1} = \frac{[H^+][HX^-]}{[H_2X]} \qquad K_{a2} = \frac{[H^+][X^{2-}]}{[HX^-]}$$

The first half-titration point occurs when one-half of the H^+ ions in the first dissociation have been titrated with NaOH, so that $[H_2X] = [HX^-]$. Similarly, the second half-titration point occurs when one-half of the H^+ ions in the second dissociation have been titrated with NaOH, so that $[HX^-] = [X^{2-}]$. Substituting $[H_2X]$ for $[HX^-]$ in the K_{a1} expression, and $[HX^-]$ for $[X^{2-}]$ in the K_{a2} expressions, the following are obtained:

$$K_{a1} = [H^+] \qquad K_{a2} = [H^+]$$

Taking the base-ten log of both sides of each equation,

$$\log K_{a1} = \log [H^+] \qquad \log K_{a2} = \log [H^+]$$

the following expressions are obtained:

$$pK_{a1} = \text{pH} \qquad pK_{a2} = \text{pH}$$

Thus, the pH value at the first half-titration volume is equal to the pK_{a1} value. The first half-titration point volume can be found by dividing the first equivalence point volume by two.

Similarly, the pH value at the second titration point, is equal to the pK_{a2} value. The second half-titration volume is midway between the first and second equivalence point volumes.

Materials

pH electrode	stirring bar
unknown diprotic acid, 0.120 g	ring stand
milligram balance	2 utility clamps
distilled water	250 mL beaker
~0.1 M NaOH solution (standardized)	100 ml beaker
magnetic stirrer (if available)	wash bottle
50 mL buret	funnel to fill buret

Procedure

1. Always wear goggles.
2. Weigh out about 0.120 g of the unknown diprotic acid on a piece of weighing paper. Record the mass to the nearest 0.001 g. Transfer the unknown acid to a 250 mL beaker and dissolve in 100 mL of distilled water.
3. Place the beaker on a magnetic stirrer and add a stirring bar.
4. Use a utility clamp to suspend a pH electrode on a ring stand. Position the pH electrode in the unknown acid solution and adjust its position toward the outside of the beaker so that it is not struck by the stirring bar. See Figure 10.3 of Oxtoby et. al. fifth edition.
5. Obtain a 50 mL buret and rinse the buret with a few mL of the ~0.1 M NaOH solution. Record the precise concentration of the NaOH solution. Use a utility clamp to attach the buret to the ring stand .

6. Fill the buret a little above the 0.00 mL level of the buret. Drain a small amount of NaOH solution so it fills the buret tip *and* leaves the NaOH at or below the 0.00 mL level of the buret. Dispose of the waste solution in this step as directed by your instructor. Follow the directions at the end of the procedure for setting up and calibrating the pH meter.
7. You are now ready to begin the titration.
 - Before adding any NaOH titrant, monitor pH for 5-10 seconds. After the pH has stabilized, record the pH and record the initial buret level. This entry is the first data pair.
 - Add enough NaOH to raise the pH by about 0.20 units. After the NaOH has been added and the pH has stabilized. Record the new pH and buret level to the nearest 0.01 mL.
 - Continue adding NaOH solution in increments that raise the pH about 0.20 units and record the pH and buret reading after each addition.
 - When pH 3.5 is reached, change to 2-drop increments. Record the pH and buret reading after each increment.
 - After pH 4.5 is reached, again add larger increments that raise the pH by about 0.20 units and record the pH and buret reading after each addition. Continue in this manner until a pH of 7.5 is reached.
 - When pH 7.5 is reached, change to 2-drop increments. Record the pH and buret reading after each increment.
 - When pH 10 is reached, again add larger increments that raise the pH by 0.20 units. Record the pH and buret reading after each increment. Continue in this manner until you reach a pH of 11.

To dispose of your titrant solution, add one drop of phosphoric acid to the solution in its beaker. This will bring the pH below 11 and you can pour it down the sink.

Processing the Data (Classical Method)

1. Calculate the volume of NaOH added by subtracting the initial buret reading from each buret reading made when the pH data was also collected. The values of pH vs volume of NaOH added constitute your data table. Make a graph of pH vs volume of NaOH added.
2. On your printed graph, one of the two equivalence points is usually more clearly defined than the other; the two-drop increments near the equivalence points frequently result in larger increases in pH (a steeper slope) at one equivalence point than the other. Indicate the more clearly defined equivalence point (first or second) in the Data and Calculations Table below.
3. Use your graph and data table to determine the volume of NaOH titrant used for the equivalence point you selected in Step 1. To do so, examine the data to find the largest increase in pH values during the 2-drop additions of NaOH. Find the NaOH volume just *before* this jump. Then find the NaOH volume *after* the largest pH jump. Underline both of these data pairs on your data table and record them in the Data and Calculations table.
4. Determine the volume of NaOH added at that equivalence point you selected in Step 1. To do this, add the two NaOH volumes determined in Step 2, and divide by two. For example:

$$\frac{12.34 + 12.44}{2} = 12.39 \text{ mL}$$

5. Calculate the number of moles of NaOH used at the equivalence point you selected in Step 1.
6. Determine the number of moles of the diprotic acid, H₂X. Use Equation 3 or Equation 5 to obtain the ratio of moles of H₂X to moles of NaOH, depending on which equivalence point you selected in Step 1.
7. Using the mass of diprotic acid you measure out in Step 1 of the procedure, calculate the molecular mass of the diprotic acid, in g/mol.
8. From the following list of six diprotic acids, identify your unknown diprotic acid.

Diprotic Acid	Formula	Molecular Weight
Oxalic Acid	H ₂ C ₂ O ₄	90
Malonic Acid	H ₂ C ₃ H ₂ O ₄	104
Maleic Acid	H ₂ C ₄ H ₂ O ₄	116
Malic Acid	H ₂ C ₄ H ₄ O ₅	134
Tartaric Acid	H ₂ C ₄ H ₄ O ₆	150
Phthalic Acid	H ₂ C ₈ H ₄ O ₄	166

9. Determine the percent error for your molecular weight value in Step 6.
10. For the *alternate* equivalence point (the one you did *not* use in Step 1), use your graph and data table to determine the volume of NaOH titrant used. Examine the data to find the largest increase in pH values during the 2-drop additions of NaOH. Find the NaOH volume just before and after this jump. Underline both of these data pairs on your data table and record them in The Data and Calculations table below. Note: Dividing or multiplying the other equivalence point volume by two may help you confirm that you have selected the correct two data pairs in this step.
11. Determine the volume of NaOH added at the alternate equivalence point, using the same method you used in Step 3.
12. On your graph, clearly specify the position of the equivalence point volumes you determined in Steps 3 and 9, by drawing a vertical dotted reference lines from the equivalence point on the graph to the horizontal axis. Write the NaOH volume of each equivalence point on the horizontal axis of the graph.

Now use the method described below to determine the K_{a1} and K_{a2} values for the diprotic acid you identified in this experiment.
13. Determine the precise NaOH volume for the *first* half-titration point using one-half of the first equivalence point volume (determined in Step 3 or Step 9 of Processing the Data) Then determine the precise NaOH volume of the *second* half-titration point halfway between the first and second equivalence points.
14. On your graph of the titration curve, draw horizontal reference lines from the point on the graph midway to the first equivalence point to the y axis and midway between the first and second equivalence point to the y axis. Start with the first half-titration point volume (Point 1) and the second half-titration point volume (Point 2). Determine the pH values on the vertical axis that correspond to each of these volumes. Estimate these two pH values to the nearest 0.1 pH unit. These values are the pK_{a1} and pK_{a2} values respectively. (Note: See if there are volume values in your data table similar to either of the half-titration volumes in Step 1. If so, use their pH values to confirm your estimates of pK_{a1} and pK_{a2} from the graph.)
15. From the pK_{a1} and pK_{a2} values you obtained in the previous step, calculate the K_{a1} and K_{a2} values for the two dissociations of the diprotic acid.














Processing the Data (Modern Method)

You will analyze your data further in the coming simulation lab. You should have the analysis described in this handout ready by that time.

Data and Calculations Table

Mass of diprotic acid	_____ g
Concentration of NaOH	_____ M
1. Equivalence point (indicate the one you will use in the calculations below)	first equivalence point _____ or second equivalence point _____
2. NaOH volume added before and after largest pH increase	_____ mL _____ mL
3. Volume of NaOH added at the equivalence point	_____ mL
4. Moles NaOH	_____ mol
5. Moles of diprotic acid, H ₂ X	_____ mol
6. Molecular weight of the diprotic acid	_____ g/mol
7. Name, formula, and accepted molecular weight of the diprotic acid	_____ _____ _____ g/mol
8. Percent error	_____ %
9. Alternative equivalence point (indicate the one used below)	first equivalence point _____ or second equivalence point _____
10. NaOH volume before and after largest pH increase (alternate equivalence point)	_____ mL _____ mL
11. Volume of NaOH added at the alternate equivalence point	_____ mL

Instructions for calibrating the Beckman 32 pH Meter

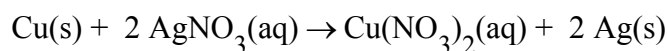
1. Connect the pH electrode to the input on the back of the pH meter marked "pH/mV", Plug in the power supply to the instrument and to the wall socket.
2. Press  to turn on the pH meter, then press  to clear. The display will show [Clr, AUTO]. If the [AUTO] does not appear press .
3. Rinse the electrode with deionized water. Blot excess.
4. Immerse the electrode in standard pH=4.0. Stir briefly with the electrode to remove bubbles from the electrode surface. Press  to put the instrument in the pH measurement mode.
5. Press  to simultaneously enter the standardization mode and begin the instrument standardization on the first standard. When  stops flashing you will see the pH value locked.
1. Rinse the electrode with deionized water. Blot excess. Immerse the electrode in standard pH=10.0. Stir briefly with the electrode to remove bubbles from the electrode surface. Press  to measure the a standard at the second pH value. The instrument is set to recognize standards of either 4,7 or 10 and set a linear calibration curve between whichever two of these values is used. When  stops flashing, the display will show the pH value of the second standard.
7. Rinse electrode with deionized water. Blot excess.
8. Immerse electrode in sample. Press  to begin measuring samples.
9. Press  for continuous measurements. The  will blink continuously.
10. When finished collecting data press  to turn off the instrument. This will also clear all standardization data. If  accidentally press this button during lab you must re-standardize the pH meter.

EXPERIMENT 3 ELECTROCHEMISTRY

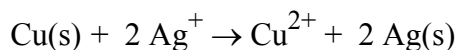
Redox Reactions

Chemical reactions that involve a change in the oxidation state of chemical species are called *redox reactions* (an abbreviation of **re**duction-**oxi**dation reaction). Redox reactions can be identified, and the movement of electrons can be followed, by using a type of formal "bookkeeping" of the number of electrons associated with atoms. This accounting of electrons involves assigning *oxidation numbers* to individual atoms within a chemical species. Redox reactions are reactions in which there are changes in oxidation numbers. Every redox reaction can be divided into two *half-reactions*: one that involves a gain of electrons and one that involves a loss of electrons. The gain of electrons is called *reduction* and the loss of electrons is called *oxidation*.

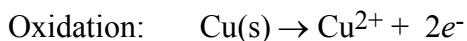
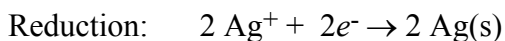
Consider the following chemical reaction in which a copper coin is dropped into a dilute solution of silver nitrate (AgNO_3). Needles of metallic silver crystals grow slowly from the copper surface, especially if the solution is not disturbed. The solution also slowly changes from colorless to a pale blue color, indicating that Cu^{2+} ions are being produced. (See Figure 12.2 of Oxtoby.) The overall chemical equation is



for which the net ionic equation is



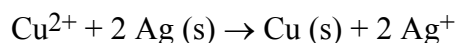
This reaction is a redox reaction because the oxidation number of copper is changing from 0 to +2 (Cu(s) to Cu^{2+}) and that of silver is changing from +1 to 0 (Ag^+ to Ag(s)). The NO_3^- ion remains unchanged during the reaction and is called a *spectator ion*. The reaction can be divided into two half-reactions:



which add together to give the redox reaction. As this reaction proceeds, the concentration of copper ions increases, and that of silver ions correspondingly decreases. The equilibrium constant for the reaction is:

$$K = \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}$$

and is a very large number, because the forward direction (as written) is favored. The backward reaction



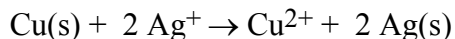
balances the forward reaction only when the silver ion concentration is very small. Then the reaction is at equilibrium and the free energy change $\Delta G = 0$ (Oxtoby, eqn 9.6). As long as the silver ion concentration is greater than the equilibrium value, ΔG is negative and the forward reaction is spontaneous.

The spontaneous reaction in which the copper coin reduced Ag^+ to silver crystals is exothermic; the energy released by the reaction is lost as heat to the solution. The redox reaction will eventually come to equilibrium, and no more heat will be released.

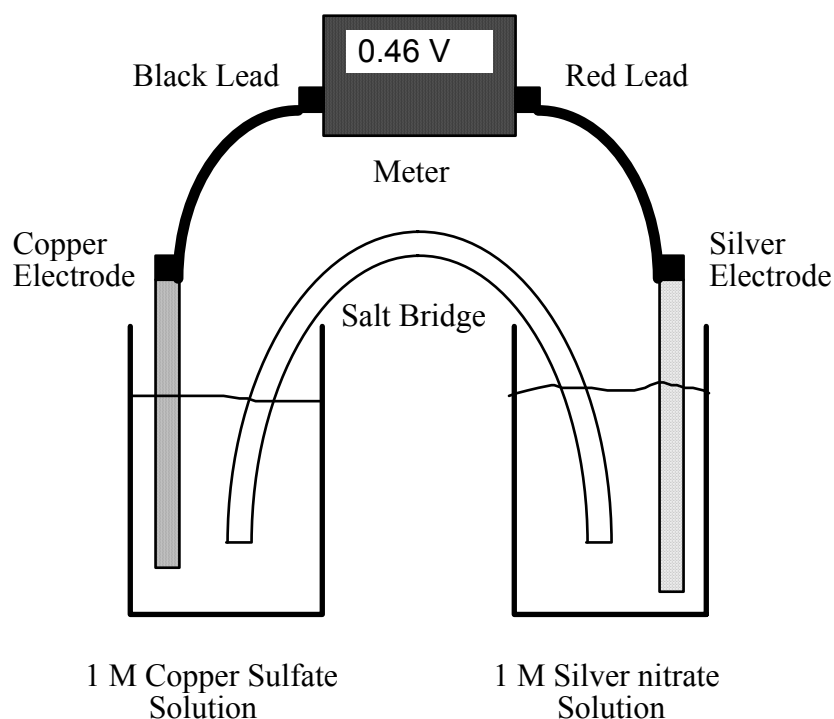
Electrochemistry

Redox reactions in which electrons are completely lost by one species and completely accepted by another are very useful because the two half-reactions can often be physically separated. The electrons that are transferred may then be allowed to flow through external wires in a circuit and be made to do useful work. *Electrochemistry* is the study of redox reactions that either produce or utilize electrical energy (moving electrons and/or ions) in devices called electrochemical cells.

