CHEMISTRY 1010
Lab Manual

University of Louisiana at Monroe
Freshman Chemistry Lab Staff
Revised: Fall 2010

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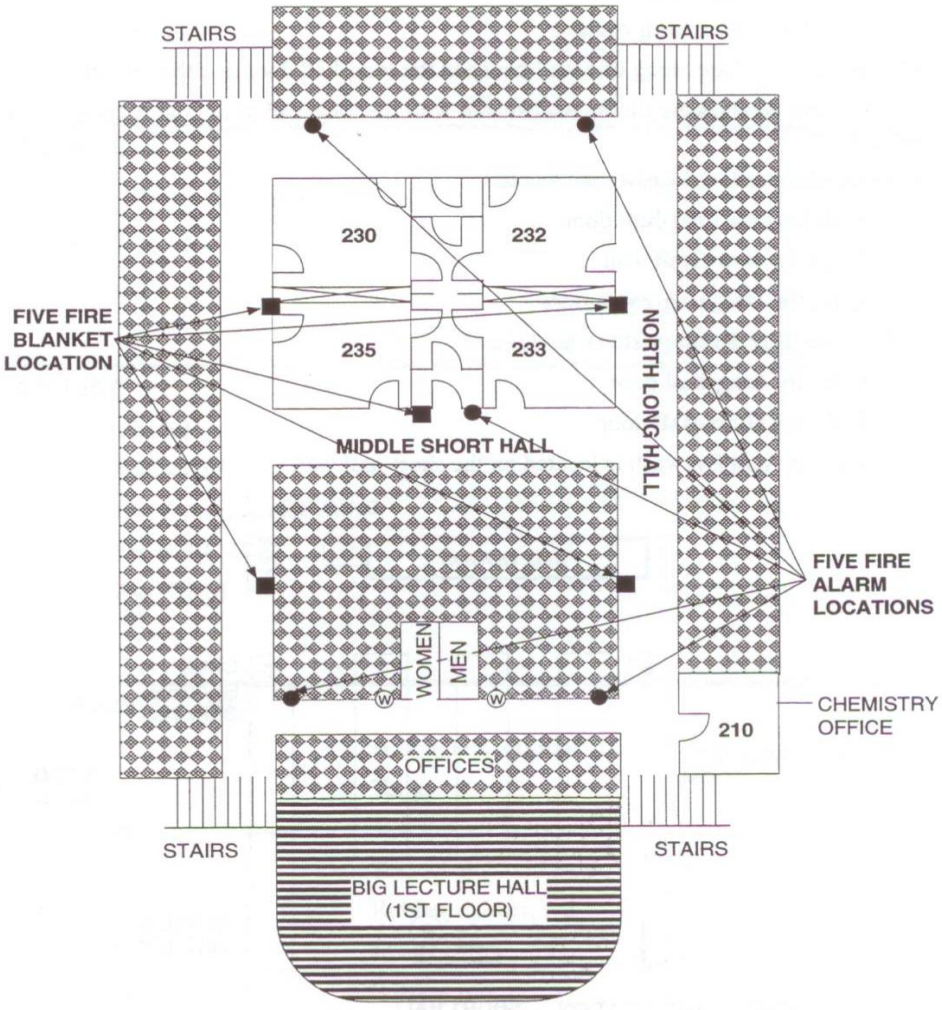
MAP

CNSB Second Floor

Locations of fire alarms, fire blankets, and stairwell exits are indicated on the map of the second floor below. Familiarize yourself with the location of these important safety features.



Floor-plan of the Freshman Laboratories

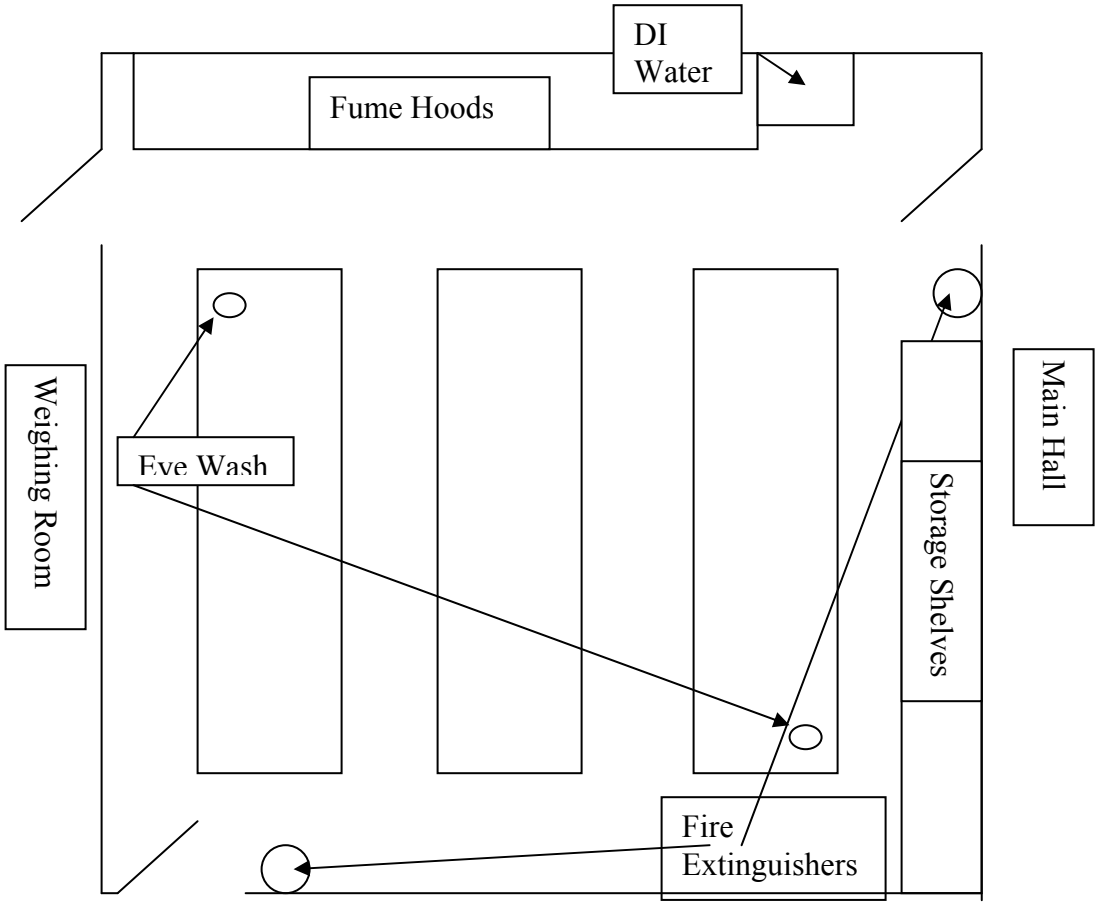
Become familiar with the location of the important safety devices in the freshman laboratories. Since there are four freshman laboratories and each has a different orientation, you should learn the locations relative to the common features of the labs.

Exits: Each room has three exits, one each on the north and south wall near the fume hoods. The third is located on the wall opposite the fume hoods and diagonal to the DI water station.

Fume Hoods: Four fume hoods are located on one wall of the lab between the main entrance door and the door to the weighing room.

Eye Wash/Shower Stations: Two eye wash/shower stations are located in each laboratory. One is located by the sink on the end of the bench near the fume hood and the weighing room door. The second is located diagonally across the lab at the end of the bench.

Fire Extinguishers: Two fire extinguishers are located in each laboratory. One is located on the wall by the main entrance door. The second in located diagonally across the lab by the second exit door.



CHEMISTRY 110 Desk Assignment Sheet

PLEASE PRINT!

Student's Name_____

CWID_____

Section #_____ Room #_____ Desk #_____

ITEMS	**QUANTITY**
Basket	1
Beaker, 100 or 150 ml	2
Beaker, 250 ml	1
Beaker, 400 ml	1
Casserole, 60 ml	1
Clamp, Test-tube	1
Cylinder, Graduated, 10 ml	1
Cylinder, Graduated, 100 ml	1
Funnel, Short-stem, filling	1
Flame Loop	1
Flask, Erlenmeyer, 125ml	2
Red Rubber-Dubber	1
Spatula	1
Stirring Rod	1
Test Tube, 13 X 100	10
Test Tube, 15 X 125	10
Test Tube Brush	1
Test Tube Rack	1
Tongs	1
Wash Bottle	1
Watch Glass	1

Student's Signature_____

Check in by_____ ***Date***_____

Check out by_____ ***Date***_____

I MUST PROVIDE AND WEAR SAFETY GOGGLES DURING EACH LAB PERIOD.

Initials_____ Date_____

Safety

Laboratory Safety Rules

(Rules listed are minimum standards and additional safety requirements may be imposed by each individual instructor).

Eye protection **must** be worn in the laboratory and in the balance room at all times.

Eating and/or drinking in the laboratory and in the pre-lab lecture room are forbidden.

Students wearing shorts and/or shoes that are not solid and cover the foot will not be allowed to work in the laboratory. A lab coat or apron which extends below the knee is required if clothing does not cover the knee or if the mid-riff is exposed. Stated dress code conditions may not be waived; improperly clad students will be told to leave the laboratory.

Students must not handle broken glass. If any glass item breaks, inform the Instructor. A brush and plastic dust/glass pan that can be used to collect glass fragments are located on the wall near the DI water container. Broken glass may also be found on the floor, in your drawers, and in the sinks. Don't reach carelessly into drawers or sinks, and wear shoes that protect you. When broken glass is present see that it gets cleaned up. All broken glass should be placed in a box marked for that material only. Your instructor will help you.

Students may not use cell phones in the laboratory; laboratory work demands full attention, and responsible behavior (see University cell phone policy). Cell phones must be turned off during pre-lab lecture and in the laboratory.