In the redox reaction



the two half-reactions can actually be separated by placing the reactants in different compartments, partitioned by some type of porous medium that prevents mixing, but not ion flow. Such a device is called a *salt bridge*. Each compartment, called a *half-cell*, contains a metal electrode in contact with a solution containing its corresponding metal ion, as shown in the figure below.



An Electrochemical Cell Made Up of Two Half-Cells

An external connection between the two electrodes completes the circuit, and electrons will flow from the copper electrode through the external wire and meter and into the silver electrode. The copper electrode will dissolve, forming Cu^{2+} ions in solution, and Ag^+ ions will pick up electrons at the surface of the silver electrode and be deposited as silver atoms. The electrode at which oxidation takes place (the copper electrode) is called the *anode*, and the electrode at which reduction takes place (the silver

electrode) is called the *cathode*. The combination of the two half-cells is called an *electrochemical cell*.

When an electrochemical cell voltage is measured, ΔG is typically not zero:

$$\Delta G = -nFE_{\text{cell}}$$

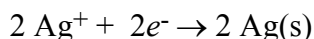
where n is the number of electrons in the redox reaction as written, and F is the faraday, 96,500 coulombs per mole of electrons, and E_{cell} is the potential (electromotive force, emf) in volts measured between the two electrodes (Oxtoby, p. 395). At reasonable values for the concentrations of both ions, the reaction proceeds in the forward direction as written. As current flows the voltage drops to zero and so does ΔG . This final state is the same equilibrium reached without electrical connections. If we measure the emf of the reaction when both ions have unit concentration we measure the standard emf or E° (Oxtoby, p. 395).

Standard Potentials

In the electrochemical cell under discussion, it is a fact that oxidation,



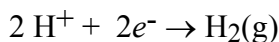
occurs at the copper electrode (anode) and that reduction,



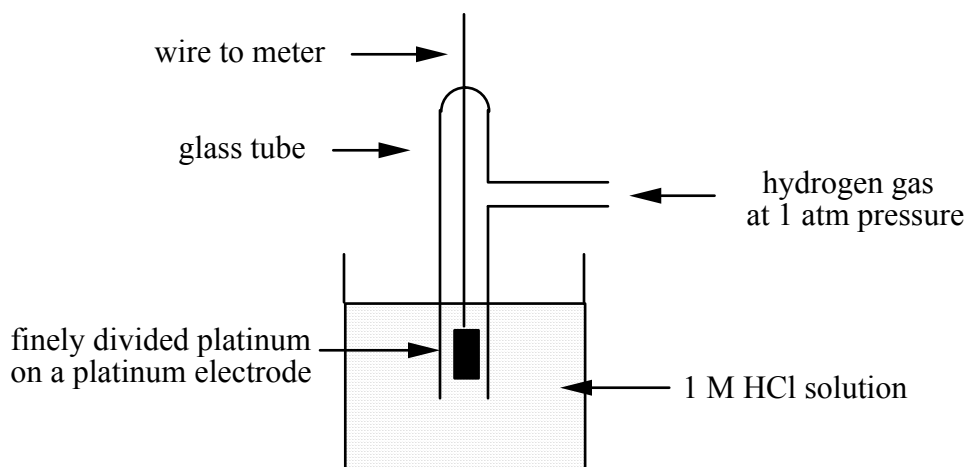
occurs at the silver electrode (cathode). The relative tendency of a particular species to give up or accept electrons is manifested as a *potential*, which is measured in volts, between the two electrodes. This potential may be considered as being the sum of two potentials called *half-cell potentials* or *single-electrode potentials*.

The tendency of a species to give up or accept electrons can only be compared relative to another species. In order to obtain consistent electrochemical data, it is necessary to compare all single electrodes to a standard reference electrode. The universal reference electrode, chosen by international agreement, is the *standard hydrogen electrode* (SHE), which is shown in the diagram below.

The half reaction at the SHE,



is arbitrarily written as a reduction. An arbitrary assignment of *zero* electrode potential (0.00 V) is given to the SHE. If the reverse reaction were written, its standard *oxidation* potential would also be zero.



A Standard Hydrogen Electrode

All other electrode potentials are referred to the SHE. It is now customary to report *single* electrode potentials in tables, and it must be remembered that these single half-cell potentials are expressed in combination with a SHE at 0.00 V.

The single-electrode potential value is dependent on the concentration of the ion surrounding the electrode and on the temperature. Standard conditions of 1 M concentration and 298 K (25°C) have been chosen, and by international agreement all standard electrode potentials are reported as *standard reduction potentials* (\mathcal{E}°). Some examples are given below in Table I.

Table I.

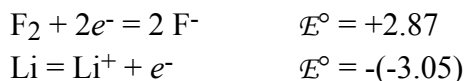
$\text{Al}^{3+} + 3e^- \rightarrow \text{Al(s)}$	$\mathcal{E}^\circ = -1.66 \text{ V}$
$\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn(s)}$	$\mathcal{E}^\circ = -0.76 \text{ V}$
$\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe(s)}$	$\mathcal{E}^\circ = -0.41 \text{ V}$
$\text{Pb}^{2+} + 2e^- \rightarrow \text{Pb(s)}$	$\mathcal{E}^\circ = -0.13 \text{ V}$
$2 \text{H}^+ + 2e^- \rightarrow \text{H}_2(\text{g})$	$\mathcal{E}^\circ = 0.00 \text{ V}$
$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu(s)}$	$\mathcal{E}^\circ = 0.34 \text{ V}$
$\text{Ag}^+ + e^- \rightarrow \text{Ag(s)}$	$\mathcal{E}^\circ = 0.80 \text{ V}$

A useful way of thinking about these \mathcal{E}° values is to remember that the more *positive* the \mathcal{E}° value, the more that reaction goes to the right. The \mathcal{E}° value for oxidation reactions is obtained simply by changing the *sign* of the appropriate reduction reaction, e.g.,

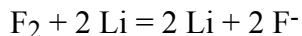


A larger table of standard reduction potential is in Appendix E of Oxtoby.

You will note that the values are arranged in increasing order of the voltage. This indicates that, for example, Li is hard to reduce and (change sign) easy to oxidize. Exactly the opposite is true of F₂ at the bottom of the table. To find the voltage of a cell made of these two half-cells we reverse one of them so that the sum is positive:



The sum is +5.93. To balance the equation multiply the second half-reaction by 2 and add:



Note that you do NOT multiply \mathcal{E}° for lithium by 2. This is best seen from the formula $\Delta G^\circ = -nFE$. If you double the number of electrons ΔG° also doubles, Therefore \mathcal{E}° must stay the same.

Note that the voltage of the whole cell is always positive. With the corresponding half-reactions written so that \mathcal{E}° is positive, the positive pole is the half-reaction where the electrons enter the cell and the negative pole is where they exit to the meter or load. If you use the silver electrode as the reference instead of the hydrogen electrode, examination of Table 19.1 shows that all \mathcal{E}° would be 0.80 V lower (F₂ would be 2.07 volts and Li = -3.85). Thus if you measure against silver-set to zero, you have to *add* 0.80 to compare with Appendix E of Oxtoby.

Comparison of Electrode Potentials

One very important practical consideration in the measurement of cell potentials is that the cell reaction must be carried out under standard conditions. A simple wire connection between the two electrodes would allow the electrons to flow and the redox reaction to go to completion. In the process the concentrations of ions in each half-cell would change dramatically, and the cell voltage would drop to zero, its equilibrium value. Cell potential measurements are, therefore, usually made with instruments that have very high resistance in order to minimize the flow of electrons during the measurement.

Another important consideration is the electrical connection that must be made between the two half-cell solutions before the cell voltage measurement can be made. The connection is called a *salt bridge*. The salt bridge allows electrical neutrality to be maintained in each half-cell. During the voltage measurement, electrons must flow from the anode, through the meter, and into the cathode. Cations are generated in the anode half-cell solution, and to maintain a charge balance, anions flow from the salt bridge into this half-cell (and cations flow into the cathode half-cell where metal cations are reduced and deposit as neutral metal). The net result is simply a flow of inert electrolyte from the salt bridge into the cell.

NOTE: Equilibrium constants for redox reactions are not tabulated in the usual reference literature (as are equilibrium constants for acid-base reactions, etc.). Instead,

redox reaction equilibrium constants are calculated from standard reduction potential data.

Experimental Setup

Equipment you must check out from the stockroom

Fluke Multimeter with alligator clamps and wire leads.

Thermometer

Labeled wires (Ag, Cu, Pb, Zn)

platinum wire

50 ml beaker

2 - 100 ml beakers

250 ml beaker

stir bar

10 ml burette

10 ml pipette

pipette bulb

Materials found in the lab

1 M Metal ion solutions in dropper bottles (CuSO₄, AgNO₃, PbNO₃, ZnSO₄)

1 M solution (KNO₃) to be put in a 100 ml beaker.

0.005 M Fe²⁺ Solution

0.01 M Ce⁴⁺ Solution

Saturated KCl

0.1 AgNO₃ Solution

test tubes for holding metal ion solutions

salt bridges (tygon tubing filled with 1% Agar dissolved in 1 M KNO₃ solution)

electrodes (syringes with porous tips)

Hot plate, stir plate combination.

Thermometer holder and ring stand

Waste disposal

The metals you will be using are present in toxic concentrations, harmful to the environment. Deposit each solution into it's proper waste container. There is a separate waste container for each solution containing a metal. The Potassium Nitrate and unused 0.005 M Fe²⁺ may go down the drain. Do not mix the solutions.

Part I. Determination of Standard Half-Cell Potentials

The standard half-cell potentials of Zn/Zn^{2+} , Pb/Pb^{2+} , and Ag/Ag^+ will be determined using a copper electrode as a reference. This experimental setup involves cells under near standard conditions (1.0 M, 25°C, 1 atm) so the standard potentials are directly measured.

In order to interpret potential results obtained from a voltmeter, it is necessary to understand electrical conventions and how a voltmeter displays the potential it measures. From Ohm's law we know that $V = I \cdot R$. Resistance (R) always opposes the flow of current and is always positive. Therefore if the current is positive, the voltage reading also is positive. Positive current from a battery (Galvanic cell) flows from the positive pole at high electrical potential to the negative pole at low electrical potential. Convention dictates that the positive lead (red) be attached to the positive pole and the negative lead (black) be attached to the negative pole to measure the voltage difference of the positive pole relative to the negative pole. If this is done with the batteries found in the laboratory, you will obtain a positive voltage reading. **The voltmeter displays the difference of the potential at the positive pole minus the potential at the negative pole.** Electrons however flow in the opposite direction as current. So electrons tend to flow from the negative pole of the battery to the positive pole. This means that if the voltage reading on the voltmeter is positive, electrons tend to flow through the black lead into the meter, and out the red lead of the meter. This fact is important to correctly evaluate at which electrode half-cell reduction is occurring.

Because we are using the copper half-cell as the reference, it is connected to the common (negative) terminal of the multimeter. For the copper electrode 0.34 half-cell potential to be taken as the reference value for these experiments, the over all reaction must be written so that $\text{Cu}(s)$ appears as the reactant. Then the voltage measured by the voltmeter will be the potential that tends to push electrons toward the copper electrode. The voltmeter is measuring the difference in the potentials between two half-cells, one of them being copper. The potential displayed is the potential difference of the positive pole minus the negative pole, which would be at a potential of 0.34 V relative to the SHE. If a half-cell of potential X relative to the SHE is attached to the red lead of a voltmeter and a 1.0 M Cu^{2+}/Cu half-cell is attached to the negative terminal of the voltmeter, and if $\Delta\mathcal{E}$ represents the voltmeter reading, then:

$$\Delta\mathcal{E} = X - 0.34$$

or

$$X = \Delta\mathcal{E} + 0.34$$

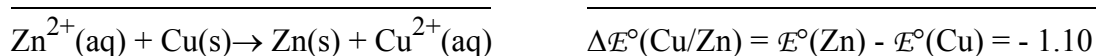
If the potential, $\Delta\mathcal{E}$, is positive then ΔG is negative and the over all reaction occurs in the direction written. Electrons are flowing from the half-cell attached to the negative terminal. If $\Delta\mathcal{E}$ is negative then ΔG is positive, and electrons are flowing to the half-cell attached to the negative terminal. When reactions that involve other pairs half-cells are measured, the voltmeter will be measuring the potential of the half-cell attached to the positive terminal minus the potential of the half-cell connected to the common (negative) terminal as it tries to push electrons into the negative terminal. A negative value for $\Delta\mathcal{E}$ simply means that a negative push is a pull. The metal ions originally written as

reactants in the half-cell attached to the common (negative) terminal must be written as products to describe the reaction as it occurs spontaneously.

For example, for the cell $\text{Cu}/\text{Cu}^{2+}//\text{Zn}^{2+}/\text{Zn}$, the standard reduction potentials are as follows:



The symbol // represents a salt bridge, which provides electrical contact between the electrode couples without allowing mixing and, in the ideal case, contributes no liquid junction potential to the cell potential. Because for this experiment we are measuring potentials with the copper electrode at the negative terminal of the voltmeter, we must write the overall reaction with $\text{Cu}(\text{s})$ as a reactant:



We can see from this example, that the reaction will occur spontaneously in the direction opposite to the one which it was written. Experimentally we could determine $\Delta\mathcal{E}^{\circ}(\text{Cu}/\text{Zn})$ by measuring a potential of -1.10 with a voltmeter. From this measurement we can calculate the half-cell potential for $\mathcal{E}^{\circ}(\text{Zn})$ by substituting for $\Delta\mathcal{E}$ in the equation:

$$X = \Delta\mathcal{E} + 0.34$$

$$X = -1.10 + 0.34 = - 0.76$$

Experimental Procedure

Plug the wire leads into the multimeter. The red lead plugs into the $V\Omega$ hole and the black lead plugs into the COMM hole.

Attach the alligator clips to the leads if they are not already attached.

Obtain a lead, zinc, copper, and silver wire.

Obtain a salt bridge containing the agar/ KNO_3 gel.

Obtain four test tubes with a marker label them: Ag, Cu, Pb, Zn.

Using the plastic pipettes supplied fill each test tube 4/5 full with the salt solution of the appropriate metal.

Turn on the multimeter to read volts - DC.

Attach the alligator clip to the black multimeter lead to the copper wire. Attach the alligator clip to the red multimeter lead to the silver wire.

Holding the copper wire by the alligator clip, dip the wire into the copper salt solution in the test tube labeled Cu.

Holding the silver wire by the alligator clip, dip that wire into the silver salt solution in the straw labeled Ag.

Read and record the potential on the multimeter. (It should read 0.000 V)

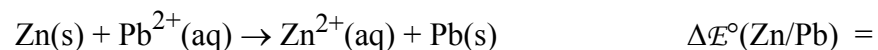
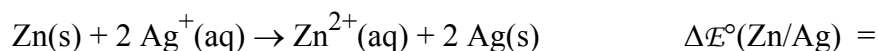
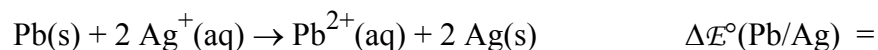
Place one end of the salt bridge into the test tube labeled Cu and the other end into the test tube labeled Ag.

Now read and record the potential on the multimeter.

Leaving the copper wire in place remove the silver wire from the solution and release it from the alligator clip.