Students may not entertain visitors in the laboratory. Again, the laboratory work demands full attention and appropriate safety precautions. (Also, visitors are not authorized to be there.)

When no longer required, equipment should be returned to its original space (e.g. drawer or side shelf), and solids must not be disposed of down the sink. Most solid waste can be placed in the trash receptacles located at the end of each bench. You may be instructed to place some waste solids and liquids in marked containers in the hoods.

Eye Protection:

Because tragic and irreversible eye injuries are a constant danger, eye protection must be worn at all times in the lab. The best protection is given by goggles which have a strap to pull them flush with your face. However, we currently allow safety glasses which have side-shields (so-called "weed-eating" glasses). You may wear your regular prescription glasses if they can be worn under goggles or if they are fitted with side shields. If you store your glasses/goggles in your drawer, your first action during any lab session is to put them on; do not make any other moves toward lab work before that. If you get anything in your eye, proceed to the eye wash and use it. But let your instructor know; don't be quiet about it.

Although dress code may be mitigated by religious beliefs, eye protection is not negotiable – any instructor can remove you from the lab for disregarding this rule.

Corrosives:

There are some very corrosive chemicals used every day in the lab. You must learn to handle them with respect. You may get small amounts on your hands and clothing. Wash immediately and thoroughly. The rarer but greater danger is from large spills on the body. Don't be embarrassed to use the eyewash/shower. You may need to shed some clothing. Just do it and use lots of water. Concentrated H_2SO_4 in large amounts should be wiped off first but for all the other corrosives, get the water going fast. The solutions to be most concerned about are 18 M H_2SO_4, 16M HNO_3, 12M HCl, 8M NaOH, and 15M NH_3. Help your neighbors if they have a spill, especially if on the body, and let your instructor know immediately.

Poisons:

Consider every chemical in the lab a danger in this respect but learn from your instructor those chemicals that are most dangerous. No eating or drinking can be tolerated in the lab. Even chewing of gum in lab is forbidden. Wash your hands thoroughly before you leave lab after completion of the day's experiment.

Fire:

Fire danger is not unusually high in this lab, however we do use the Bunsen burner continually. Be careful of your hair and clothing (particularly in cool weather). Before lighting your burner, look to see that it is whole and well connected. Always follow the procedure given by your instructor for lighting the burner. Always turn a burner off by reversing the lighting procedure. Though we use few flammables in this course, and these only in small amounts, large quantities may be in the hoods. Do not use the burner in the hoods that contain flammables. Your instructor will indicate hoods in which a burner may be lit.

Gases:

Poisonous, corrosive, and noxious gaseous compounds are used regularly in the course. Pay attention to these:

- H_2S is extremely poisonous as well as horribly smelly. You will smell it! However, it is critical to avoid direct inhalation even of the dilute solution of H_2S we make up. Never convert a basic solution of sulfide to acid unless under a functioning fume hood.
-
- HCl and NH_3 concentrated solutions give off gases which are very corrosive and damaging to your respiratory system. Use these carefully.
-
- HCl and SO_3 are created by boiling down acid solution. Do such work in the hood!

Solubility

Solubility, the extent to which one substance (the solute) can be dissolved in another (the solvent), is quantitatively conveyed by the concentration of a saturated solution, that is a solution in equilibrium with pure solute. In terms of molar solubility, where concentration is on the molar scale, the obvious lower limit is zero (or virtually so) and the upper limit of observed solubility for ionic substances in water are in the 'tens'. For example, the molar solubility of KCl is about 4.2 M and that of AgC1 is about 1.7 x 10^{-5} M (at 25 ºC). Another way solubility is communicated is the solubility product constant, K_{sp}, the product of molar concentrations in a saturated solution, with each ionic molarity raised to the power of its coefficient in the solubility equation.

$$AgCl(s) \rightleftarrows Ag^{+}(aq) + Cl^{-}(aq);\ K_{sp} = [Ag^{+}]^{1}[Cl^{-}]^{1} = 2.8 \quad X \quad 10^{-10}$$

$$PbCl_{2\,(s)} \rightleftarrows Pb^{2+}{}_{(aq)} + 2\ Cl^{-}{}_{(aq)},\ K_{SP} = [Pb^{2+}][Cl^{-}]^{2} = 1.6 \times 10^{-5}.$$

You will find K_{sp}'s recorded for sparingly soluble salts (sometimes called "insoluble" salts).

Our current interest is **qualitative** and the rules to be expounded here are to be used to give us a quick expectation as to whether a salt is "soluble" or "insoluble" ("sparingly soluble" is a better description). The rules below have been tailored for our needs in this course and you should **learn them in detail** and apply them. Experiments dealing with qualitative analysis of cations and anions in aqueous solution (Experiments 2, 3, and 4) will require that we know whether certain salts are sparingly soluble, thus liable to form precipitates.

Solubility Rules

1) All salts of Na^{+}, K^{+}, and NH_4^{+} are soluble.
2) All acetates and nitrates are soluble.
3) Exception: $AgC_2H_3O_2$ is moderately soluble.
4) All chlorides, bromides, and iodides are soluble.
5) Exceptions: Pb^{2+}, Hg_2^{2+}, and Ag^{+}
6) All sulfates are soluble.
7) Exceptions: Ba^{2+}, Pb^{2+}, and Hg_2^{2+}
8) Note: $CaSO_4$ and Ag_2SO_4 are moderately soluble
9) All arsenates, borates, carbonates and phosphates are insoluble
10) Exceptions: Na^{+}, K^{+}, and NH_4^{+}
11) All hydroxides are insoluble
12) Exceptions: Na^{+}, K^{+}, and NH_4^{+}. Note: $Ca(OH)_2$ and $Ba(OH)_2$ are moderately soluble.
13) All sulfides are insoluble

14) Exceptions: Na^+, K^+, and NH_4^+

15) Note: *CaS*, *BaS*, *and MgS* are slightly soluble

The rules above deal qualitatively with solubility of salts in unadulterated water. As you may already realize, there are ways (we're particularly interested in two) by which a third component in the solution can change the apparent solubility of a salt. The two categories of most interest in this course are 1) strong acids and 2) complexing agents.

In the first case insoluble salts of weak acids usually show increased solubility, sometimes dramatic increases, if strong acids (high $[H^+]$ concentration) are added. The result is formation of the weak acid, usually quite soluble itself, with the release of the cation. Such as

$$ZnS_{(s)} + 2\,HCl_{(aq)} \rightleftarrows Zn^{2+}{}_{(aq)} + 2\,Cl^-{}_{(aq)} + H_2S_{(aq)}.$$

This is, of course, a chemical reaction, not just simply ZnS dissolving. Nevertheless, we could now discern the presence of zinc ion and hydrogen sulfide for that matter, in the solution.
Another important case is where insoluble salts are 'solubilized' by reaction with a cation complexing agent. These agents are "Lewis base" molecules or ions called **ligands**) which react with cations which are "Lewis acids". An examples is

$$AgCl(s) + 2\,NH_{3\,(aq)} \rightarrow [Ag(NH_3)_2]^+{}_{(aq)} + Cl^-{}_{(aq)},$$

in which silver chloride is seen to be dissolved in ammonia solution by formation of a complex cation, often denoted by brackets. A new salt is formed, diamminosilver chloride, which is soluble. We also see how this reaction is readily reversed by addition of strong acid, H^+.

$$[Ag(NH_3)_2]^+{}_{(aq)} + Cl^-{}_{(aq)} + 2\,H^+{}_{(aq)} + \rightarrow AgCl_{(s)} + 2\,NH_4{}^+{}_{(aq)}.$$

General Terms and Fundamental Techniques

The Pasteur pipets we use are disposable, which is to say that when they become too difficult to clean or become unusable for any other reason, toss them and get another. As long as you are not wasteful, the disposable pipets will be available. You may have occasion to use an old-fashioned Pasteur pipet which consists of a glass pipet (dropper) fitted with a rubber bulb (called a rubber-dubber). To be useful the glass pipet should fit snuggly with the 'red' or the 'latex' rubber-dubber, the 'blue' have too much volume, the 'black' are hopelessly small. Tight fit of the rubber-dubber is critical: it should hold the solution so that it does not drop out until you squeeze.

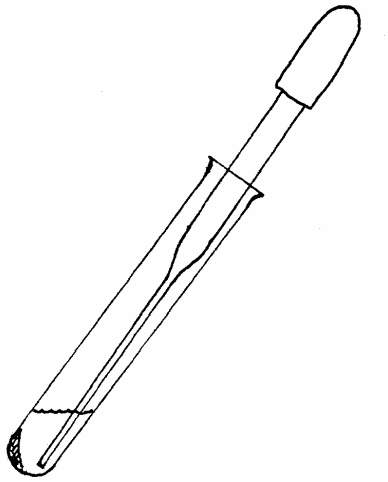


Figure 1

The main use of the pipet is to decant the supernatant off the precipitate. The word 'decant' really means to pour off, which by the way, is often possible. When the precipitate is not packed well enough by centrifugation, the supernatant can still easily be sucked away with the pipet. After centrifugation you will note that the precipitate pellet will be packed to one side at the bottom of the tube. First exhaust the pipet by squeezing the bulb, then place it on or near the bottom of the tube opposite the pellet with tube tilted as shown. Then slowly relax the squeeze. Usually this picks up the solution/supernatant/decantate leaving the precipitate. Practice this patiently a few times and you'll become a pro.

Centrifuging

Always balance the tube containing your sample to be centrifuged with another of the same size, shape, and thickness containing very nearly the same amount of water as you have sample solution, placed opposite your sample in the centrifuge. This will avoid the raucous and dangerous vibrations which accompany misbalance. If the centrifuge vibrates when run empty ask your instructor to fix it. Different sized rubber spacer plugs (not visible) are placed in the metal holder-tubes so that different sizes of test tubes may be used. The metal holder tubes should have been matched in weight with their opposite, but not necessarily with their adjacent tubes. Please don't rearrange these unadvisedly. So, your tubes, sample and counter weight, should fit into the metal holder tubes to an equal extent. Never let your glass tubes set against each other as they will surely break and fling glass during centrifugation.

How long one should centrifuge depends on the sample. Thirty seconds at high speed will pack most, but some may require two or more minutes. Clarity (no mention here of color) of the supernatant solution is the best measure of completion. Sometimes total clarity cannot be reached but don't give up without some extended centrifugation. As mentioned above, most precipitates pack so well that you could pour the supernatant/decantate off. In other cases, as you will learn, any kind of agitation breaks the pellet up.

To “wash” a precipitate requires **three** operations:

1) Add to the precipitate the wash solvent which may be water or a particular solution.
2) Always stir or shake to re-suspend the precipitate but heat only if specified;
3) Centrifuge; and
4) Decant the supernatant, which may be combined with some previous decantate or discarded. This leaves you the washed precipitate.

To “check for completeness of precipitation” you will need to clarify the supernatant by centrifugation but you need not decant. Then add a drop of the precipitating reagent gently and observe where it mixes with the solution you’re testing for cloudiness, which would indicate more reagent is needed. When no cloudiness occurs, precipitation is complete.

The “unknown tube”: For the qual scheme experiments (Experiments 2, 3, and 4), you will turn in a test tube to your instructor in which he/she will put your unknown. The best policy is to place your tube for the next unknown when you pick up an unknown. Each instructor has his own specification for these as to size, where to label, what to label, and where to place it. You **must** meet his/her specifications. Your instructor will simply add the “unknown” to the tube without any cleaning, so if you want a clean sample give a clean tube.

Lab Reports

The student is expected to prepare and submit a detailed lab report for each experiment done. The format for these reports will vary according to the individual instructor, and will be specified in the course syllabus or in pre-lab lectures. The medium for the lab reports (print and/or electronic) will also vary from one instructor to another. Some of the experiments contain directions (on data treatment and graphing procedures) that specify minimum report content. Your instructor will probably require a more extensive report. Typical lab reports might consist of the following sections:

A separate **Title Page**, to consist of Date, Experiment #, Experiment Name, Your Name, Names of People in Your Group, Name of Instructor, Lab Section Number.

1. Theory and Principles. This section should be reflective of the prelab lecture, supplemented by material from the text or other references. It should not be copied from the sources, but should be presented in the student's own words. This section should describe the chemistry being demonstrated by the experiment, thus should contain balanced chemical equations.

2. Experimentation. This section should outline the following.

> **2A. Procedures.** Describe procedures followed and describe any instruments used. This should be written in the past tense and should not be a detailed step-by-step recanting of steps performed. It should tell what general procedures were followed. Flow charts fit well in this section of the report. It may also include a listing of chemicals used, with specification of any safety hazards.
>
> **2B. Experimental Data**. This is usually presented in tabular form as prescribed in the lab manual.

3. Results

> **3A. Sample Calculations.** Applicable only if the experiment involves calculations. Most do.
>
> **3B. Results**. Results are often presented in the form of a graph, but may be numerical or tabular. Graphs may be plotted on graph paper or may be produced using graphing software like EXCEL. It is important that axes be clearly labeled and that scales be chosen to make the graph span the entire page as much as possible.
>
> **3C. Error Analysis.** Calculate % errors, average deviations, etc, if your instructor tells in advance what value should have been obtained. For a quantitative determination, your instructor may calculate the percent error and deduct points for poor results.
>
> **3D. Discussion of Results**. Discuss sources of error and assess the reliability of the experimental results.

Neatness, **spelling and grammar count.** Further discussion of expectations for lab reports will occur during the semester. Lab reports should be as brief as possible while adequately addressing

the stipulations listed above. For many of the experiments, specifics are provided on how to present the results for that given experiment.

The students are expected to hand in a lab report of each completed experiment at the beginning of the next week's prelab. Failure to meet this deadline will result in a grade of zero for that experiment. If for some legitimate reason you must miss lab, you should plan to submit the lab report early or have someone turn it in for you on or before the deadline. Thus it is unwise to wait till the last moment to prepare a lab report.

Lab reports must be typed, not hand written. If you do not routinely use a word processor, this is the chance to start doing so. Entries in data tables must either be typed or written neatly in ink, as dictated by your instructor. Whether graphs are plotted by hand or produced using graphing software such as that included in a spreadsheet like EXCEL, is decided by your instructor. Unless otherwise specified, each graph should occupy its own page. It is mandatory that axes chosen for graphs cause the plot to fill the page as much as possible. Plot smooth curves (including straight lines). Do not connect the dots.

Do not copy any part of the lab report directly from a book or from another individual's lab report. Lab reports should be written in your own words. Utilize the spelling and grammar checker provided by the word processor you are using. Your grade should be based on your work, not that of others. The instructor will be vigilant in looking for plagiarism. Conclusive evidence of plagiarism will result in a grade of zero for that experiment and may result in expulsion from the course.

Experiment 1: Colligative Properties

Determination of the Molar Mass of a Compound by Freezing Point Depression.

Objective: The objective of this experiment is to determine the molar mass of an unknown solute by measuring the freezing point depression of a solution of this solute in a solvent as compared to the freezing point of the pure solvent.

Background: **Colligative properties** are properties of a solvent, such as freezing point depression and boiling point elevation, which depend on the concentration of solute particles dissolved in the solvent. The decrease in freezing point, ΔT_f (freezing point depression) for a near ideal solution can be described by the equation:

$$\Delta T_f = k_f \cdot m \qquad \text{Eq 1}$$

where k_f is the **molal freezing point depression constant** of the solvent with units °C · kg solvent/mole solute. *m* is the molal concentration of the solute dissolved in the solvent expressed as moles of solute/kg solvent.

Since the molar mass $\mathcal{M}$ (traditionally and often, but erroneously called the molecular weight) of a compound has units g/mole, we can solve for moles and substitute the result into the molal concentration relationship, and then into Eq 1 as is shown below.

$$\mathcal{M} = \text{g/ mole} \qquad \text{Eq 2}$$

Rearranging Eq 2 gives

$$\text{moles} = \text{g}/\mathcal{M} \qquad \text{Eq 3}$$

Now substituting Eq 3 into the unit definition of molality yields

$$m = \text{g}/(\mathcal{M} \cdot \text{kg solvent}) \qquad \text{Eq 4}$$

And substituting Eq 4 into Eq 1 gives

$$\Delta T_f = (k_f \cdot \text{g})/(\mathcal{M} \cdot \text{kg solvent}) \qquad \text{Eq 5}$$

We can rearrange Eq 5 and solve for the molar mass, mol wt, as is shown in Eq 6, below.

$$\mathcal{M} = (k_f \cdot \text{g})/(\Delta T_f \cdot \text{kg solvent}) \qquad \text{Eq 6}$$

Therefore, if we know the mass of unknown compound added to a known mass of solvent and determine the change in freezing point of the solution, relative to pure solvent, we can use Eq 6 to determine the molar mass of the unknown compound.

At the freezing point of any substance, an equilibrium exists in which both liquid and solid are present.

$$\text{liquid} \rightleftarrows \text{solid} \qquad \text{Eq 7}$$

The temperature at which this equilibrium exists is the freezing point of the substance. Sometimes this temperature is difficult to determine, so the use of **cooling curves** is required. To construct a cooling curve one would warm their sample, pure solvent or solution, to well above its melting point, then allow it to cool. As the sample cools the temperature of the sample is monitored as a function of time. As the sample begins to solidify the change in temperature will slow, and at the equilibrium shown by Eq 7 the temperature will be constant until all of the sample has solidified. A graph is made by plotting the temperature vs. time. An example of a cooling curve is shown below in Figure 1.

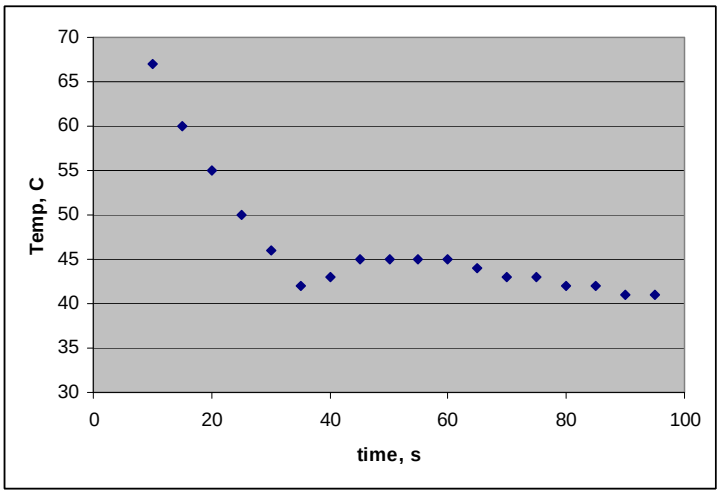


Figure 1: Cooling curve for a pure solvent.

In this cooling curve you see a steady decrease in temperature followed by a dip which is followed by a slight rise in the temperature. This dip is not unusual and results from **supercooling** during the early stages of the freezing process. In this example the dip is followed by a short plateau in the temperature. This plateau is at the freezing point of the pure solvent as shown in Figure 1.

When solute is added to the solvent the shape of the cooling curve sometimes changes so that we don't see a clear horizontal plateau as the example shown in Figure 1.