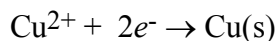
In sequence pick up the lead then zinc wires with the red alligator clip and measure and record the potential differences with respect to the copper electrode when these wires are dipped into the salt solutions of their metals and the test tubes are linked with the salt bridge

From the potential differences obtained with the Cu^{2+}/Cu half-cell and the rest of the half-cells, predict and then measure the potential differences for the following reactions:

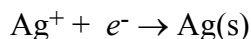


Calculations and Results

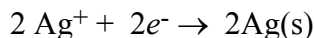
1. (a) Calculate the standard reduction potentials for each half-cell vs the SHE from the data you collected using the Cu^{2+}/Cu half-cell, given that the \mathcal{E}° is 0.34 V for



Note that \mathcal{E}° for a half-reaction is not dependent on the coefficients, provided, of course, that the reaction is balanced, i.e., \mathcal{E}° for



is the same as \mathcal{E}° for



- (b) Compare your values with those in Appendix E of Oxtoby. Determine your experimental accuracy for each (deviation of your average value from the true value).

Summarize these results in a table.

2. (a) Tabulate the results of the whole cell potential differences that were measured along with their predicted values using the Cu^{2+}/Cu as a reference and the per cent error.

$$\% \text{error} = 100\% \times \frac{|\text{predicted result} - \text{experimental result}|}{\text{predicted result}}$$

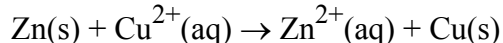
Part II. Concentration Effects and the Nernst Equation

Oxtoby, (section 12.3) derives the Nernst equation :

$$E = E^\circ - \left(\frac{RT}{nF} \right) \ln Q$$

where $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, T is the absolute temperature, n is the number of electrons in the overall reaction, $F = 96,487 \text{ J V}^{-1} (\text{mol e}^-)^{-1}$, and Q is the reaction quotient, the ratio of the molarities (M) of the products to the reactants. Actually, to be rigorous, Q is a ratio of activities, and one should use activity coefficients and molarities instead of molarities - but with dilute solutions the difference is not significant.

For the reaction



Q is given by

$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

Substitution of Q into the Nernst equation gives:

$$E = E^\circ - \left(\frac{RT}{nF} \right) \ln \left(\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right)$$

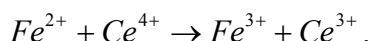
Replacing the \ln term with $2.303 \log$ and substituting values for R , T and F gives:

$$E = E^\circ - \frac{0.059}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

at 25°C .

What is not shown in the above equation is the activity of the solid metals Cu and Zn because by convention they are equal to 1. Oxidation and reduction potentials don't

arise solely between a solid metal and its ions. Redox potentials also arise between two different oxidized states of the same ions such as ferrous and ferric ions or cerous and ceric ions. These ion pairs react as follows:



The first half-reaction is: $Fe^{2+} \rightarrow Fe^{3+} + e^{-}$;

and the second half-reaction is: $Ce^{4+} + e^{-} \rightarrow Ce^{3+}$.

The second part of this lab will apply the Nernst equation to these half-reactions to look at the effects the concentration of these ion pairs has. The Nernst equation applies to half-cells in exactly the same way as it does to complete electrochemical cells. For any half-cell potential at 25° C,

$$E_{hc} = E_{hc}^{\circ} - \frac{0.059V}{n_{hc}} \log_{10} Q_{hc}$$

where n_{hc} is the number of electrons appearing in the half-reaction and Q_{hc} is the reaction quotient for the half-cell reaction written as a reduction (Oxtoby 5th Ed. Eqn 12.7).

This reaction has two important features. First, like most inorganic redox reactions it is fast. Second, it has a huge equilibrium constant of 1.7×10^{14} . Reactions with large equilibrium constants are said to be irreversible because once the products are formed, very, very little of the reactants are ever seen again. The large equilibrium constant makes it possible change the ratio of the oxidized and reduced states of one species without the other species affecting the electrochemical potential as measured against a reference electrode. In this experiment a homemade silver-silver chloride reference electrode will be used.

To a solution of a known amount of ferrous, Fe^{2+} , ions ceric, Ce^{4+} , ions will be added. While the Fe^{2+} is in excess, so much of the Ce^{4+} will be converted to cerous Ce^{3+} ions that it is inconvenient to determine the amount of Ce^{4+} present in the solution. However ferric, Fe^{3+} , ions will be created equal to the number of Ce^{3+} , and prior to the equivalence point enough ferrous, Fe^{2+} , ions are present that the Fe^{2+}/Fe^{3+} ratio can be easily calculated. Therefore prior to reaching the equivalence point the easiest form of the Nernst equation to use is the following:

$$E_{hc} = E_{Fe^{3+} \rightarrow Fe^{2+}}^{\circ} - \frac{0.059V}{1} \log_{10} \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

Lets look at how to determine the concentrations of $[Fe^{2+}]$ and $[Fe^{3+}]$. The oxidation reduction reaction shows that for every Fe^{3+} ion created a Ce^{3+} is created.

$$[Fe^{3+}] = [Ce^{3+}].$$

Since the equilibrium constant is large for this reaction it is the case that before the equivalence point all of the Ce^{4+} is converted to Ce^{3+} so that:

$$[Ce^{4+}] = [Ce^{3+}].$$

If x is allowed to equal the volume of Ce^{4+} titrated and C the original concentration of the Ce^{4+} titrant, then $x C$ is the number of moles of Ce^{4+} delivered to the solution.

Before the equivalence point all of the Ce^{4+} is converted to Ce^{3+} creating an equal amount of Fe^{3+} . That is :

$$Fe^{3+} = Ce^{3+} = x C$$

All of the ions are present in the same solution so in calculating the ratio of their concentrations the volume of the solution can be ignored. Let F = the number of moles of ferrous ions present at the start of the titration. Since the total amount of iron present can not change then:

$$F = Fe^{2+} + Fe^{3+} \text{ or}$$

$$Fe^{2+} = F - Fe^{3+}$$

Substitution for Fe^{3+} gives:

$$Fe^{2+} = F - x C.$$

The Nernst equation in terms of F , x , and C with $n = 1$ becomes

$$E_{hc} = E_{Fe^{3+} \rightarrow Fe^{2+}}^{\circ} - 0.059 \log \frac{F - xC}{xC}.$$

After the equivalence point all of the Fe^{2+} has been converted to Fe^{3+} and no more Ce^{3+} can be created. With almost no Fe^{2+} present it now becomes inconvenient to determine its value. However the Ce^{3+} present will equal the original amount of Fe^{2+} present and the concentration of Ce^{4+} will increase directly as more Ce^{4+} ions are added to the solution. So after the equivalence point the Ce^{4+}/Ce^{3+} ratio is easy to determine and following form of the Nernst equation is easy to apply.

$$E_{hc} = E_{Ce^{4+} \rightarrow Ce^{3+}}^{\circ} - \frac{0.059V}{1} \log_{10} \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

During this phase of the titration :

$$F = Fe^{3+} = Ce^{3+}.$$

The total amount of cerium added continues to equal $x C$, which must equal the sum of Ce^{3+} and Ce^{4+} . In other words:

$$x C = F + Ce^{4+}$$

or

$$Ce^{4+} = x C - F.$$

The Nernst equation after the equivalence point is:

$$E_{hc} = E_{Ce^{4+} \rightarrow Ce^{3+}}^{\circ} - 0.059 \log \frac{F}{xC - F}$$

For the titration curve used in this discussion and for the experiment to be performed during the laboratory

$$F = 0.05 \text{ millimol.},$$

$$C = 10.0 \text{ mM, and}$$

$$x = 0 \text{ to } 5 \text{ ml.}$$

It is important to remember during this experiment that E_{hc} cannot be measured. What is measured is the ΔE between $E_{hc} - E_{Ag/AgCl}$. Standard potential values for the theoretical plot were obtained by subtracting the standard potential for the silver - silver chloride half reaction from the standard potentials for the ferric - ferrous and ceric - cerous half reactions. These values are given below in Table II.

Table II

Half - Reaction	Standard Potential (Volts)
$Ce^{4+} + e^{-} = Ce^{3+}$	1.44 (in 1 M H_2SO_4)
$Fe^{3+} + e^{-} = Fe^{2+}$	0.771
$AgCl + e^{-} = Ag + Cl^{-}$	0.228 (1 M KCl)

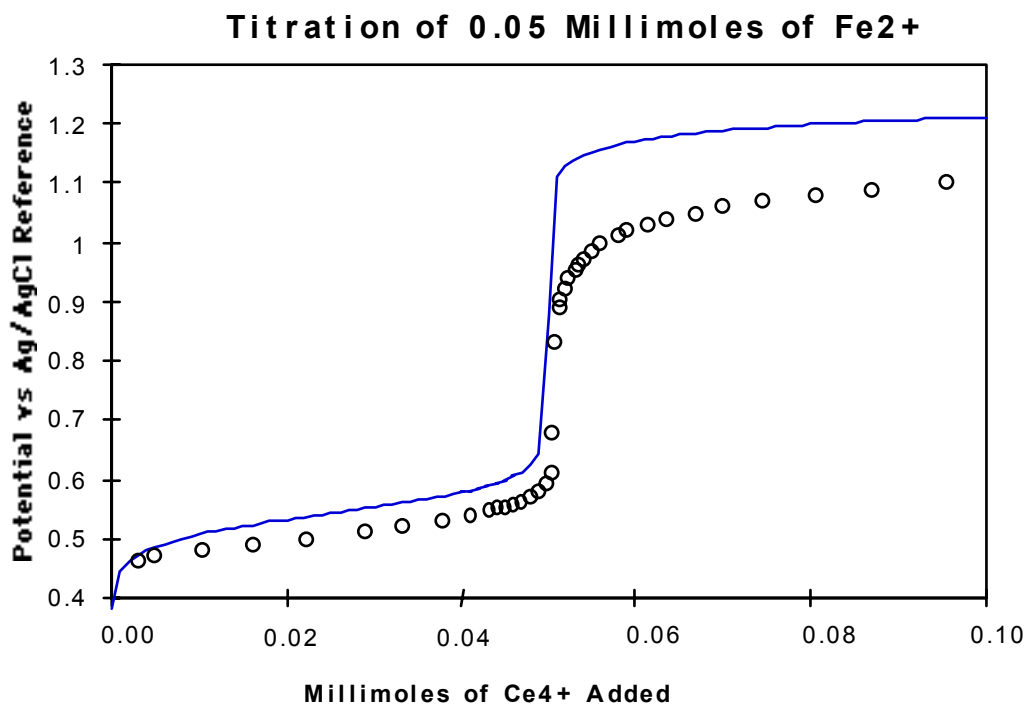
From **Analytical Chemistry**, Christian. Gary .D. Wiley 5th Ed.

Potentials vs Ag/AgCl Reference (Volts)

$$E^{\circ}_{Ce^{4+} \rightarrow Ce^{3+}} = 1.44 - 0.228 = 1.21$$

$$E^{\circ}_{Fe^{3+} \rightarrow Fe^{2+}} = 0.771 - 0.228 = 0.54$$

Measuring the electrical potential during the addition of ceric ions to a solution of ferrous ions is a potentiometric titration. A theoretical titration curve (solid line) using the two Nernst equations developed above before and after the equivalence point is shown below with data from an actual titration (circles).



The first data point with zero titrant added can not be assigned a theoretical value because no ferric ions are present before the titration begins. After the first data point there are two obvious differences between the theoretical curve and the experimental data. First the experimental electrical potential is less than the theoretical potential throughout the titration. This is due to differences between the values obtained from a assembled reference electrode and the literature values. The second difference is that the experimental values deviate from the theoretical values more after the equivalence point than they do before it. The theoretical values are based on assumptions that only cerium and iron react in the solution and that the reference electrode has an instantaneous and constant response. However, cerium ions can complex with other ions such as sulfate in the solution and errors in potential readings can occur due to delays that might arise from a lag in the reference electrode's response. Sulfuric acid is required to dissolve cerium and electrode readings change over time so the theoretical assumptions can not be relied on.

The form of the Nernst equation can still give a good description of the concentration effects on the electrode potential. Look again at the two Nernst equations used to calculate the electrical potential of the solution

$$E_{hc} = E_{Fe^{3+} \rightarrow Fe^{2+}}^o - \frac{0.059V}{1} \log_{10} \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

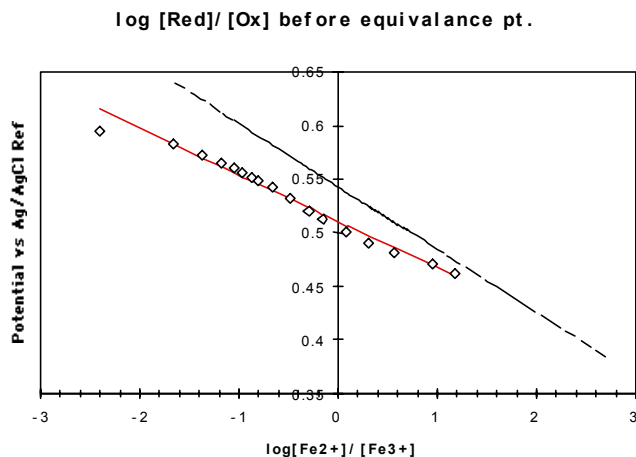
$$E_{hc} = E_{Ce^{4+} \rightarrow Ce^{3+}}^o - \frac{0.059V}{1} \log_{10} \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

If we let $\log_{10} \frac{[Fe^{2+}]}{[Fe^{3+}]} = x_1$, $\log_{10} \frac{[Ce^{3+}]}{[Ce^{4+}]} = x_2$, $y_1 = E_{hc}$ before the equivalence point and $y_2 = E_{hc}$ after the equivalence point, we can write the following two linear equations:

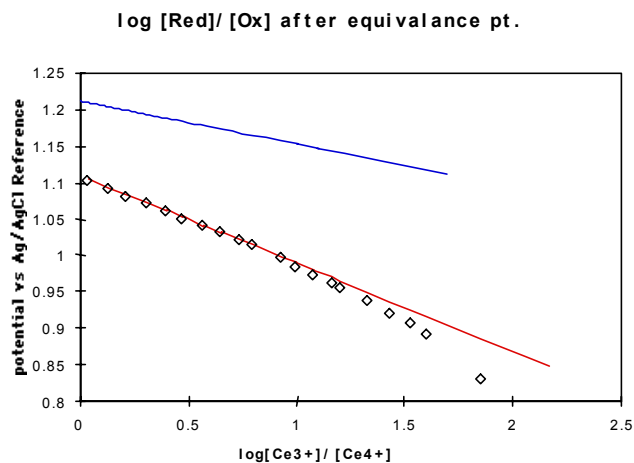
$$y_1 = b_1 + m_1 x_1$$

$$y_2 = b_2 + m_2 x_2.$$

Where b_1 and b_2 are substituted for $E_{Fe^{3+} \rightarrow Fe^{2+}}^o$ and $E_{Ce^{4+} \rightarrow Ce^{3+}}^o$, and m_1 and m_2 are substituted for $-\frac{0.059V}{1}$. By plotting E_{hc} vs $\log_{10} \frac{[Fe^{2+}]}{[Fe^{3+}]}$ before the equivalence point and E_{hc} vs $\log_{10} \frac{[Ce^{3+}]}{[Ce^{4+}]}$ after the equivalence point and using linear regression to determine the values for b_1 , m_1 , b_2 , and m_2 the experimental data can be fitted to a titration curve that takes on the form of the Nernst equation with adjusted parameters. Below are linear plots before and after the equivalence point using the data from the previous plot.



The upper line represents what the log plot would look like using the exact parameters of the Nernst equation. The lower plot shows where the actual data points for the titration would lie with a line fitted through them using the least squares method of linear regression. **Ferric ions increase** as the line moves from **right to left**. Where the lines cross zero along the horizontal axis the concentrations of the ferrous and ferric ions are equal. As the equivalence point is reached the electrode becomes unstable and the data deviates from linearity. m_1 equals -0.044V versus -0.059V for the Nernst equation; and b_1 equals 0.51V versus 0.54V for the Nernst equation.



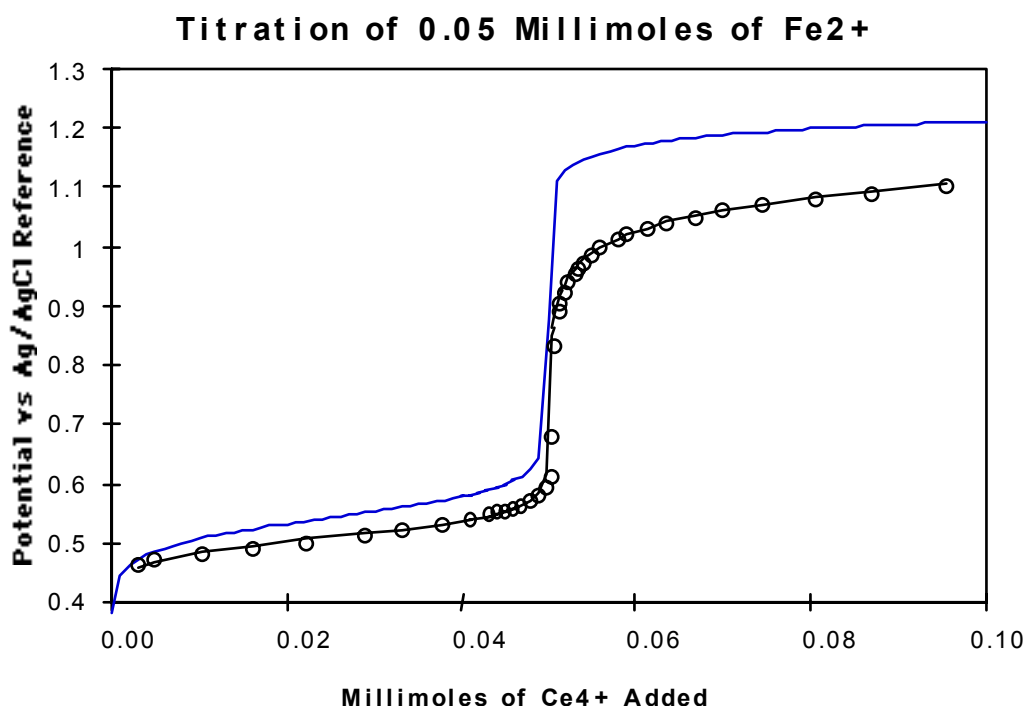
Again the upper plot represents the exact Nernst equation while the lower plot represents actual data along a line fitted by linear regression. **Ceric ions increase** as the line moves from **right to left**. As the data moves well past the equivalence point it becomes more linear. This titration was only carried out until twice the number of equivalents of ceric ions were added to those of the ferrous ions originally present. At that point half of the cerium was in the ceric form and half in the cerus form and the titration stopped at zero along the horizontal axis. m_2 was -0.121V vs -0.059V (quite a difference), and b_2 was 1.11V vs 1.21V as predicted by the Nernst equation.

By calculating the electrical potentials (y1 and y2) from the equations:

$$y1(\text{before equivalence pt.}) = b1 + m1 \log_{10} \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$y2(\text{after equivalence pt.}) = b2 + m2 \log_{10} \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

the data can be fitted quite well to the Nernst equation with adjusted parameters. In the next graph the experimental data points are represented as circles that follow the solid line representing the adjusted Nernst plot. The actual Nernst plot is also shown.



Procedure

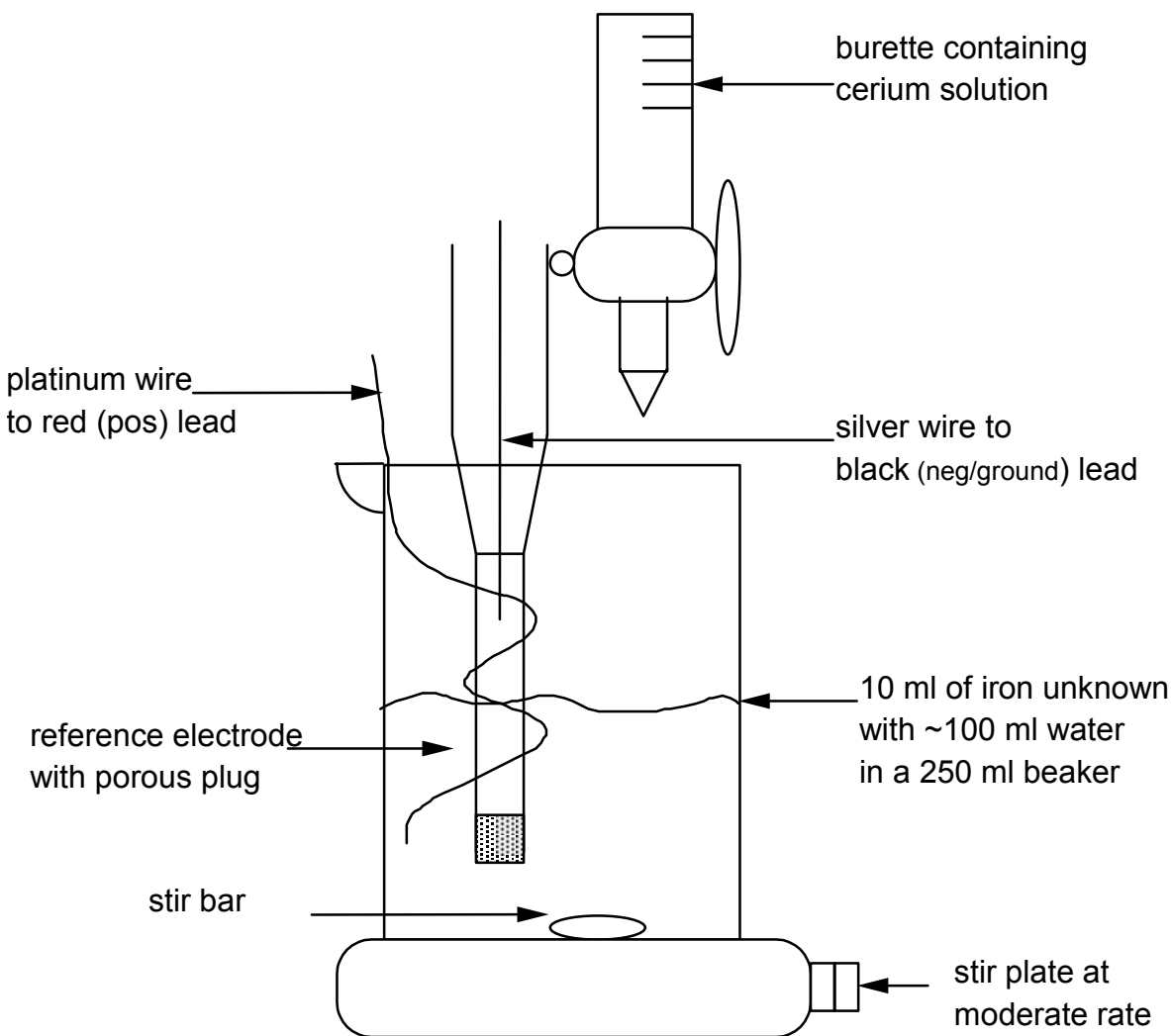
During this second part of the lab you are to titrate 0.05 millimoles of Fe²⁺ with a solution of 10.0 mM Ce⁴⁺ ions while measuring the electrical potential with a multimeter and Ag/AgCl reference electrode. Then use Excel Chart Wizard to find the appropriate parameters and present your data in graphical form.

Obtain approximately 30 ml 10.0 mM Ce⁴⁺ in a 100 ml beaker. Rinse out the 10 ml burette with several small portions of the 10.0 mM Ce⁴⁺ solution emptying the waste in to a small beaker you decide to set aside strictly for cerium waste. Be careful handling this solution as it contains sulfuric acid. Next close the stopcock and fill the burette past the 0 line at the top. Place the burette on a burette holder and ring stand. Let the solution

run out of the burette slowly into the beaker used to fill it and stop it when it reaches the 0 line.

Obtain 20 - 30 ml of 5.00 mM Fe^{2+} solution in a 50 ml beaker. Accurately pipette 10 ml of this solution into a 250 ml beaker and add 100 ml of distilled water. Add a stir bar to the beaker and place it on a stir plate under the burette. Start the solution stirring at a moderate speed.

Obtain a Pasteur pipet with a porous agar plug in the tip filled with saturated potassium chloride (KCl) solution. Add a drop of silver nitrate using a plastic pipette. Insert a silver wire into the syringe and wrap a piece of platinum wire around it as shown in the diagram below. Place the syringe in a clamp and insert it into the solution to be titrated. Attach the alligator leads from the multimeter to the platinum wire (red lead) and silver wire (black lead) and turn on the multimeter to read DC Volts.



Add cerium solution to the beaker below in 1 ml portions and recording the volume added. Wait precisely 1 minute after each addition and then read and record the

potential. The following volumes are suggested for obtaining data that will track the electrode response well when it is most susceptible to change. [1 2 3 3.5 4 4.2 4.4 4.6 4.8 5 5.2 5.4 5.6 5.8 6 6.5 7 8 9 10].

When finished place the contents of the electrode in the silver waste container. Rinse out the burette into the beaker you set aside for waste. Empty this waste beaker and the titrated solution into the general waste container reserved for cerium. Excess 5.00 mM Fe^{2+} that wasn't used can go down the drain.

Return the electrode to the beaker it came from and return the other items to the stockroom.

Lab Report for Part II

1. Use Excel Chart Wizard to apply linear regression to a plot of the measured potential E vs $\log \frac{F-xC}{xC}$ before the equivalence point and a separate plot of E vs $\log \frac{F}{xC-F}$ after the equivalence point. Determine the slope (m_1 and m_2) values and intercept (b_1 and b_2) values for the best fit lines from these two plots.

2. On a graph plot the individual data points of E vs xC .

3. **On the same graph**, plot $b_1 + m_1 \log \frac{F-xC}{xC}$ vs xC for all volumes x titrated before the endpoint, and plot $b_2 + m_2 \log \frac{F}{xC-F}$ vs xC for all volumes x titrated after the endpoint. **Plot this data as solid lines.**

4. Finally **on the same graph** plot the actual Nernst equations:

$E_{Fe^{3+} \rightarrow Fe^{2+}}^o - 0.059 \log \frac{F-xC}{xC}$ vs xC for all volumes titrated before the equivalence point and

$E_{Ce^{4+} \rightarrow Ce^{3+}}^o - 0.059 \log \frac{F}{xC-F}$ vs xC for all volumes titrated after the equivalence point See

Table II above for the standard potentials. **Also plot this data as solid lines.**

Indicate clearly what information represents actual data, the adjusted Nernst equation and the actual Nernst equation.

5. For each mole of Fe^{3+} created a mole of Ce^{3+} is created. Therefore at all times:

$$(1) \quad [Fe^{3+}] = [Ce^{3+}]$$

At the equivalence point the total number of moles of Fe equals the total number of moles of Ce. Therefore at the equivalence point:

$$(2) \quad [Fe^{2+}] + [Fe^{3+}] = [Ce^{3+}] + [Ce^{4+}].$$

Subtracting equation (1) from equation (2) we see that at the equivalence point:

$$(3) \quad [Fe^{2+}] = [Ce^{4+}].$$

At all times the Nernst half cell equations apply:

$$(4) \quad E_{hc} = E_{Fe^{3+} \rightarrow Fe^{2+}}^o - \frac{0.059V}{1} \log_{10} \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

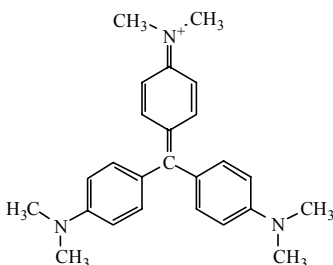
$$(5) \quad E_{hc} = E_{Ce^{4+} \rightarrow Ce^{3+}}^{\circ} - \frac{0.059V}{1} \log_{10} \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

Add equations (4) and (5) above. Then, using the equalities from equations (1) and (3), substitute all [Ce] terms for [Fe] terms in the expression. Solve the resulting equation for E_{hc} at the equivalence point. Using the values from Table II predict what the potential should be at the equivalence point if no adjustments to the Nernst equation were necessary.

EXPERIMENT 4 RATE OF A CHEMICAL REACTION

Introduction

When chemical reactions occur they proceed at rates which span an extremely wide range. For example, H^+ (aq) and OH^- (aq) ions react at almost every encounter. On the other hand, studies of the depletion of the ozone layer by chlorinated fluorocarbons (CFCs) suggest that the rate of diffusion of CFCs to the stratosphere (where the ozone layer is located) is so slow that even if the production of CFCs were to stop immediately, the maximum damage to the ozone concentration would occur 10 to 20 years later. It is obvious that knowing how fast a reaction occurs, and what factors influence that rate, has extremely important industrial, biological and environmental significance.



Crystal Violet (D^+)

In this experiment you will measure the rate of the reaction of a dye, crystal violet (also called Gentian Violet), with OH^- . The dye undergoes a dramatic change in color that is easy to follow with a spectrophotometer. When the dye, in the violet D^+ form, is mixed with OH^- , it begins to form the colorless DOH . The time-dependence of the $[\text{D}^+]$ form is measured with a spectrophotometer.

You will mix together D^+ and OH^- , which will initiate the reaction. Then you will measure the absorbance of the D^+ ion as a function of time. From a calibration curve you will be able to calculate how much D^+ is present from the transmittance (or absorbance) data. Then you will plot D^+ (and various functional forms of D^+ , such as $\ln[\text{D}^+]$) against time. From this you will determine the rate constant for the reaction and the dependence of the rate on $[\text{D}^+]$ (the dependence is referred to as the "order"). The experiment will be repeated with different amounts of OH^- to determine the dependence of the rate on this species too.

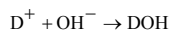
There are also some technical skills to be acquired: You will learn the procedure of making serial dilutions and developing a calibration curve.

Overview

Part 1

Analysis of Data

Schematically the reaction looks like this:



The back reaction is negligible. D^+ stands for the highly colored cation and DOH is the colorless product of the reaction. The rate law for this reaction can be written as:

$$\text{rate} = -\frac{d[D^+]}{dt} = k[D^+]^n[OH^-]^m$$

Our objective is to measure k , n and m . n and m are the orders of the reaction for D^+ and OH^- respectively and k is the rate constant. From a mathematical and physical perspective these three numbers will completely characterize the kinetics of the reaction.