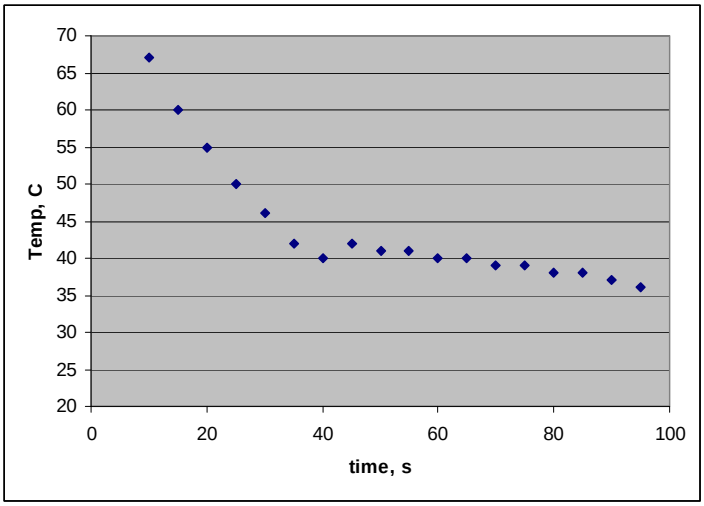


Figure 2: Cooling curve for a solution.

In Figure 2 we don't see a clear horizontal plateau. In this case we must draw a trend line through the data points corresponding to the cooling of the liquid and a trend line through the data points corresponding to the freezing of the liquid. The temperature at the point where those two lines intersect is the freezing point of the solution.

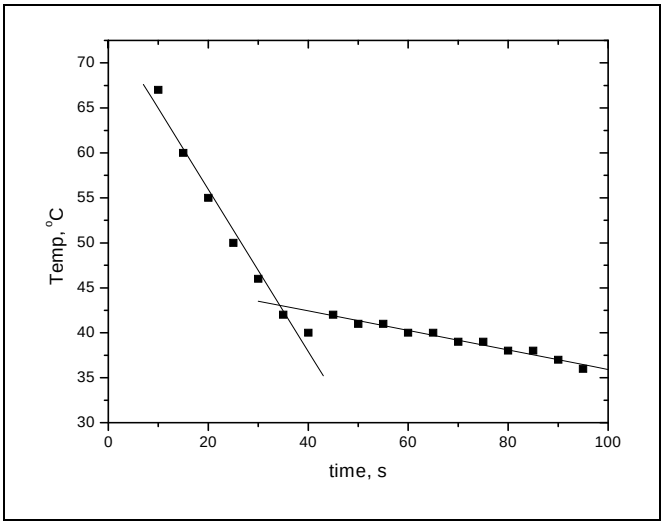


Figure 3: Solution cooling curve
showing best fit straight lines through the two portions of the curve discussed in the text.

Figure 3 shows an example with the trend lines drawn in and the intersection of the lines. In the example shown in Figure 3 the freezing point would be measured as about 43 °C. If we continue to record and plot the temperature of the solid, the data points may start to deviate from the trend line shown in Figure 3 corresponding to the freezing of the liquid. In this case you would not include those points in the trend line.

In this experiment you will determine the freezing point of pure tertiary butyl alcohol (*t*-butanol) then the freezing point of *t*-butanol with an unknown solute dissolved in it. From these freezing point measurements you will be able to calculate the molar mass of the unknown solute. The *t*-butanol is a good solvent choice for this experiment. Its transition state from solid to liquid occurs near room temperature, so it has a relatively low melting point, thus a low freezing point. It also has a relatively large k_f, 9.10 ºC·kg solvent/mol solute, which is good for estimating the molar mass of a solute because it will allow us to see a greater ΔT_f relative to a solvent with a lower k_f.

Procedure: For this experiment you will need a 150 ml beaker, two 400 ml beakers, a large test tube (25 x 150 mm), a tripod stand with wire mess, a thermometer, a stirring loop and a Bunsen burner.

Freezing point of pure t-butanol:

Place a 150 ml beaker on a top loader balance and tare it. Place a clean, dry 25 x 150 mm test tube in the beaker and record the mass in the data table, line 1. Fill the test tube about half full with *t*-butanol, reweigh and record this mass in the data table, line 2. Place the beaker and test tube aside for now.

Place about 250 ml of hot tap water in one 400 ml beaker and place the test tube containing the *t*-butanol in the hot water; we want to warm the *t*-butanol to about 40 °C. You may use a tripod and Bunsen burner to warm the *t*-butanol in the water bath if needed. (**Do not heat the test tube with a**

direct flame!) Insert the stirring loop into the test tube and then insert the thermometer so that the loop of the stirrer surrounds the thermometer. Periodically stir the *t*-butanol with the stirring loop by an up and down motion while warming it.

Place about 250-300 ml of ice in the other 400 ml beaker and enough cold tap water to just cover the ice. Once the temperature of the *t*-butanol has warmed to about 40 °C, transfer the test tube to the ice-water bath making sure that most of the *t*-butanol is below the surface of the ice-water bath, add more ice if needed. Immediately begin to take temperature readings and record them in the table every 15 seconds while continually stirring the *t*-butanol with the stirring loop in an up and down motion. Continue to stir and take temperature readings every 15 seconds until the *t*-butanol has solidified. When the *t*-butanol has solidified so that the stirring loop will no longer move, stop trying to stir, but continue to record the temperature every 15 seconds for one more minute. **Do not try to pull the thermometer and stirrer from the frozen *t*-butanol!** Doing so may break the thermometer.

Freezing point of solutions:

Place the test tube in the 150 ml beaker, the test tube may now be top heavy, so use caution, or use a 250 ml beaker. Place the beaker with test tube on a top loader balance and tare the balance. With a disposable pipette add about 0.5 g of our unknown to the test tube and record the mass, line 4. Reheat the test tube as before to about 40 °C, this is sample solution 1. If you need fresh hot tap water in which to warm your sample, get it. Try to make sure all your unknown is dissolved in the *t*-butanol. Use the stirring loop to aid the dissolution of the solute, if needed. If you need more ice for your ice-water bath get it. As before, once the temperature is about 40 °C, transfer the test tube to the ice-water bath. Begin stirring and take temperature readings every 15 seconds until the solution has solidified. When the solution has solidified so that you can no longer stir it, stop trying to stir, but continue to record the temperature every 15 seconds for one more minute.

Return the test tube to the 150 ml beaker and place the beaker with test tube on a top loader balance and tare the balance. With a disposable pipette add about another 0.5 g of the unknown to the test tube and record the mass, line 5 (this is sample solution 2). Repeat the melting and temperature recording steps outlined in the previous paragraph.

Clean-Up: Place the test tube back in the warm water bath to melt the solid. Remove the thermometer and stirring loop. Pour the t-butanol solutions into the waste beaker under the fume hood. Wash the thermometer, stirring loop and test tube in the sink with soap and water, dry and return them to the side shelf. Empty all beakers and other glassware you used and return them to your drawer.

Data:

1) Mass of test tube: _____

2) Mass of test tube and *t*-butanol: _____

3) a) Mass of *t*-butanol (line 2 – line 1): _____

   b) Mass of *t*-butanol in kgs: _____

4) Mass of first sample of unknown: _____

5) Mass of second sample of unknown: _____

6) Total mass of unknown in second solution freezing point determination (line 4 + line 5): _____

Data Table:

t-butanol, pure solvent		*t*-butanol plus first sample portion, solution 1		*t*-butanol plus second sample portion, solution 2	
time	temperature	time	temperature	time	temperature

Data Handling, Calculations and Questions:

Use graph paper and plot temperature vs. time for the pure *t*-butanol and for each solution analyzed; make 3 different graphs. Use the discussion in the background section above as a guide and determine the freezing point, T_f, of *t*-butanol and of each solution. Clearly mark on each graph all your data points and the best fit lines you used to determine each freezing point. Determine the ΔT_f of solution 1 by subtracting the T_f of solution 1 from the T_f of pure *t*-butanol. Determine the ΔT_f of solution 2 by subtracting the T_f of solution 2 from the T_f of pure *t*-butanol.

Use the ΔT_f for solution 1 along with the mass of unknown in solution 1, line 4 of the data table, the mass of solvent, *t*-butanol, line 3b of the data table, and the k_f of *t*-butanol, 9.10 ºC·kg solvent/mol solute, in Eq 6 to determine the molar mass, $\mathcal{M}$, of your unknown compound.

Repeat the calculation above for solution 2 remembering to use the total mass of solute, line 6 of the data table, and the ΔT_f for solution 2.

Report:

In your lab report briefly discuss the theory behind why the freezing point of a solution is typically lower than the freezing point of pure solvent.

Reproduce the data from the Data page and the Data Table, pages 5 and 6, and turn in with your report, along with all three graphs.

Make a data and calculations page to report the T_f of pure *t*-butanol and for each solution. Show all calculations and report the molar mass of unknown as determined in each of the two solutions.

Average the two molar masses you determined and calculate the percent difference for each determination vs. the average. This should give you about a 6 or 7 page lab report, not all pages will be full of text.