The units of k are whatever is appropriate for the rate law. From looking at the rate law here, one can conclude that k has units of (liters/mole) ^{$n+m-1$} /second, assuming time is in seconds.

We are now going to play a trick on the mathematics which places requirements (or constraints) on the nature of the samples used in the experiments. We require that the $[OH^-]$ be much larger than that of $[D^+]$; that way when all of D^+ is consumed, the $[OH^-]$ hardly changes.

Mathematically then, the above expression can be modified by letting

$$k' = k[OH^-]^m$$

where k' is a constant for any particular large initial concentration of OH^- . Then the rate law has the form:

$$-\frac{d[D^+]}{dt} = k'[D^+]^n$$

This form of the rate law can be rearranged as an integral equation

$$\int \frac{1}{[D^+]^n} d[D^+] = \int -k' dt$$

and solved for different integer values of n to give:

$$n = 0 \quad [D^+] = -k't + \text{constant}$$

$$n = 1 \quad \ln[D^+] = -k't + \text{constant}$$

$$n = 2 \quad \frac{-1}{[D^+]} = -k't + \text{constant}$$

These equations are in linear form:

$$y = (\text{slope})(x) + \text{intercept}$$

where

$$y = [D^+] \ln[D^+] \text{ or } \frac{-1}{[D^+]}$$

$$\begin{array}{l} x = \text{time} \\ -k' = \text{slope} \end{array}$$

For the case of n which works, *i.e.* produces a straight line, n is the order of the reaction with respect to $[D^+]$ and $-k'$ is the slope of the line. Assuming we do a number of reactions with different concentrations of $[OH^-]$, then we have a table of k' vs $[OH^-]$. Since

$$k' = [OH^-]^m (k)$$

we can rewrite this in linear form as

$$\ln(k') = (m)\ln[OH^-] + \ln(k)$$

Then a plot of $\ln(k')$ vs $\ln[OH^-]$ will give a straight line whose slope is m and whose intercept is $\ln(k)$. The slope of the line, m , rounded to an integer (0,1,2, etc.) is the order of the reaction with respect to OH^- . Once m has been found, it is better to directly find k from the equation that defines k' , using the integer m value.

Part 2 Monitoring $[D^+]$

Now that we have discussed the analysis of the data, how do we go about determining how to measure the rate of the reaction? The details of making samples and properly running the spectrometer will be treated in the procedure section. This is just to give you an overview of what data is needed.

Since one needs to know the $[D^+]$ as a function of time, but the spectrometer reads out %T, transmittances as percent, (or A , absorbances) we need to know what %T corresponds to what $[D^+]$. Therefore it will prove necessary to make up a set of solutions of known $[D^+]$ and measure the %T. From this data, a graph of $A = -\log(\%T/100)$ can be made so that for any value of A the actual $[D^+]$ can be estimated. This is called a calibration (or standardization) curve.

Now you can perform the kinetics experiment. Take a beaker containing $[D^+]$ and mix it with a beaker containing $[OH^-]$. Choose a reference time to be the beginning of the reaction and record %T as a function of time. As a function of time the solution will become colorless so the %T will **increase** with time. The reaction must be repeated for different concentrations of $[OH^-]$ to fully determine the dependence on $[OH^-]$.

$[D^+]$ is not directly measured but is calculated from the calibration curve determined in step 1. The details of this curve are discussed later.

$[D^+]$ as a function of time is now known. We are now ready to proceed with the analysis as outlined above. From this information we know that the order of the reaction (n) with respect to the dye concentration, and (m) with respect to the hydroxide concentration and the rate constant (k) can be determined.

Equipment you will find in your kit

- Four 100 mL Beakers
- Three 150 mL Beakers
- Six 250 mL Beakers
- One 32 oz Bottles
- 50 mL Graduated Cylinder
- 110°C Thermometer
- Glass Stirring rod
- Grease Pencil
- Cuvet (test tube)
- Stopwatch

Materials found in the lab

- Spectrophotometer
- Solutions of dye and NaOH
- Kimwipes

Waste: Solutions must be between 5 and 12 pH units before being poured down the sink with water. You can lower the pH by adding phosphoric acid or raise it by adding small amounts of solid sodium bicarbonate.

Procedure

A. Stock Solution

A 1.50×10^{-4} M dye solution you will dilute 1:10 to provide you with a working stock solution whose concentration is 1.50×10^{-5} M.

B. Make Dye Solutions for Calibration of Spectrometer

Make 6 solutions of the dye according to the following instructions for a serial dilution. *Note:* a mistake anywhere along the way causes errors in all subsequent dilutions. Follow instructor's suggestions on rinsing containers. Each succeeding solution will have 1/2 the dye concentration of the previous solution. Be sure to *label* each concentration properly to avoid confusion. Put a beaker on each of 6 labelled paper towels in a row. These six solutions will be used to calibrate the spectrophotometer.

Solution 1: Mix 40 mL of your working (or stock) solution with 40 mL of deionized water.

Solution 2: Mix 40 mL of solution (1) with 40 mL deionized water.

Solution 3: Mix 40 mL of solution (2) with 40 mL deionized water.

Solutions 4, 5, and 6: Continue diluting in the same fashion. At the end of this process you should have six solutions, *not* including the stock solution.

C. The Calibration Curve

The appendix contains instructions for the use of the spectrophotometers. All measurements are made at 590 nanometers. If you have difficulty with the spectrometer, ask the instructor for assistance. Be sure to use the same clean cuvet (test tube) for all measurements. As a blank reading use the cuvet filled with distilled water. Take multiple readings and measure the *weakest* dye sample *first*, working your way up to the most concentrated to give 6 points. When through, clean up immediately or the dye will stain the beakers.

Before proceeding, make a rough plot of the absorbance A against the concentration in moles/liter. The line should go through the origin (A and dye concentration both zero). It should be fairly straight (Beer's Law) except at the highest concentration. Ignore data that falls outside the linear region. If it looks very curved, seek help from your TA.

D. Make solutions of NaOH

Begin with at least 80 mL of the NaOH stock solution. The concentration will be about 0.50 M. (Record the exact concentration in your notebook — don't forget!). Label that flask ~0.5 M NaOH. Only one run uses full strength NaOH. To make ~0.25 M NaOH, mix 40 mL of ~0.5 M NaOH with 40 mL of deionized water, and to make ~0.125 M NaOH, mix 40 mL of ~0.25 M NaOH with 40 mL of deionized water. Calculate the exact concentrations of these solutions.

The dye and hydroxide solutions should be within 1°C of the same temperature (and of room temperature) before beginning the reaction. This should not be a problem since the temperatures will equalize while you are doing the calibration. However, check the temperature before starting to collect your kinetic data.

E. Measuring the Rate of Reaction

The maximum absorbance for crystal violet is at 590 nm, so set the spectrophotometer at that wavelength. Over what range of absorbances do we record? The calibration curve provides the answer to this question. One generally does not like to extrapolate such curves so it is suggested that you record absorbances that are not higher than the most concentrated solution nor lower than the most dilute solution used in the calibration.

How often do we record data? The data should be recorded at small enough time or absorbance intervals to insure that a plot of absorbance vs. time will have a sufficient amount of data. Usually one would like to have 15 or so points.

In summary: Record absorbance data over the range of 0.1 to 1.0. Record data in short enough time steps to get an absorbance resolution of about 5%. Fill in your table first with the absorbances for which you want the times. If you miss an absorbance reading just skip it, no harm done.

F. Initial Mixing of Dye and OH⁻

Put 30 mL of the working (dye Stock) of 1.5×10^{-5} M solution in a clean beaker, and 30 mL of NaOH Solution #3 ([OH⁻] ~0.125M) in another beaker. Make sure the spectrophotometer is properly adjusted to the 0 and 100% T readings (See Appendix A). Mix the two solutions together in the 100 mL "sample beaker". Stir a second or two with the glass rod. This is "time zero", so start your stopwatch. As quickly and carefully as possible transfer an aliquot to the cuvet (test tube), insert it into the spectrophotometer, and begin taking absorbance readings. The dye concentration after mixing is initially 7.5×10^{-6} M; the OH⁻ concentration is 1/2 of its initial concentration when made up.

G. Data Table for a Single Run

Run # _____

Data Point #	Time, s	abs*	[D ⁺], M
1		1.000	Calculated later from calibration curve and absorbances
2		0.824	
3		0.699	
4		0.602	
15		0.097	

Additional data: Initial dye conc.: _____ Initial NaOH conc.: _____

Room Temperature: _____

Spectrometer Wavelength: 590 nm

NOTE: The [NaOH] is 1/2 the value shown in the table for NaOH solutions because it was mixed 50:50 with the dye. Be sure to take this into account when writing down the Conc of NaOH.

* These are just representative values; you may decide on a different set.

H. Additional Kinetics Runs

Now do the experiment with ~0.25 M NaOH and with ~0.50 M NaOH. Notice that if the reaction rate depends on [OH⁻], then the reaction will go faster with increasing [OH⁻].

Warning: This is a complex experiment, so go over the data and details of the analysis with your TA before you leave. A short amount of discussion will help enormously before you begin to do the analysis.

I. Calculations

- (1) Obtaining a Calibration Curve: You should have already plotted [D⁺] (on the y axis) vs absorbance (on the x axis), and you know where it is linear. Over that range you have the calibration:

$$[D^+] = m * \text{abs} + b \quad \text{where } b = 0$$

Find the "best" value of the slope using Excel.

- (2) Convert the absorbance values to corresponding concentrations of D⁺ using the calibration equation obtained above.
- (3) Choose one kinetics run and plot [D⁺] vs. time, ln[D⁺] vs. time, and -1/[D⁺] vs. time. Determine which function gives the most linear relationship. This is the reaction order for crystal violet.
- (4) Now that you know *n* and the proper function to use, graph the data and obtain the slope (-*k'*) from each kinetics run. Use Excel to get the best values of *k* for each run.
- (5) Determine the dependence on [OH⁻] (i.e. to get *k* and *m*)

Make a table from your values of *k'* from each run (in the notebook!):

Run #	[OH ⁻]	<i>k'</i>
1		
2		
3		

>From the definition of $k' = k [\text{OH}^-]^m$ it follows that

$$\ln(k') = m \ln[\text{OH}^-] + \ln(k)$$

is also in the form of a straight line. Make a plot of $\ln(k')$ versus $[\text{OH}^-]$ and, using Excel determine m , the slope of the line. Note that m should be an integer number. Give your actual value and the rounded-off value you choose. From the intercepts, determine k for each run and calculate the average k , including units.

- (6) You will have a lot of graphs to show. At a minimum: For one run there should be at least three different graphs (for $n=0, 1$ and 2). For each run (all with the same n value), there should be a "straight line" plot of the data. Finally, there should be a final graph of $\ln(k')$ vs. $\ln[\text{OH}^-]$. Summarize the overall rate expression using your values for k (including units), m , and n .

Questions

- (1) If a reaction is second order in species A and first order in species B, how will the rate change if both concentrations are doubled? Will k change?
- (2) What is serial dilution and what purpose does it serve?
- (3) What is a calibration curve? (Generalize from our specific use.)
- (4) What, if anything, does your rate law imply about the reaction mechanism?

Experiment 5

QUANTUM MECHANICS AND ATOMIC STRUCTURE

Work with a partner for the first four sections of this lab. Do section five on your own.

The Purpose of this lab is to:

1. Understand how gratings are used to measure electromagnetic radiation and determine the grating constant (lines/mm) of a replica grating.
2. Understand the design, calibration, and operation of a grating spectroscope using the known wavelengths of mercury spectral lines.
3. Use the grating spectroscope to test Bohr's model of the hydrogen atom for measuring the Rydberg constant and predicting the Balmer series of emission lines.
4. Record the emission spectra (color and Displacement(D)) of a number of metal ions then use this information to identify the components of an unknown mixture.
5. Apply the particle in a box model to predict the maximum absorbance wavelengths in the visible region of molecules containing delocalized pi electrons.

I

Electromagnetic Radiation

Diffraction and the Grating

Issac Newton deduced that a beam of sunlight passing through a prism was separated into its component colors. We now know that each color component of the beam matches a certain wavelength of light. Prisms are generally used to illustrate this process because of their apparent simplicity, but a far superior way to separate light according to its wavelength is to use a grating. Gratings are surfaces (flat, curved, transparent or solid) that have many closely-spaced lines or grooves embossed on them. Phonograph records and CDs are everyday examples of gratings.

The behavior of light when it strikes a grating can be understood in terms of constructive and destructive interference, in analogy to what happens when water waves pass through a pier (see figure). In fact, the behavior of light when it strikes a grating is the primary evidence we have that light exhibits wavelike properties. Figure 1 below shows what happens when water waves pass through (or are reflected from) a surface containing many regularly spaced openings. As you can see, the incoming wave breaks up into many little wavelets (this is the key idea), whose crests and 'troughs' reinforce each other only in certain directions. From a distance what one sees is a single incoming wave striking the grating and then going off in a small number of diffracted waves at angles given by the diffraction equation

$$n\lambda = d \sin\theta$$

In this formula, d is the spacing between the openings, θ is the angle of diffraction, λ is the distance between the crests (or troughs) of the waves, and n is an integer:

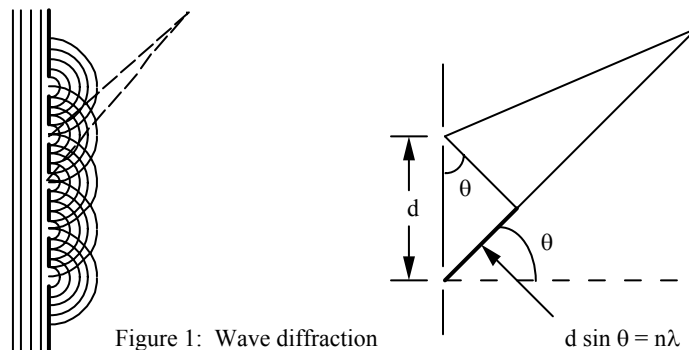


Figure 1: Wave diffraction

The meaning of the diffraction equation is that the extra distance ($d \cdot \sin\theta$) traveled by adjacent waves must be a whole number of wavelengths ($n\lambda$) in order for the crests to reinforce each other. If this distance is equal to one wavelength, the diffracted waves are first order waves, if it is equal to two wavelengths (2λ), they are second order waves, etc. For water waves one can independently measure λ , θ and d and so investigate what happens when these values are changed. Rearranging the diffraction equation gives us $\sin\theta = n\lambda/d$, and since $\sin\theta$ is limited to ± 1 , if we want to have, say, 5 diffracted waves, then λ/d needs to be $\sim 1/5$, i.e. the wavelength needs to be about 1/5 the distance between the openings. If λ/d is > 1 (i.e. if the wavelength is greater than the spacing), no value of n will solve the equation, so no diffraction will occur and the wave will not pass through the grating. If λ/d is $\sim 1/100$ (i.e. the wavelength is much smaller than the spacing), then diffraction will occur, but the angle between the different orders will be very small. This means the outgoing waves will merge into one another and the result will look as though the wave simply went through the grating without being diffracted at all. In order to see diffraction effects the wavelength must thus be $\sim 1/2$ of the grating spacing.

This behavior of waves is reproduced by light: light is normally blocked by ‘solid’ objects because the spacing of the atoms is much smaller than the wavelength, i.e. $\lambda/d \gg 1$; if the spacing is increased by vaporizing the atoms, then light passes through the vapor without apparent diffraction. But if λ/d is ~ 1 , then we see evidence of the wave nature of light. For solids this means using short wavelength light, i.e. X-rays. If we want to use visible light, we have to have a grating with the correct spacing - indeed finding the right value of ‘ d ’ both gives us a value for λ and confirms that light behaves like waves.

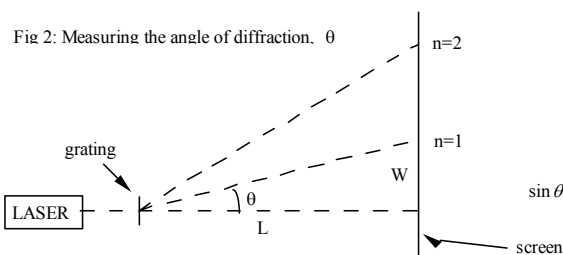
Until about 50 years ago it was very difficult to construct gratings with spacings as small as the wavelength of visible light. Great efforts went into building ‘ruling engines’ that could, over a period of about a year, slowly and methodically drag a diamond ‘chisel’ over a piece of highly polished quartz to make a series of grooves on the surface with the proper spacing. Once a master grating was made, however, the surface could be coated with a thin film of plastic, which, when peeled off, became a replica grating - much like

the process of making phonograph records from a master recording. Obviously the cost of making replica gratings is very small compared to the cost of making the original master, and although the quality is not quite as good, such gratings have brought spectroscopy to the masses. In today's exercise, for example, you will be given a replica grating with about 500 lines per millimeter. To visualize this, look at a cm ruler and try to imagine 500 divisions between each mm mark! The spacing between the lines is thus about 0.002 mm, which is the same as 2×10^{-6} m or 2000 nm.

Procedure for Part I

Measuring the Grating Constant (lines/mm)

The drawing below shows how one can measure the sin of θ , the angle of diffraction, to rather high accuracy. For this exercise



λ is 632.8 nm, the well-established wavelength of red light from a He-Ne laser. In the lab you will find a laser and with a grating positioned in front of the light source diffracting the beam onto one of the laboratory walls. Use the string and meter stick

available to determine the distance L from the grating to the wall. Also use the string and meter stick to measure the distance W along the wall from the zero order (undiffracted) beam to the first and second (and if possible third order) beam.

Treatment of data from Part I

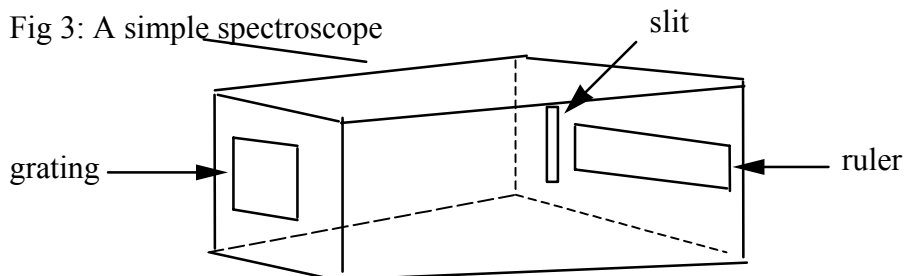
1. $\sin \theta = W / \sqrt{W^2 + L^2}$
2. Using $d = n\lambda / \sin \theta$, calculate d. ($\lambda = 632.8$ nm, $n=1,2,3?$)
3. Express d in mm
4. Calculate number of lines per mm ($= d^{-1}$)

II

The Spectroscope

As you observed in Part I, the shape of the diffracted beam is the same as the shape of the incident light, e.g. a circular spot for a laser. If the light does not come from a well-defined source it is hard to measure the angle of diffraction. To solve this problem it is customary to pass the light through a small rectangular slit before letting it fall on the grating. The diffracted beam is thus an image of the slit so the different colors appear as lines falling on the ruler.

The essential elements of a spectroscope are (a) a slit, to create a sharp image that is easy to measure, (b) a grating or prism, and (c) a recording or measuring device or ruler for identifying the lines. A sketch of these components is shown below:



You will be using a prefabricated plastic spectroscope for this lab. Spectroscopic wavelength measurements are based on the diffraction equation: $\sin\theta = \lambda/d$. Rather than actually measuring θ , however, it is easier to just measure the position where the image of the slit appears on the see-through ruler, and then use the known wavelengths of mercury lines to calibrate the scale.

Look at the wide end of the spectroscope and notice the slit and ruler. Turn the spectroscope around and so the slit is on your left. Cover the slit with your finger and look toward the light through the small end of the spectroscope. You are actually looking directly through the diffraction grating. You may see a rainbow of colors appear above the slit. This is due to light reflected from the grating and will not be used for any measurements. The ruler should appear as in Figure 4.

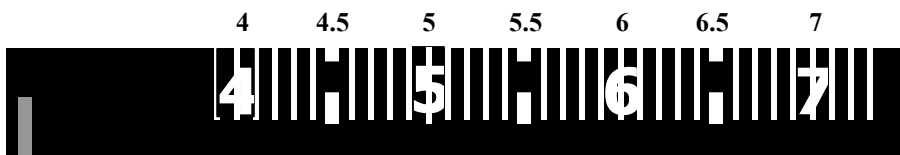


Figure 4: Spectroscopic ruler as seen looking toward the light with the slit (gray line at left of ruler) covered. Markings on the ruler indicate their distance in centimeters from the slit. For clarity their values are printed above in the ruler.

While continuing to look toward the light uncover the slit. Notice a rainbow of colors appearing below the ruler. Violet will appear about 4.5, blue at 5, green at

5.5, yellow-orange at 6, and red at 6.5. Figure 5 is an approximation of what you should see with the slit uncovered. If you can not see this pattern while looking at white light such as light coming through the window, ask the TA for help.

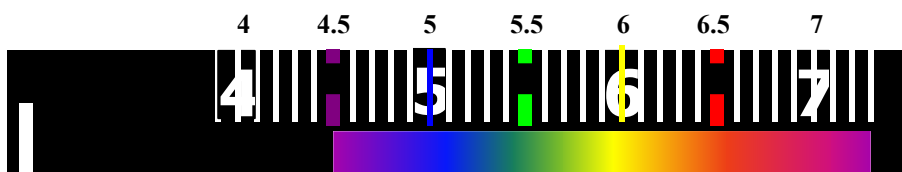


Figure 5: Spectroscope ruler with light passing through the slit.

Procedure for Part II

Calibrating the spectroscope

To calibrate the spectroscope, look at light from a mercury lamp. You should see at least five spectral lines with these wavelengths (in nm)

404.7 (violet) 435.8 (violet-blue) 546.1 (green)
579.0 (yellow-orange) 691 (red)

There is also an 'aqua' line which is due to a different element (argon?). The violet line is difficult to see unless you are near the lamp, which you should be in order to have the image on the ruler be that of the slit rather than the lamp. Note the displacement of each line on the scale. Remain the same distance from the lamp in all cases. Copy and complete the following table in your lab notebook.

Table 1. Calibration of Spectroscope Data

<u>Color</u>	<u>Wavelength (nm)</u>	<u>Expected Displacements*</u>	<u>Displacements Student A</u>	<u>Displacements Student B</u>
violet	404.7	4.05		
violet-blue	435.8	4.36		
green	546.1	5.46		
yellow-orange	579.0	5.79		
red	691.0	6.91		

* The manufacturer has built the spectroscopes such that this is true. Check that your values approximate the expected values. Check with your TA if you are having problems. If values are extremely far off the TA may choose to give you another spectroscope.

Using Excel plot wavelength vs displacement and find the slope and intercept of the best linear fit to the data.

III

Atomic Spectra and Transitions between Energy States

Atomic Spectrum of the Hydrogen Atom:

Interpretation by Bohr's Model

INTRODUCTION

One of the most important experimental observations of the 19th century was that the light given off when substances are vaporized in a flame contains only a few specific colors. Similar emission is observed when an electric current passes through gases. Light from the mercury atoms in a fluorescent lamp, for example, which appears bluish-white to the eye, in fact consists of only four colors: blue, green, yellow and red. The light emitted by an atom (called its spectrum) is characteristic of that atom, no matter what other elements it is combined with. For example, light from hot sodium vapor is the same as that from sodium chloride or sodium carbonate or sodium hydroxide, while light from hot potassium, or any potassium compound, is distinctly different.

This observation is a useful discovery, since it allows unknown substances to be analyzed just by observing the light they emit when heated in a flame. 'Atomic Emission Spectroscopy' (or 'AES', as this technique is known) is one of the most sensitive methods available for detecting trace amounts of toxic substances like lead, and the only one available for identifying the gases found in interstellar space, based on the light they emit.

A more fundamental question that might be asked, however, is why do atoms behave this way? Why do they emit only certain colors of light? This question led many people to search for a 'formula' that would predict the colors, and in 1885 the Swiss physicist Johann Jakob Balmer came up with a formula that exactly matched the light emitted by hydrogen atoms. Balmer's formula is:

$$\frac{1}{\lambda} = R \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

where λ is the 'wavelength' corresponding to a given color, n_i and n_f are integers, and R is a constant (called the Rydberg constant) which has a value of $10967758.1 \text{ m}^{-1}$. Both the simplicity of the formula and the accuracy of the results left little doubt that this equation held the key to unknown physical laws. Just what these laws were, however, took another 40 years to figure out, and in the end led to the conclusion that Nature, at the atomic level, does not obey the laws of physics discovered by Newton and other 'classical' physicists.

The spectrum of hydrogen thus served as the doorway to a much deeper understanding of our world. Using a spectroscope, you will see that hydrogen atoms really **do** behave according to the Balmer formula. The Balmer formula can be related to the quantum mechanical equation for the hydrogen atom

$$\Delta E = -2.18 \times 10^{-18} \text{J} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

where n_f and n_i are integers (principal quantum numbers). This equation is based on the fact that the electron in the hydrogen atom can only have certain discrete energies ($E_n = -2.18 \times 10^{-18} \text{J}/n^2$). Hydrogen atoms can thus only absorb or emit light that matches the difference between two of these energy levels (n_f and n_i), which gives the expression above. From the equation $\Delta E = h\nu = hc/\lambda$, one can then use Bohr's quantum mechanical model to derive the Balmer formula, where $R = 2.18 \times 10^{-18} \text{J} / hc = 10967758.1 \text{ m}^{-1}$. To see this result use equations [15.1] and [15.9] from Oxtoby. Letting $Z = 1$ solve for $1/\lambda$ and note the value of the coefficient to the $\left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$ term which corresponds to R .

$$c = \lambda \nu = 2.9979 \times 10^8 \text{ ms}^{-1} \quad \text{[Oxtoby 15.1]}$$

$$\nu = \frac{Z^2 e^4 m_e}{8 \epsilon_0^2 h^3} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = (3.29 \times 10^{15} \text{ s}^{-1}) Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad \text{[Oxtoby 15.9]}$$

$$n_i > n_f = 1, 2, 3, \dots (\text{emission})$$

Procedure for Part III

Record the displacements observed for the hydrogen emission spectra. Copy and complete all but the last column of the following table in your lab notebook.

Table 2. Hydrogen emission data

<u>Color</u>	<u>Displacement</u> <u>Student A</u>	<u>Displacement</u> <u>Student B</u>	<u>Wavelengths</u> <u>(λ's**)</u>
violet*			
violet - blue			
blue - green			
red			

* The violet line may be hard to see. Its wavelength is 410.1 nm

** Displacement x 100 = wavelength in nm.

Treatment of Data: Measuring the Hydrogen Spectrum

If the data agrees with the theory (Balmer formula), then a plot of $\frac{1}{\lambda}$ vs $\frac{1}{n_i^2}$ should be a straight line with a slope of $-R$. Because the initial state of the hydrogen atom in the hot emission lamp is unknown it is not obvious what value of n_i should be used. The solution is to try three sets of values, and then select the one which offers the most linear plot.

Set #1: $n_f = 1$; $n_i = 2, 3, 4, 5$

Set #2: $n_f = 2$; $n_i = 3, 4, 5, 6$

Set #3: $n_f = 3$; $n_i = 4, 5, 6, 7$

1. Set up and complete the three tables indicated below:

Table 3. Set #1; $n_f = 1$; $n_i = 2, 3, 4, 5$

n_i values	$\frac{1}{n_i^2}$	λ	$\frac{1}{\lambda} \text{ nm}^{-1}$
$n_i = 2$ (red)			
$n_i = 3$ (blue-green)			
$n_i = 4$ (violet-blue)			
$n_i = 5$ (violet)			

Table 4. Set #2; $n_f = 2$; $n_i = 3, 4, 5, 6$

n_i values	$\frac{1}{n_i^2}$	λ	$\frac{1}{\lambda} \text{ nm}^{-1}$
$n_i = 3$ (red)			
$n_i = 4$ (blue-green)			
$n_i = 5$ (violet-blue)			
$n_i = 6$ (violet)			

Table 5. Set #3; $n_f = 3$; $n_i = 4, 5, 6, 7$

n_i values	$\frac{1}{n_i^2}$	λ	$\frac{1}{\lambda} \text{ nm}^{-1}$
$n_i = 4$ (red)			
$n_i = 5$ (blue-green)			
$n_i = 6$ (violet-blue)			
$n_i = 7$ (violet)			

2. Show your values to your TA.
3. Plot the data using Excell. Determine which plot is most linear based on the data having a correlation coefficient closest to one and obtain the slope and intercept for that line. You may use the table below to report the values of m , b , r and n_f ($n_f = \sqrt{(-m/b)}$).

Table 6. Least Squares Data

Set	m	b	r	n_f
Set #1				
Set #2				
Set #3				

4. Based on the fact that the quantum number n_f must be an integer, select the best set. If your data does not give clear-cut results, consult your TA for help.

5.* Express the result of the best fit set.

$$\frac{1}{\lambda} = \frac{R}{n_i^2} + b$$

6.* Convert R (presently in units of nm^{-1}) to \mathbf{R} in units of m^{-1} by multiplying by 10^9 nm/m . Do the same for \mathbf{b} . How does your \mathbf{R} compare with the literature value of $10,967,758.1 \text{ m}^{-1}$?

7.* Rewrite the equation in step #5 in terms of m^{-1} :

$$\frac{1}{\lambda} = \frac{\mathbf{R}}{n_i^2} + \mathbf{b}$$

Calculate the Ionization Energy from the n_f state. Calculate the energy levels for the hydrogen atom ($n = 1, 2, 3, 4$). To be done at home.

The y-axis intercept (the value of the line when $x=0$, i.e. when $n_i=8$, so $1/(8)^2 = 0$) should give you the wavelength corresponding to the transition $n_8 \rightarrow n_f$. This transition corresponds to minus the energy needed to ionize the atom (i.e. remove the electron) from the n_f th level. Note that this ionization energy will differ from that calculated last week or the ground state.