Reference:

Some information at the following lab experiment was used for this experiment.

http://infohost.nmt.edu/~jaltig/FreezingPtDep.pdf

Experiment 2: The Qual Scheme
Cation Group I

Note About Notation:

When describing chemical reactions by writing chemical formulas and chemical equations, it is important to balance the equations (with respect to charge and mass) and to specify the physical state (solid (s), liquid (l), gas (g), or dissolved in water (aq)) of each chemical species (elements, molecules, salts, or ions). For example,

$$NaHCO_{3\,(s)} + HCl_{\,(aq)} \rightarrow NaCl_{\,(aq)} + H_2O_{\,(l)} + CO_{2\,(g)}$$

or alternately written in ionic form as

$$NaHCO_{3\,(s)} + H^+_{(aq)} \rightarrow Na^+_{\,(aq)} + H_2O_{\,(l)} + CO_{2\,(g)}.$$

For the qualitative analysis experiments in this manual (Experiments 2, 3, and 4), it is understood that most species (all ions) are in aqueous solution. For these solute species, no physical state notation is used. To indicate a solid species (like a precipitate), the formula is underlined. Thus the previous equation might be written as follows:

$$\underline{NaHCO_3}_{\,(s)} + HCl \rightarrow NaCl + H_2O + CO_{2\,(g)}.$$

$$\underline{NaHCO_3}_{\,(s)} + H^+ \rightarrow Na^+ + H_2O + CO_{2\,(g)}$$

Group I Reactions

You will note from the solubility rules that three cations, (Ag^+, Hg_2^{2+}, Pb^{2+}), those having insoluble chloride salts, are easily separated from all others.

$$Ag^+ + 6\text{M}\ HCl(no\ xs) \rightarrow \underset{\text{white}}{\underline{AgCl}}$$

$$Hg_2^{2+} + 6\text{M}\ HCl(no\ xs) \rightarrow \underset{\text{white}}{\underline{Hg_2Cl_2}}$$

$$Pb^{2+} + 6\text{M}\ HCl(no\ xs) \rightarrow \underset{\text{white}}{\underline{PbCl_2}}$$

Silver and mercurous chlorides are very insoluble in water and are not greatly affected by excess chloride. Lead chloride, however, is much more soluble in water and also forms a soluble complex ion

$$Pb^{2+} + 4\,Cl^- \leftrightarrow PbCl_4^{2-}$$

Therefore in Proc 1 we try to keep the excess chloride ion concentration low. In Proc 2 we take advantage of the relative large solubility of $PbCl_2$ and its favorable temperature coefficient to separate $PbCl_2$ from AgCl and Hg_2Cl_2 which we have no chance of dissolving in mere hot water. In Proc 3 final testing for lead involves two separate reactions which each form a precipitate.

$$Pb^{2+} + 0.2\text{M } K_2CrO_4 \rightarrow \underset{\text{yellow}}{\underline{PbCrO_4}}$$

$$Pb^{2+} + 3\text{M } H_2SO_4 \rightarrow \underset{\text{white}}{\underline{PbSO_4}}$$

Since K_2CrO_4 solution is vivid yellow the color of the test solution will be yellow even without the presence of lead: there must be a precipitate for a positive lead test. Note here, as with most of the qual scheme, many cations form yellow insoluble salts with chromate and some form white precipitates with sulfate; therefore, the separation done in Procs 1 & 2 must precede Proc 3.

The second application of hot water to the precipitate from Proc 1 is necessary to dissolve all the $PbCl_2$ which will otherwise confuse your decision about the presence of silver. In Proc 4 concentrated ammonia (aq) [sometimes called ammonium hydroxide (See endnote of this experiment)] is added directly to the white precipitate from Proc 2. If Hg_2Cl_2 is present the following overall reaction will occur.

$$\underset{\text{white}}{\underline{Hg_2Cl_2}} + 2\,NH_3 \rightarrow \underset{\text{black}}{\underline{Hg}} + \underset{\text{white}}{\underline{HgNH_2Cl}} + NH_4^+ + Cl^-.$$

This involves the disproportionation of Hg_2C1_2 in base,

$$\underset{\text{white}}{\underline{Hg_2Cl_2}} + 2\,NH_3 \rightarrow \underset{\text{black}}{\underline{Hg}} + HgCl_2,$$

followed by precipitation of the salt of an unusual anion NH_2^- (amide)

$$HgCl_2 + 2\,NH_3 \rightarrow \underset{\text{white}}{\underline{HgNH_2Cl}} + NH_4^+ + Cl^-$$

In any case, the distinct behavior of white precipitate turning black (or dark grey) identifies the presence of Hg_2^{2+} in the original solution.

If AgC1 is present in the precipitate from Proc 2 it will dissolve on addition of 15M NH_3

$$\underline{AgCl} + 2\,NH_3 \rightarrow Ag(NH_3)_2^+ + Cl^-$$

so that the decantate after the addition of 15M NH_3 should contain any silver as a complex cation. When this decantate is made acidic by 16M HNO_3 the complex is disrupted and AgC1 reprecipitates

$$Ag(NH_3)_2^+ + Cl^- + 2\,HNO_3 \rightarrow \underset{\text{white}}{\underline{AgCl}} + 2\,NH_4^+ + 2\,NO_3^-$$

Group I Procedures

Procedure 1

Take about 6 drops of the "solution to be analyzed" in a test tube and dilute it with an equal volume of water. Add 3 drops of 6M HC1 and mix. If a precipitate appears indicating the presence of one or more Group I ions, centrifuge. "Test for completeness of precipitation" by adding a single drop of 6M HC1, letting it run down the side, and examine for cloudiness where the solutions mix. When you are satisfied that precipitation is complete decant the supernatant. Since analysis of Group II, etc., will not be done, the decantate may be discarded. "Wash" the precipitate with 6 drops of water (discard wash) and take the precipitate to Proc 2.

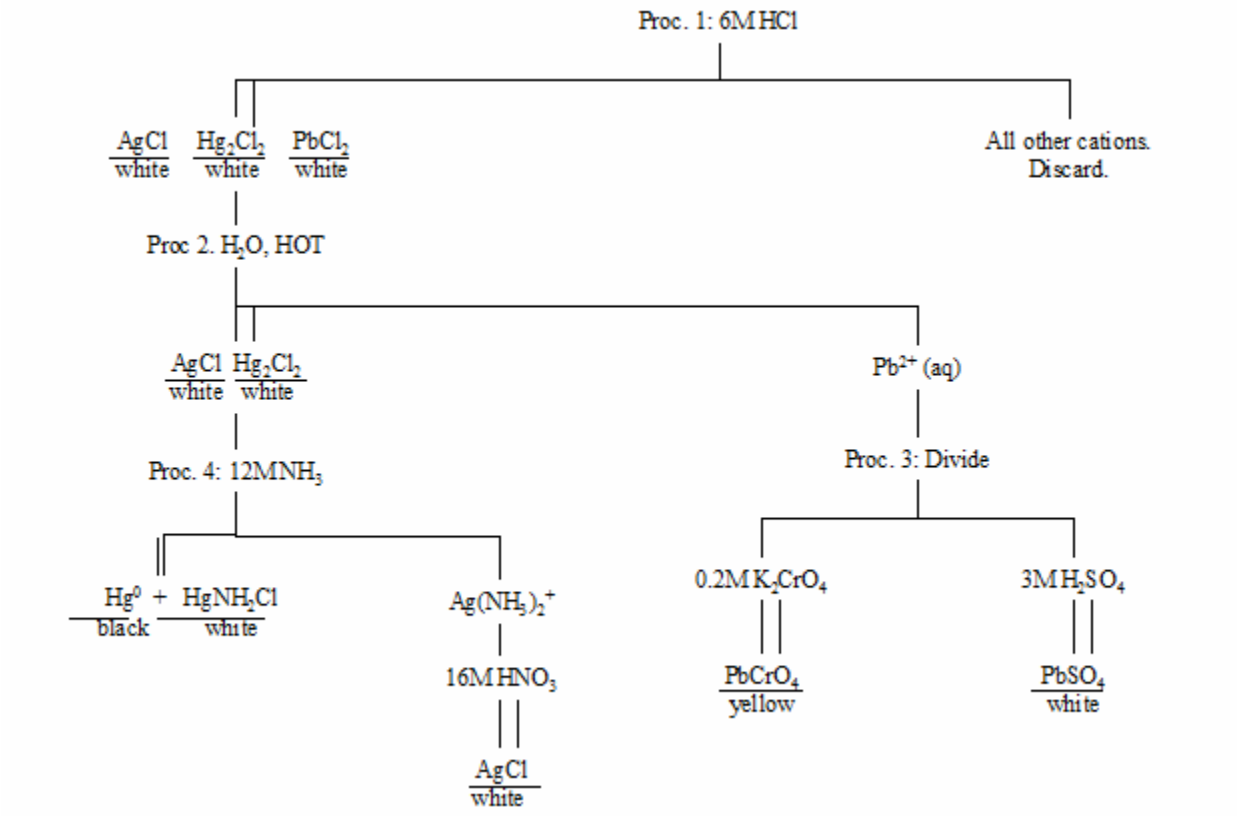
Flow Diagram for Group I: Procedures 1-4

Ag^+, Hg_2^{2+}, Pb^{2+} (Group I)

Cu^{2+}, Cd^{2+}, Sb^{3+} (Group II)

Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+} (Group III)

NH_4^+, Ba^{2+}, Ca^{2+}, $Na+$, K^+ (Group IV)



Procedure 2

Put 20 drops of water in with the precipitate from Proc 1 and place the tube in your boiling water bath, stirring for 1 min. The next operations should be carried out quickly. Get a balance tube ready and spot an available centrifuge before taking the sample out of hot water. Then quickly spin about 30 sec. and decant quickly to minimize cooling. The decantate will contain most of the $PbC1_2$ if present. Test it according to Proc 3. Wash the remaining precipitate with 10 drops of hot water (in the same manner) but discard the wash. Save the precipitate for analysis according to Proc 4.

Procedure 3

Divide the decantate from Proc 2 into two equal parts.
To one part add 2 drops of 0.2M K_2CrO_4. If Pb^{2+} is present a yellow precipitate is produced. To the other part add 2 drops of 3M H_2SO_4, a white precipitate will form if Pb^{2+} is present in solution. The chromate test is more sensitive, there must be precipitate, significant cloudiness at the least.

Procedure 4

Add 5 drops of 15M NH_3 (hood) to the washed white precipitate from Proc 2. Immediate conversion of the precipitate to dark grey or black indicates the presence of mercurous ion, Hg_2^{2+}. If at this stage some white cloudiness persists, it usually is $PbC1_2$, which was not washed out in Proc 2 and will require a little extra centrifugation. Centrifuge and separate the clear decantate.
Take the decantate to the hood and add 16M HNO_3 dropwise (a very vigorous reaction) until a white precipitate appears or until the solution is acid to litmus. The white precipitate is AgC1, appearing as the ammonia complex is decomposed by acid, and proves the presence of Ag^+.