The y-intercept is just the value of **b** in your equation. Therefore the ionization energy (I.E.) from the n_f state may be calculated using the equation

$$\text{I.E.} = h \cdot c \left(\frac{1}{\lambda} \right) = h \cdot c \cdot \mathbf{b}$$

1. Calculate I.E. from n_f in kilojoules per mole (kJ/mol).
2. Calculate E_n with $n = 1, 2, 3$ and 4 ($E_n = -hc\mathbf{R}/n^2$). Remember that **R** is now in units of m^{-1} (step #6 from previous section).

$$h = 6.6261 \times 10^{-34} \text{ Js}, \quad c = 2.9979 \times 10^8 \text{ m/s}$$

IV

EMISSION SPECTRA FOR ANALYSIS OF UNKNOWN ELEMENTS

Procedure for part IV Qualitative identification of metal ions by identifying their “fingerprint” atomic emission spectra.

1. Take your spectroscope to the various stations around the lab which are set up with bunsen burners for doing flame tests. Each station has a metal ion solution and cotton applicators.

Caution: In the next step one individual will hold the sample in the flame while the other will observe the emission through the spectroscope. The partner holding the sample must watch carefully that the partner observing through the spectroscope does not come into contact with the flame.

2. One partner is to dip the cotton applicator tip into the metal ion solution then hold the Q-tip just above the inner blue cone of the bunsen burner flame (where the flame is the hottest). The second partner should observe the color emitted by the heated solution - both visually (which you should note in your lab book) and through the spectroscope. Be sure that the 'lines' seen are actually coming from the heated material and not from scattered room light. Check this by pointing the spectroscope slightly away from the flame and seeing if the lines are still there. It is very important that you do not do the flame test on more than one solution at the same bunsen burner as the burners can become contaminated. All used cotton applicators should be placed in the trash.
3. Copy and complete the following table in your lab notebook:

Table 8. Metal Ion Emissions

Metal Ion	Colors Observed	Displacements (mm)	Wavelengths (nm)
Lithium			
Sodium			
Calcium			
Strontium			
Unknown			

Based on your knows, identify the components in your unknown.

V

The Particle in a Box

Absorption bands in the visible region of the spectrum arise from transitions from the ground state of a molecule to an excited electronic state, which is 180 to 300 kJ mol^{-1} above the ground state. Those compounds that are colored (i.e. absorb in the visible region of the spectrum) usually have delocalized electrons such as the π electrons in a conjugated organic molecule. In this part of the laboratory session you will interpret the spectra of several symmetric polymethine dyes with conjugated π bonds in terms of the "free electron" (particle in a box) model.

Figure 4 shows two possible structures of a polymethine dye (3,3'-Diethyl-thiatricarbocyanine iodide) you will examine in this experiment.

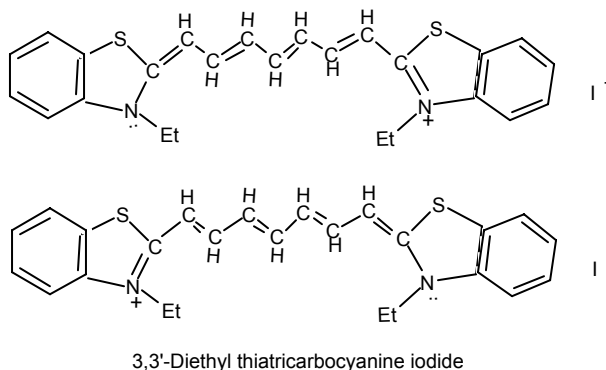


Figure 6.

Representing the molecule with these two structures of equivalent energy is useful because it shows on what atoms charges are allowed to reside as well as what atoms are able to share single and double bonds. However the two structures above can be considered as limiting structures of a resonance hybrid structure shown below in Figure 5.

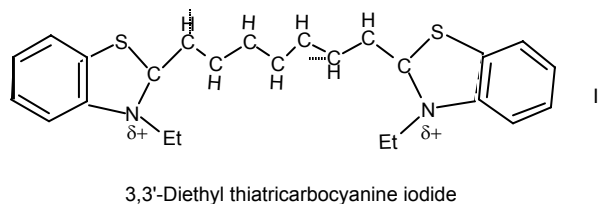


Figure 7.

In this representation the skeleton of the structure is made up of localized (sigma) bonds. The pi bonds along the conjugated double bond chain between the two benzene rings are equivalent (i.e. they are equal in energy and hence hold electrons with equal strength). The nitrogen atoms are also equal and hold partial positive charges represented by δ^+ . Because of the equality of the bonds along this conjugated chain system extra valence electrons participating in these bonds have no preference for localizing near any

particular atoms along the chain and hence form a mobile cloud free to move along the chain until they are restrained by the electropositive nitrogen atoms which allow them to extend no more than one bond length past the nitrogen nuclei. Thus all of the bonds along the (polymethine) chain can be considered equivalent, with bond order approximately 1.5, similar to the C-C bonds of benzene. In all, there are 9 carbon atoms and 2 nitrogens which make up the polymethine chain. The carbons contribute 9 electrons and the nitrogens 3 electrons to the π system.

To apply the particle in a box model assume that the potential energy is constant along the chain and rises sharply to infinity at the ends; i.e. the π electron system is replaced by free electrons moving in a one-dimensional box of length L . The quantum mechanical expression for the energy levels of this model is

$$E_n = \frac{h^2 n^2}{8mL^2} \quad n = 1, 2, 3, \dots \quad [\text{Oxtoby equation 15.20}] \quad (1)$$

where m is the mass of an electron and h is Planck's constant.

Since the Pauli exclusion principle limits the number of electrons in any given energy level to two, the ground state of a molecule with N π electrons will have $N/2$ lowest levels filled (if N is even) and all higher levels empty. When the molecule absorbs light, it causes a one-electron jump from the highest filled energy level ($n_1 = N/2$) to the lowest unoccupied energy level ($n_2 = N/2 + 1$). The energy change for this transition is

$$\Delta E = \frac{h^2}{8mL^2} (n_2^2 - n_1^2) = \frac{h^2}{8mL^2} (N + 1) \quad (2)$$

Since $\Delta E = h\nu = hc/\lambda$, where c is the speed of light and λ is the wavelength,

$$\lambda = \frac{8mc}{h} \frac{L^2}{N + 1} \quad (3)$$

If the number of carbon atoms in a polymethine chain is represented by p ; then $N = p + 3$ (note: each carbon (p) contributes one electron and the nitrogen atoms which are fixed in number contribute 3 electrons). If free electrons can travel the length of the chain between nitrogen atoms plus one bond distance on each side of the nitrogen atoms then $L = (p + 3)l$, where l is the bond length between atoms along the chain. Therefore,

$$\lambda = \frac{8mc}{h} \frac{(p + 3)^2}{p + 4} \quad (4)$$

Putting $l = 1.39$ nm (the bond length in benzene, a molecule with similar bonding) and expressing λ in nanometers,

$$\lambda(\text{nanometers}) = 63.7 \frac{(p + 3)^2}{p + 4} \quad (5)$$

If there are easily polarizable groups at the ends of the chain (such as benzene rings), the potential energy of the π electrons in the chain does not rise so sharply at the ends. In effect, this lengthens the path L . This lengthening effect requires the addition to the

formula of a parameter (α) which should remain constant for a series of dyes of a given type.

$$\lambda(\text{nanometers}) = 63.7 \frac{(p + 3 + \alpha)^2}{p + 4} \quad (6)$$

By adjusting the parameter α you will apply the particle in a box model to a series of polymethine dyes of a single type and compare the predicted absorption wavelength with the actual maximum absorbance wavelength (λ_{max}) from the visible spectra of the dyes.

Procedure for Part V

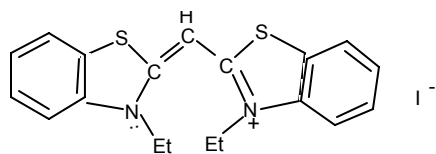
Below you will find the structures of four polymethine dyes followed by their spectra in the visible range of wavelengths. The wavelength of maximum absorbance is indicated on each spectrum.

1. From equation 6 above predict the direction of the shift in λ_{max} as the center carbon chain becomes longer .
2. Pick one of the dyes and its spectrum and determine the number of consecutive carbon atoms in the chain linking the conjugated carbon atoms (i.e. the number of carbon atoms between the two nitrogen atoms). This is the value for p . Using the above formula and the value for λ_{max} on the spectrum solve the equation for α .
3. Using the value for α calculated in step 2, use equation 6 to predict λ_{max} for the other dyes in the series. Divide the difference between the predicted and experimental values by the predicted value and multiply this number by 100% to determine the relative error of each prediction. Does this error appear to depend on the length of the carbon chain?
4. In part 1 of this exercise you correlated the length of each dye molecule with the wavelength at which it most strongly absorbs light. In the laboratory you will find solutions of each dye. Realize that when a transparent, colored material absorbs light from one region of the spectrum it allows light from other regions of the spectrum to be transmitted. The intensity and complementarity of the colors **transmitted** determine the color you see.

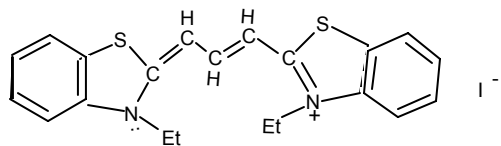
To further appreciate the value of spectroscopy for isolating and identifying particular wavelengths, use your observations of the color of the solutions in the vials, figure 15.3 in Oxtoby and the spectra given below try to correlate each dye vial with the structure of its dye and its λ_{max} .

Next hold each vial in front of the slit of the spectroscope while pointing the spectroscope to the light coming in from a window. Earlier you were looking at the emission spectra of various elements in the visible range. Now you are observing the absorption spectra of the solutions in the vials. If visible light is being absorbed by the

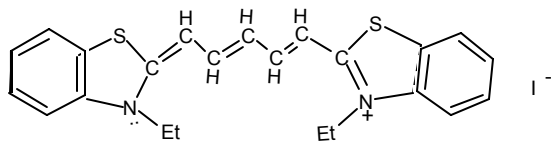
dye compound in the vial you should see a dark region along the ruler corresponding to the wave lengths and hence energy of the light that matches the transition states for the dye molecule being observed. Do your absorption spectra observations cause you to alter your conclusions on the correlations you made earlier?



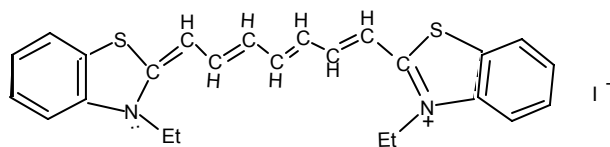
3,3'-Diethyl thiacyanine iodide



3,3'-Diethyl thiacyanine iodide



3,3'-Diethyl thiacyanine iodide



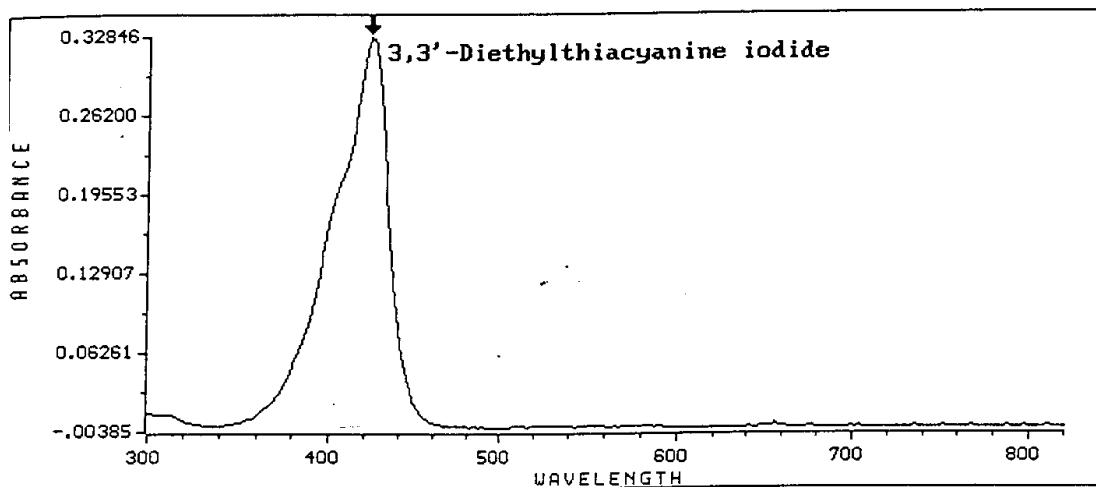
3,3'-Diethyl thiacyanine iodide

----> WAVELENGTH SCAN REPORT <----

Date : 02-24-1997
Time : 12:19:21
Operator : Not Entered

Sample Name : #7
Solvent Name : Methanol
Concentration : 0.40E-05
Units : Molar

Function : Absorbance
Wavelength Range : 300 to 820 nanometers
Integration Time : 2 seconds
Std Deviation : OFF



Unnotated Wavelengths:

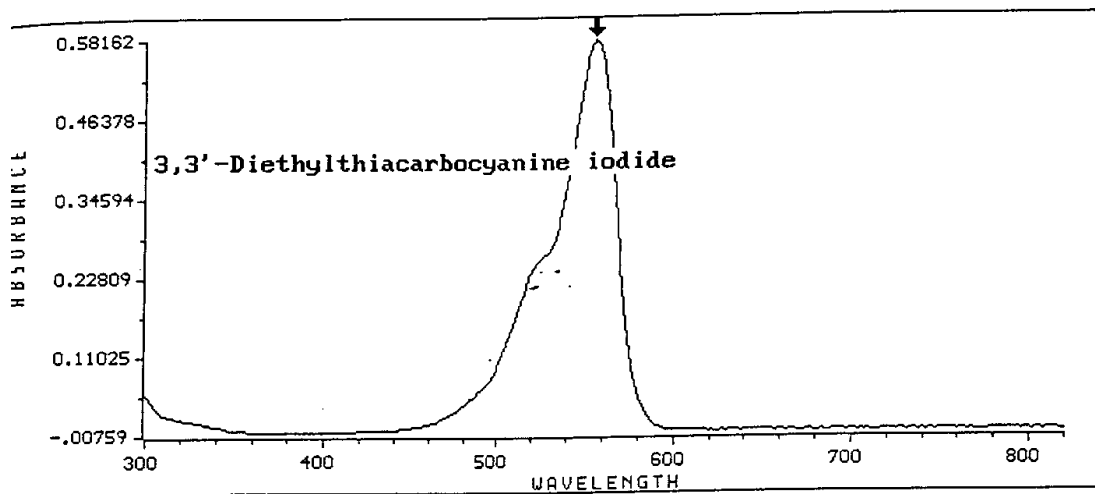
1 : Wavelength = 422 Result = 0.328461

----> WAVELENGTH SCAN REPORT <----

Date : 02-24-1997
Time : 12:27:11
Operator : Not Entered

Sample Name : #8
Solvent Name : Methanol
Concentration : 0.40E-05
Units : Molar

Function : Absorbance
Wavelength Range : 300 to 820 nanometers
Integration Time : 2 seconds
Std Deviation : OFF



notated Wavelengths:

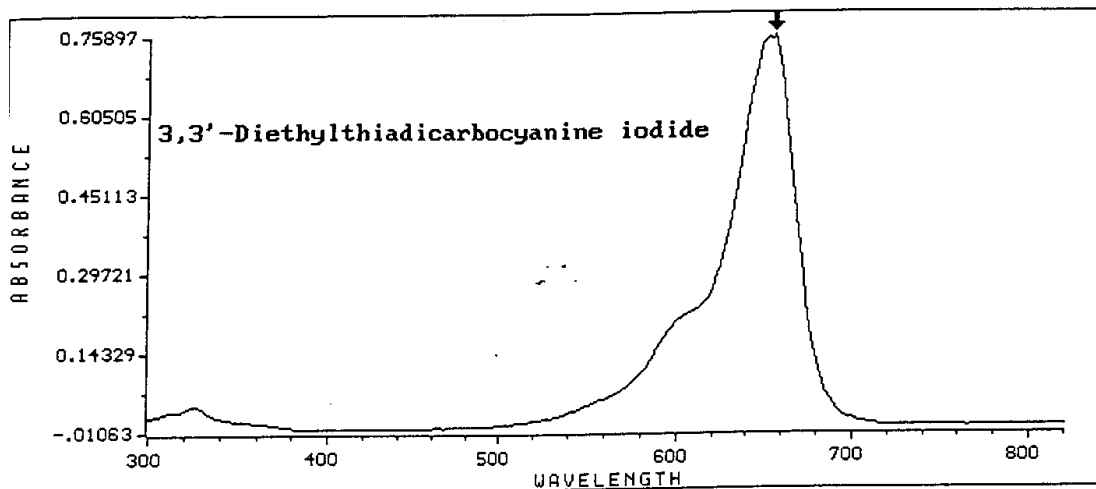
1 : Wavelength = 556 Result = 0.581619

---> WAVELENGTH SCAN REPORT <---

Date : 02-24-1997
Time : 12:31:11
Operator : Not Entered

Sample Name : #9
Solvent Name : Methanol
Concentration : 0.40E-05
Units : Molar

Function : Absorbance
Wavelength Range : 300 to 820 nanometers
Integration Time : 2 seconds
Std Deviation : OFF



Annotated Wavelengths:

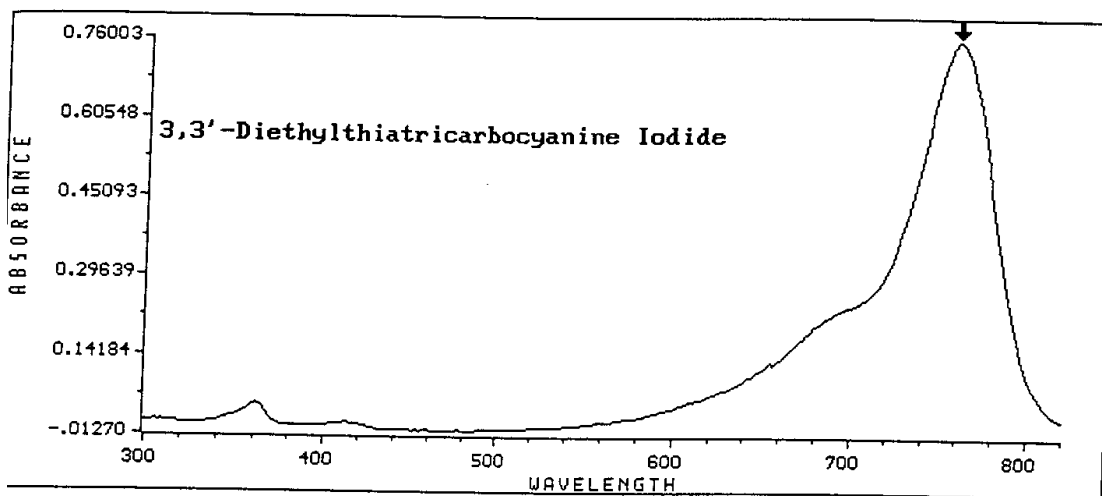
1 : Wavelength = 656 Result = 0.758972

---> WAVELENGTH SCAN REPORT <---

Date : 03-07-1997
Time : 12:23:05
Operator : Not Entered

sample Name : #10
solvent Name : Methanol
Concentration : 0.40E-05
Units : Molar

Function : Absorbance
Wavelength Range : 300 to 820 nanometers
Integration Time : 1 seconds
Std Deviation : OFF



notated Wavelengths:

1 : Wavelength = 758 Result = 0.760025

Lab Report

All calculations should be carefully documented in your lab notebook. You may, but are not required to use either Excel or Mathematica for linear plots and calculations :

Part I

1. Grating constant: values for L , W , $\sin \theta$, and d^{-1} (the grating constant in lines/mm).

Part II

2. Calibration of the spectroscope: Displacement values for each wavelength measured, the slope and intercept of the best fit line for predicting the wavelength on the vertical axis from the line displacement on the horizontal axis.

Part III

3. Hydrogen emission λ s
4. Trial sets: Table 3, Table 4, & Table 5
Plot $\frac{1}{\lambda}$ vs $\frac{1}{n_i^2}$ for each of the the three trial sets
5. Table 6: Least squares data and corresponding n_f values
6. Select the best fit line and write the corresponding equation
$$\frac{1}{\lambda} = \frac{\mathbf{R}}{n_i^2} + \mathbf{b}$$
7. E_n values with $n = 1, 2, 3$ and 4 ($E_n = -hc\mathbf{R}/n^2$)
8. I.E. from n_f state. Report value in kJ/mole.

Part IV

9. Color, displacement, and wavelength chart of the known elements.
10. Color, displacement, and wavelength lines of the unknown.
11. The identity of the unknown metal ion sample

Part V

12. Hand in a chart for the four polymethine dyes that contain the following:
 - I. α value used for the set of four at the top
 - II. Name and color of each dye with the following:
 - A. λ_{\max} (experimental)
 - B. λ_{\max} (predicted)
 - C. % error of λ_{\max}

MATERIALS

Spectroscopes
He-Ne lasers (1/section)
Replica transmission gratings (1/section)
String and meter sticks for θ measurements.
Hydrogen (H_2) and Mercury (Hg) discharge lamps (1 ea/section)
Containers of LiCl, NaCl, $CaCl_2$, $SrCl_2$, and an unknown at defined
stations (1 ea/section)
Cotton tip applicators (Q-tips)
Bunsen Burners
Matches
Clear numbered containers of the four polymethine dyes

Waste Disposal:

All used cotton tip applicators should be placed in the trash. DO NOT PLACE IN THE SINK!

Appendix

SAMPLE MEASUREMENT: SPECTRONIC 20D

Transmittance and Absorbance

The sequence for sample measurement is:

1. Turn on the instrument by turning the left knob on the front of the instrument clockwise.
2. Select the wavelength using the wavelength control knob on top of the instrument, while watching the LED display of wavelengths.
3. Set the mode to TRANSMITTANCE (press the MODE select control until the transmittance LED on the right of the display is lit).
4. With the sample compartment empty and the cover closed, adjust the Zero Control so that the meter reads 0%T. The Zero Control is the same left front knob used to turn on the instrument.
5. Choose the mode that you require by pressing the MODE selector control until the appropriate LED (on the right of the display) is lit.
6. Insert reference blank into the sample compartment and set 100%T or 0.000A using the right knob on the front of the instrument.
7. Insert an unknown sample into the sample compartment and read the measurement from the display in percent transmittance or absorbance.
8. Recheck the 0%T after removing the sample. Periodically check to blank to be sure it reads 100%T or 0.000A. If the instrument readings drift from 0%T or 100%T, then readjust the appropriate knob in the front of the instrument, and reread the samples affected by the instrument drift.
8. Turn off the instrument when finished.

Experiment 1

Physical Measurements and Error Analysis

Experiment 1

Physical Measurements and Error Analysis

Introduction

Objectives. (a) To become proficient in using the analytical balance and measuring volumes of liquids and solids, and (b) to understand the concepts of accuracy and precision, how they are specified and how they are used to investigate the above measurement tools.

Density. One of the fundamental properties of any sample of matter is its density (ρ), which is its mass (m) per unit of volume (V):

$$\rho = \frac{m}{V} \quad (1)$$

The density of water is exactly 1.00000 g/cm^3 at $4 \text{ }^\circ\text{C}$ and is slightly less than one at room temperature (0.9970 g/cm^3 at 25°C). Densities of liquids and solids range from values less than that of water to values considerably greater than that of water. Osmium metal has a density of 22.5 g/cm^3 and is probably the densest material known at ordinary pressures. It should be noted that cm^3 and mL (milliliters) are identical and are typically used interchangeably.

In any density determination, two quantities are measured: the mass and the volume of a given quantity of matter. The mass can easily be determined by weighing a sample of the substance on a balance. The quantity we usually think of as "weight" is really the mass of a substance. In the process of "weighing" we find the mass, taken from a standard set of masses, that experiences that same gravitational force as that experienced by the given quantity of matter we are weighing. The mass of a sample of liquid in a container can be found by taking the difference between the mass of the container plus the liquid and the mass of the empty container.

The volume of a liquid can easily be determined by means of a calibrated container. In the laboratory a graduated cylinder is often used for routine measurements of volume. In titration experiments where it is necessary to add a precise series of volumes of liquid to another container, a buret is employed. However, the most accurate measurements of liquid volume are made by using a *pycnometer*, which is simply a container having a precisely definable volume. In the case where the pycnometer is used to deliver the volume to another vessel, we have a pipet. These three instruments are shown in Figure 1.

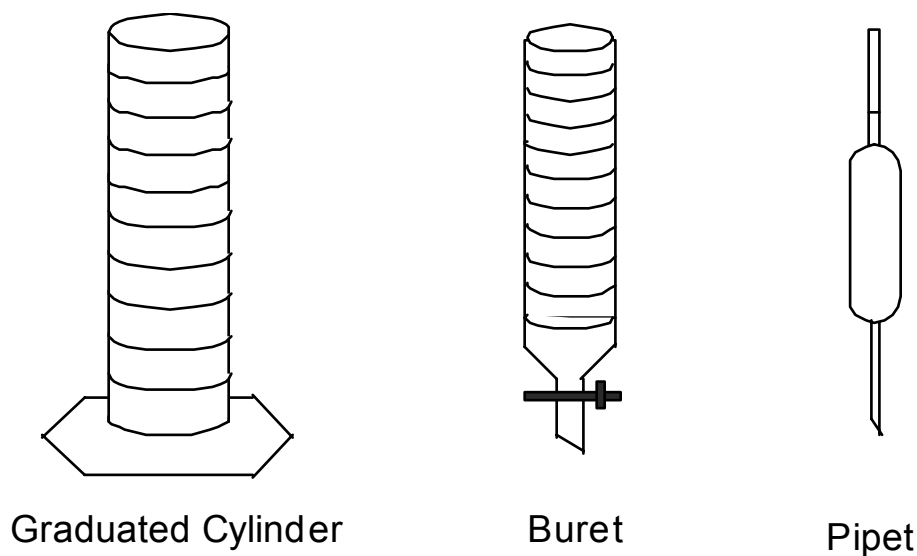


Figure 1. Volumetric Devices

The volume of a solid can be determined by direct measurement of its dimensions if it has a regular geometrical shape. However, many solid samples have an irregular shape. In these cases, a convenient way to determine the volume of a solid is to measure accurately the volume of liquid displaced when it is immersed in the liquid. The volume of the solid will equal the volume of liquid which it displaces.

In this experiment we will determine the density of a liquid and a solid by procedures involving the determination of the mass of a sample together with its volume. Along the way, we will evaluate the precision with which the three volumetric devices depicted in Figure 1 can deliver a known volume to a second container. We will judge the precision by weighing the volumes of liquid. Thus, the more precise method of weighing will be used as the reference technique for comparison of the volumetric devices.

Error Analysis

In any scientific experiment it is necessary to know how good the results are. We evaluate our results by determining their error. The word error does not necessarily imply that one has been careless. Even with the best technique, measured values are never perfectly well known, but contain some uncertainty. Errors in experimental measurements may be divided into two classes: (a) systematic errors and (b) random errors.

Systematic errors. Systematic errors are quite reproducible and arise from failure or incompleteness of underlying theory, a shortcoming in the instrumentation or procedure, or failure to account for an experimental variable. We characterize the magnitude of systematic errors by specification of the *accuracy*. This term is defined as the difference

between the observed value and the true value of the quantity. Thus accuracy is a measure of the correctness of the result. An accurate measurement is one in which the systematic errors have been eliminated in so far as possible.

The ultimate goal of any analysis is to have the measured value be the same as the true value. Of course, one of the fundamental difficulties in real scientific investigations, is that the true value is not known. However, in the student laboratory, the true value has been established through use of independent reference methods as performed by well-trained personnel.

In the world of science, a central preoccupation is to arrive at the "true" answer by reduction of systematic error. Often this involves repeating the experiment many times, systematically changing as many variables as possible: trying a different location, a different source for the starting materials, a different instrument, etc. In practice such experimental manipulations are difficult to carry out, but for crucial experiments, (such as testing a fundamental theory of nature), they are always done. More common, one simply analyzes the experiment carefully, checking each step to see what 'hidden' influences might be present. This requires the scientist to think through the entire experiment to find all the flaws in it. For example, if temperature variations seem to be a problem, a little heat can be applied to see if any results change.

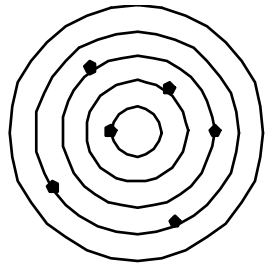
How then do we specify accuracy? It seems obvious that by calculating a % deviation of the measured value from the true value we can get a mathematical value for accuracy of the measurement. This quantity is calculated as

$$\% \text{ deviation} = \frac{|x_{\text{meas}} - x_{\text{true}}|}{x_{\text{true}}} \cdot 100\% \quad (2)$$

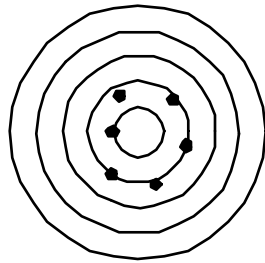
where x_{meas} is the measured value and x_{true} is the true value.

Random errors. Random errors are deviations (irreproducibilities) in observations which yield results which differ from experiment to experiment. We characterize these irreproducibilities by their *precision*. The precision of a series of measurements thus reflects how closely each measurement in a series agrees with the others. In Figure 2, we illustrate the difference between accuracy and precision using the analogy of firing a rifle at a target.

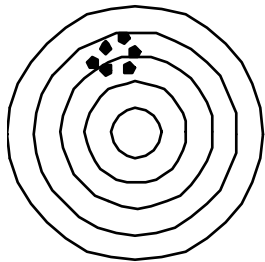
In many cases, precision is influenced by physical effects beyond the control of the operator. In other cases, precision is influenced by how consistent one is in performing a technique. For example, the precision of pipetting a volume of a liquid generally improves with practice.



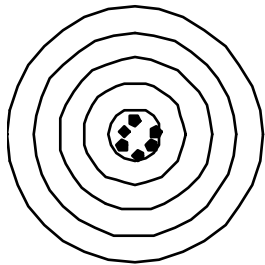
Low Accuracy and Low Precision



High Accuracy and Low Precision



Low Accuracy and High Precision



High Accuracy and High Precision