Endnote:

When an aqueous solution is created which contains ammonia ($NH_{3\,(aq)}$) molecules, ammonium cations ($NH_4^+{}_{(aq)}$), and hydroxide anions ($OH^-_{(aq)}$), the following equilibrium is established.

$$NH_{3\,(aq)} + H_2O_{\,(l)} \rightleftarrows NH_4^+{}_{(aq)}) + OH^-_{(aq)}.$$

This equilibrium is strongly shifted to the left. Thus, regardless of how the solution was prepared, ammonia is by far the major component (other than water). Hence the solution should be labeled as aqueous ammonia, rather than as aqueous ammonium hydroxide. You will find that under the hood, it is erroneously labeled as 15M ammonium hydroxide. Don't be confused if the lab manual calls for 15M ammonia.

Experiment 3: The Qual Scheme
Selected Cations in Group IV

Note: Procedures start with Procedure 19, rather than Procedure 1 because this is part of an extensive qual scheme containing Cation Groups I, II, III, and IV. We did not investigate Groups II and III, and will examine only three of the five cations in Group IV.

In Proc 19 we test for the presence of the ammonium ion outside the flow of the qual scheme. The test depends on the volatility, thus mobility, of NH_3 which is readily formed from NH_4^+.

$$NH_4^+(aq) \; + \; 8M \;\; NaOH \;\; \rightarrow \;\; NH_3 \uparrow \; + \; H_2O \; + \; Na^+$$

$$NH_3 \; + \; H_2O \;\; \rightarrow \;\; NH_4^+ \; + \; OH^- \; (\text{litmus} \rightarrow \text{blue})$$

Barium is separated in Proc 20 by precipitation as the sulfate.

$$Ba^{2+}(aq) \; + \; 0.2M \;\; (NH_4)_2SO_4 \;\; \rightarrow \;\; \underset{\text{white}}{\underline{BaSO_4}} \; + \; 2 \;\; NH_4^+$$

Calcium is separated in Proc 21 by precipitation as the oxalate, then dissolved for the flame test.

$$Ca^{2+}(aq) \; + \; 0.2M \;\; (NH_4)_2C_2O_4 \;\; \rightarrow \;\; \underset{\text{white}}{\underline{CaC_2O_4}} \; + \; 2 \;\; NH_4^+$$

$$CaC_2O_4 \; + \; 6M \;\; HCl \;\; \rightarrow \;\; Ca^{2+} \; + \; 2 \;\; Cl^- \; + \; H_2C_2O_4$$

Flame Test Procedures

Your flame tester consists of a 2 – 3 inch piece of nichrome wire with one end fused into a glass rod to act as a handle. The other end is shaped into a loop of about 2-mm diameter. If dipped into an aqueous liquid solution, the loop will support a thin film of the liquid.

Use a small but hot flame for the test (usually the hottest part). Position yourself so that the flame has a background of the black bench top. Then dip the wire loop in the solution to be tested and in to the flame; watch for color. Be patient and just keep doing it.

We rely on flame test for barium and calcium. Sodium (which is also in Group IV but for which we are not testing) gives *fluffy* yellow (to orange) flame and is so intense and persistent that when it is present all other flame tests are hard (or impossible) to see. Aqueous solutions, on standing in glass containers, will leach sodium ions from the glass and give a positive sodium flame test.
The 'apple' green barium flame is also easily seen in the absence of sodium but is difficult with sodium present. In Proc 20 you will try to dissolve washed $BaSO_4$ for a flame test. The washing is to reduce the sodium present. However, $BaSO_4$ is scarcely soluble and you will need to flame it

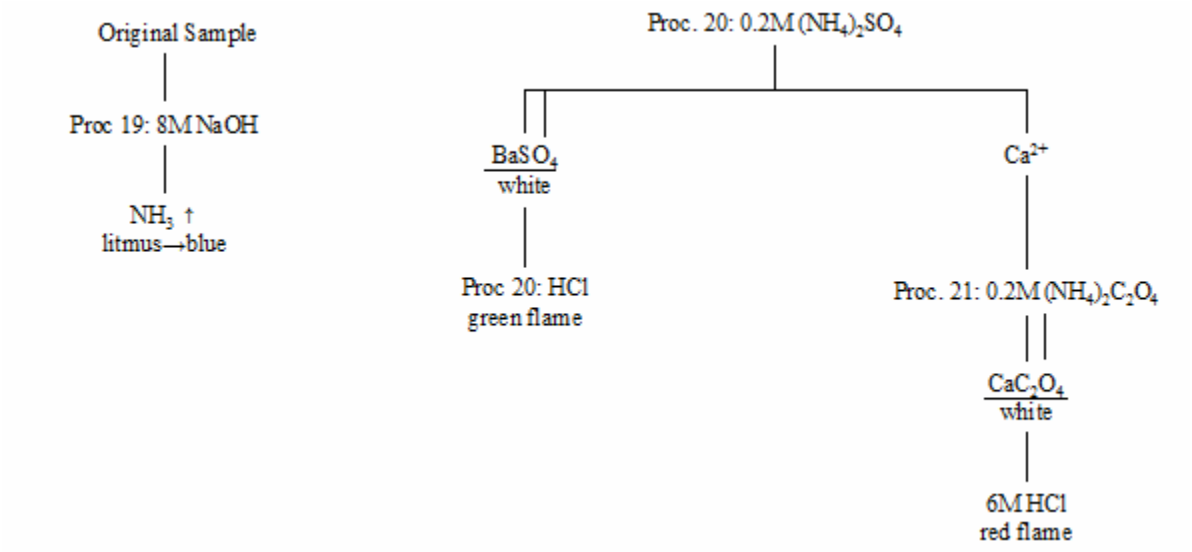
repeatedly. After several tries, barium (probably as the oxide) often tends to build up on the wire making the test easier to see.

The calcium flame is a distinct brick-red but always of short duration and seems to sputter. However, if you allow calcium oxide to build up on the wire through several flamings, then dip once into l2M HCl, this often gives a more intense and more persistent test.

When starting flame test you should clean your wire thoroughly with l2M HC1 a couple of inches deep in a test tube, repeatedly dipping and burning for a sustained period until the yellow-orange sodium flame is minimized and no other flame color is noted. If your wire becomes too dirty you could clip off the worst part and role yourself another loop or install a new piece of wire.

Flow Diagram for Group IV : 19-21

Ba^{2+}, Ca^{2+}, NH_4^+
(all colorless)



Group IV Procedures

Procedure 19

The test for ammonium ion is performed on the most original, unadulterated, sample you have. We will do the procedure so as to include a reagent blank test. Using a clean casserole mix a few drops of water and a few drops of 8M NaOH. Cover this with a watch glass which has a wet piece of red litmus stuck to it on the bottom so it faces the solution in the bottom of the casserole. Now warm the casserole by holding it over your water bath (do not heat on direct flame). Now watch the litmus paper; if it turns blue in under a minute there is too much NH_3 in the air or in your reagents. If not, lift the watch glass and drop in a few drops of the solution to be tested. The litmus should turn blue smoothly, starting from the edges, within 30 seconds for a positive ammonium test.

Note: An astounding number of students either use a sample to which an ammonium reagent has been added or use NH_3 instead of NaOH in the procedure.

Procedure 20

This is a good time to do a flame test on your Group IV sample. Consult the special section on flame tests just prior to Proc 19. Use 6 drops of a Group IV sample.

Add a single drop of 0.2M $(NH_4)_2SO_4$, mix and look for the beginnings of white precipitate. Add one more drop; if there is still no precipitate present, there is no Ba^{2+}. Take the solution on to Proc 21. If a precipitate, $BaSO_4$, shows up, centrifuge and test for complete precipitation by sliding in one more drop of $(NH_4)_2SO_4$ solution. Do not add more than 4 drops altogether. Centrifuge, decant, and take the decantate to Proc 21. Wash the precipitate with two 10-drop portions of hot water to free it of sodium ion. Attempt to dissolve the washed precipitate in 3 drops of 12M HC1, with heating and stirring. Do a flame test for barium. However, you will proba1y have to depend on the white precipitate to prove the presence of Ba^{2+}.

Procedure 21

Test the decantate from Proc 20 by first adjusting its pH to just basic (to litmus) by adding 5M NH_3 one drop at a time, testing after each drop. Then add 2 drops of 0.2M $(NH_4)_2C_2O_4$. If no c1oudiness appears, no calcium is present. If a white precipitate, CaC_2O_4, is seen, test for complete precipitation but limit the $(NH_4)_2C_2O_4$ additions to no more than 5 drops. Centrifuge, separate, and discard the decantate. Wash the precipitate twice with 10-drop portions of hot water then dissolve it in a minimal amount (2-3 drops) of 6M HC1 (kit). Flame test this solution to confirm the presence of Ca^{2+}.

Experiment 4: The Qual Scheme

Selected Anion Analysis

Anion Elimination Tests

In this experiment you will analyze for the presence of five anions. The knowns are provided as sodium salts (all white crystals) and 0.2M solutions of the same salts. The anion unknown provided is a mixture of the solids ground together. While many anions are known by their intrinsic color, none of these five are colored. Nor will there be any keys to identification by knowing the cation since all sodium salts are soluble. Known samples are to be used separately in three experiments described below. In these experiments you may want to join with a partner.

Experiment 1 (Essentially Procedure 22)

Using a few drops of each of the 0.2M solutions of anion knowns in separate labeled tubes, add 0.2M $AgNO_3$. Note which anions produce precipitates (all are insoluble silver salts) and note the color of each. For each anion write an equation of this form:

$$Cl^-(aq) \; + \; 0.2M \;\; AgNO_3 \;\rightarrow\; \underline{AgCl} \; + \; NO_3^-{}_{(aq)}.$$

white

Where precipitates occurred, centrifuge the sample and discard the decantate. Treat the precipitates with 3M HNO_3 (watch for bubbles) to find which dissolve. Write equations for those silver salts which dissolve in 3M HNO_3 in this form:

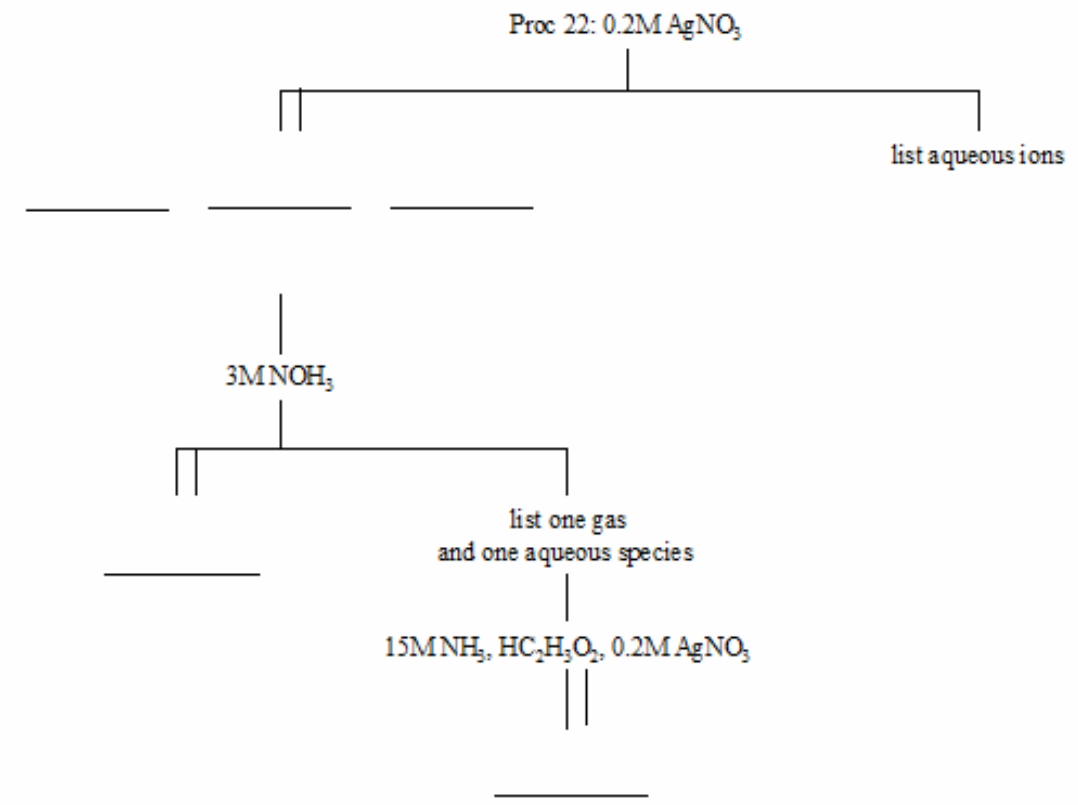
$$AgBO_2 \; + \; 3M \;\; HNO_3 \;\rightarrow\; Ag^+ \; + \; NO_3^- \; + \; HBO_2 \;\; (or \;\; H_3BO_3)$$

Finally, for those silver salts which did dissolve in acid, make those solutions just basic with 15M NH_3, then just acidic with 5M $HC_2H_3O_2$ and add two drops of 0.2M $AgNO_3$. Note which analyte anions form their silver salts.

Fill out the flow diagram "Anion Experiment One" with the formulas of products and colors on the basis on your experimental results. Try to get this right because you'll need to consult it later. Because testing a basic solution with silver nitrate may cause the precipitation of AgOH, you should also do this experiment. Take one small drop of 8M NaOH and dilute it to l0mL in your 10-mL graduated cylinder, mix thoroughly. Take about one half mL of this, and add a drop of 0.2M $AgNO_3$. Observe the brown precipitate. When testing basic salts such as Na_2CO_3, this brown precipitate may surprise you.

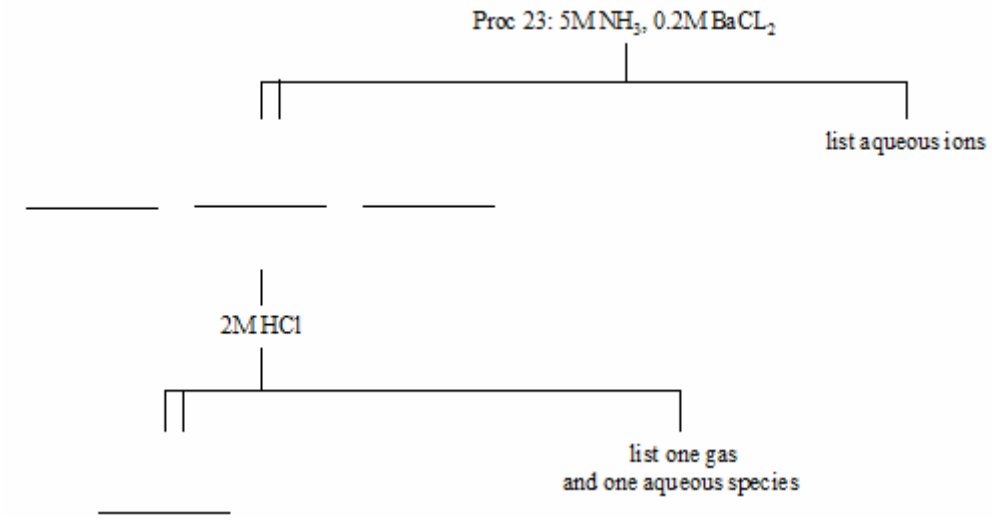
Anion Experiment One Diagram

$BO_2^-, CO_3^{2-}, Cl^-, NO_3^-, SO_4^{2-}$



Anion Experiment Two Diagram

$BO_2^-, CO_3^{2-}, Cl^-, NO_3^-, SO_4^{2-}$



Experiment 2 (Essentially Procedure 23)

Using two drops of each of the known solutions in separate labeled tubes, first add a drop of 5M NH_3 to each. Then add 2 or 3 drops of 0.2M $BaCl_2$. Note which produce precipitates and their color. Write equations for precipitate formations in this form:

$$SO_4^{2-} + 0.2M\ BaCl_2 \rightarrow \underline{Ba(SO_4)} + 2\ Cl^-$$
white

Where precipitates are formed, centrifuge and discard the decantates. Treat the precipitates with 2M HC1 (look for bubbles). Write equations for precipitate dissolution in acid in this form:

$$Ba(BO_2)_2 + 2M\ HCl \rightarrow 2HBO_2 + Ba^{2+} + 2Cl^-$$

Fill out the flow diagram "Anion Experiment Two" with the formula of products and colors on the basis of your experimental results.

Experiment 3 (Essentially Procedure 24)

Take a small pinch of each of the five known sodium salts of the anions in five separate dry test tubes and treat each successively with 2 or 3 drops of 18M H_2SO_4. At this time let us remind you how corrosive is concentrated H_2SO_4. Treat it with great respect. Don't point the tube towards anyone, especially later when heating. And of course many acid gases are produced; smell them only by wafting. As you add the conc H_2SO_4, watch for effervescence (bubbles) and discoloration in the acid solution.

Two of the five salts produce gases. Carbonates produce the mildly acid, colorless, odorless gas CO_2, with any strong acid solution. But the other will bubble only with very concentrated strong acids. Chlorides, on treatment with 18 M H_2SO_4 produce HC1, a colorless sharply acidic gas which fumes in moist air.

Write two equations for the formation of these gases.

_____

_____

Then, with the three salts which did not produce gases, take each mixture and heat it carefully till hot and look for further activity. You will note that nitrate produces yet another yellow brown gas by decomposition of the nitric acid formed.

$$2\ NaNO_3 + 18M\ H_2SO_4 \xrightarrow{\Delta} HNO_3 + Na_2SO_4.$$

$$4HNO_3 \rightarrow 2H_2O + O_2 + 4NO_2(yellow\ brown\ gas)$$

Procedure 22

When analyzing the "anion unknown," remember that you must interpret the results in view of the fact that more than one anion is present. In the case of 'single salt' unknown consider whether any acid was used to put the salt in solution.

Place three drops of the solution to be analyzed in a test tube and add 2 drops of 0.2M $AgNO_3$. Note the color of any precipitate. Centrifuge and test for complete precipitation with 0.2M $AgNO_3$. Centrifuge and discard the decantate. Treat the precipitate with plenty of 3M HNO_3, look for bubbles and any remaining precipitate. Centrifuge and treat the decantate with 15M NH_3 dropwise until just basic, then with 5M $HC_2H_3O_2$ until just acid. Add another drop of 0.2M $AgNO_3$ and note the color of any precipitate. Under these conditions no problem with AgOH or Ag_2O should occur.

Procedure 23

As with Proc 22 interpretation will depend on whether the sample has several or a single anion. To three drops of solution to be analyzed add 5M NH_3 until the sample is just basic, usually one drop if the sample had not been acidified. Add 2 drops of 0.2M $BaCl_2$. If a precipitate is produced, isolate the precipitate and treat it with 6M HCl. Look for bubbles and note if any precipitate remains.

Procedure 24

Treat a small pinch of the solid unknown to be tested with 3 drops of 18M H_2SO_4. Look for bubbles, color in the solution, color in the gas, and test the gas with wet blue litmus. If strongly acid, colored gases are not observed, carefully heat the mixture over a small flame. Now yellow-brown gas on heating indicates nitrate. These latter tests are usually feasible only if no strongly acidic gas producing anions are present.

Specific Anion Procedures

Procedure 25 Test for Borate Ion

With a small quantity of the solid salt to be tested for borate in a casserole, add 3 drops 18M H_2SO_4 (hood) and 20 drops of methanol. Heat this mixture over a burner in the hood about 5 seconds then set it afire by tipping the casserole so the flame lights the fumes. The immediate appearance of a green flame indicates the presence of borate ion. Though the cations Ba^{2+} and Cu^{2+} have distinct green flames they are not volatile and don't give the immediate color.

Equations for Procedure 25

$$NaBO_2 + H^+ + 3CH_3OH \rightarrow (CH_3O)_3B + 2H_2O + Na^+$$

$$2(CH_3O)_3B + 9O_2 \xrightarrow{ignite} 6CO_2 + 9H_2O + B_2O_3(s)$$

Procedure 26 Test for Carbonate Ion

Place a small amount of solid sample of the salt or mixture to be tested in a dry test tube. Get about one mL of saturated $Ba(OH)_2$ from the reagent shelf. If this solution is not clear, centrifuge it and draw some up in your Pasteur pipet. Now, squirt a portion of 2M HC1 onto the solid you are testing. If carbonate is present there will usually be vigorous effervescence. Insert the Pasteur pipet about half way into the tube and squeeze out a drop so that it hangs on the pipet. Immediate clouding of the suspended drop implies the presence of CO_2, thus carbonate. If any $Ba(OH)_2$ is dropped in the solution it doesn't matter.

Equations for Procedure 26

$$Na_2CO_3 + 2M\ HCl \rightarrow 2Na^+ + 2Cl^- + CO_2\uparrow + H_2O$$

$$CO_2 + satd\ Ba(OH)_2 \rightarrow \underline{BaCO_3}$$

white

Procedure 27 Test for Sulfate Ion

Use a few drops of the solution to be tested and acidify it with 6M HCl. Add one or two drops of 0.2M $BaCl_2$. A white precipitate indicates the presence of sulfate ion.

Equation for Procedure 27

$$SO_4^{2-}{}_{(aq)} + 0.2M\ BaCl_{2\,(aq)} \longrightarrow BaSO_{4\,(s)} + 2\ Cl^-_{(aq)}$$

Procedure 28 Test for Chloride Ion

Test for chloride by first acidifying a 5 drop sample with 3M HNO_3. Add two drops of 0.2M $AgNO_3$. A white curdy precipitate proves the presence of Cl^-.

Equations for Procedure 28

$$Ag^+ + Cl^- \longrightarrow \underline{AgCl}\ \text{(white)}$$

Procedure 29 Test for Nitrate Ions

Use only 2 drops in the nitrate test and add 10 drops of 18M H_2SO_4 and mix. Now carefully layer a few drops of freshly prepared $FeSO_4$ solution—do not mix. After a few minutes, you will observe a brown discoloration at the interface between the heavy 18M H_2SO_4 and the lighter $FeSO_4$ solutions. The brown species is $Fe(NO)^{2+}$, nitrosyliron(II) ion, in solution.

Fresh $FeSO_4$, solution — put a pinch of $FeSO_4{\cdot}7H_2O$ in a test tube and add a few drops of 3M H_2SO_4 then add about 2 mL of water. Stir until dissolved.

Equation for Procedure 29

$$3\ Fe^{2+} + NO_3^- + 4\ H^+ \longrightarrow 3\ Fe^{3+} + NO + 2\ H_2O$$

$$NO + Fe^{2+} \longrightarrow Fe(NO)^{2+}\ \text{(brown)}$$

Experiment #5: Qualitative Absorption Spectroscopy

One of the most important areas in the field of analytical chemistry is that of spectroscopy. In general terms, spectroscopy deals with the interactions of radiant energy with matter (i.e., atoms, ions, or molecules) in various physical and chemical states. This energy is usually some type of electromagnetic radiation, abbreviated EMR, consisting of electric and magnetic components. In most spectroscopic methods, only interactions of the electric component of the EMR are of interest.

Electromagnetic radiation exhibits a "dual nature", showing characteristics of both a cyclic wave motion and discrete particles of energy called photons. Wave properties explain such phenomena as reflection, refraction, and optical interference, while particulate properties are required to explain the photoelectric effect and optical emission and absorption processes.

The major cyclic wave motion properties are wavelength (λ) and frequency (ν).The wavelength is the distance between corresponding points on the EMR wave, and frequency refers to the number of complete wave cycles which pass a given point per unit time. Thus, the velocity, c, of the EMR wave is given by the equation: velocity = wavelength x frequency (or $c = \lambda\nu$). EMR is often classified with respect to the number of different energies or wavelengths in the beam of radiation. Monochromatic EMR has only one energy or wavelength; polychromatic EMR has more than one type of energy or wavelength.

The EMR photon characteristics include intensity (P) and energy (E). Intensity describes the number of photons present in the EMR beam or the number of photons emitted by an energy source per unit time. The energy of a photon is given by the equation: $E = h\nu = hc/\lambda$, where "h" is Planck's constant. Thus, the energy of a photon is controlled by the EMR frequency (which is determined by the energy source). As the EMR frequency increases (or the corresponding wavelength decreases), the photon energy increases.

In matter–EMR interactions, radiation may be transmitted (pass through the matter with no measurable effect), absorbed (part or all of the energy is permanently transferred to the matter), or scattered/reflected (the EMR beam direction changes, but no energy is lost). In most chemical systems, absorption is the transition of primary importance. With respect to matter, absorption is viewed as an irreversible, two-step process: (1) energy gain (via transfer of photon energy to the absorbing species, promoting change to a higher energy state followed by (2) energy loss (in which the excited absorber gives up the gained energy via thermal/collisional decay, photochemical reaction, or a photo-luminescence process).

Absorption spectroscopy involves interactions over the entire spectrum, ranging from very high energy gamma-rays (which cause nuclear changes) to very low energy radiowaves (which cause spin alignment changes in the atom). Transitions may involve nuclear, electronic, vibrational, rotational, and spin alignment changes, listed in order of decreasing relative energies. In all absorption processes, however, the EMR photon can be absorbed in the chemical species. That is, absorption is an "all-or-nothing" process.

In the absorption of visible light, the transition involves promoting an outer (valence) shell electron from a low energy or ground state orbital into a higher or excited energy state. When a solution illuminated by white light appears colored, some of the light is absorbed, and the color seen is due to the residue. Such a solution may be described in terms of the colors or the EMR wavelengths which

pass through the solution. Thus, a “blue” solution is one which transmits wavelengths corresponding to the color “blue”. However, it is equally valid (and of more interest chemically) to describe a solution in terms of the colors or wavelengths of light which are absorbed. A “blue” solution then, is one which absorbs the color complementary to blue, namely yellow.

Physiologically, the human eye can detect three primary bands of color: magenta, cyan, and yellow. All perceived colors are various combinations of intensities of light in these three ranges! The absorption of light by three different dye-like compounds in the human eye is the first step in the biochemical process of color vision.

A range of instruments have been developed for spectroscopic applications. The fundamental designs are similar, differing only in the specific components used to perform various functions. Instruments are designated as photometers, spectrometers, or spectrophotometers, depending upon the components utilized in the system. Irrespective of the purpose or application, spectroscopic instruments contain similar components, including:
an energy source (to emit stable, continuous EMR of the appropriate energy), a wavelength-control (to select appropriate wavelengths from the source output), a sample cell (to hold the gas, liquid, or solid absorbing species in the EMR path), a detector (to measure incident and emergent EMR intensities), and a recorder (to give a mechanical or electrical response to the detector output).

Instruments which use only visible light are called “colorimeters”, and the Spectronic 20 is a typical member of this group. The source consists of an incandescent-lamp with a tungsten filament which glows when heated; the cell is a glass cylinder; the wavelength-control system is made up of slits, lenses, and a reflection grating; the detector is a phototube containing a cathode coated with a photosensitive alkali oxide which emits electrons when struck by photons and an anode which collects the released electrons to give a complete flow of electricity; and a meter which converts the phototube current into a digital read-out.

The Spectronic 20 source emits EMR wavelengths over the entire visible region, but not in equal intensities. In fact, the source emits much more red and infrared radiation, while giving off much less violet and ultraviolet radiation.

Conversely, although the detector responds to all visible wavelengths, it is more sensitive toward the more energetic ultraviolet end of the EMR spectrum. This opposing interplay of source intensity and detector sensitivity must he balanced at each different wavelength of interest.
The Spectronic 20 wavelength-control system is rather simple in design and capability. The reflection grating contains 600 grooves/mm and provides a wavelength accuracy of ± 2.5 nm, although the meter scale has a wavelength readability of 1 nm. The grating dispersion is of minor quality, resulting in a nominal spectral width of 20 nm across the entire range from 340 nm to 950 nm. Thus, the instrument can completely separate and differentiate two wavelengths only if they differ by more than 20 nm.

The Spectronic 20’s will generally be turned on and warmed up when the students arrive in the laboratory. If not, the turn-on is as follows: Using the left control, turn the Spectronic 20 on, and allow a five minute warm-up period.

EMR wavelength and visual color correlations

Each student will make a correlation series of wavelengths and perceived colors, using the EMR spectral output of a Spectronic 20 colorimeter. Place a slanted piece of white chalk in a clean, dry

cuvette, and insert the cuvette into the sample compartment. Leave the compartment cover up so the EMR beam can be observed as a reflection on the smooth, slanted surface of the chalk. Leave the left control in the counter-clockwise position, turned just enough to turn on the instrument. Looking down at the chalk, turn the right control until the color band can he clearly seen.

Set the top wavelength dial to 400 nm, and examine the color of the light band shown on the chalk. Record a personal description of the observed color in Table I. Change the wavelength dial to a new setting (using 25 nm intervals) and repeat the process. It may be necessary to change the position of the right control to sharpen the color band as the wavelength is changed. Record the associated color at each wavelength setting from 400 nm to 625 nm.

Bausch & Lomb Spectronic 20^{R}

Table I

λ, nm	Color Description

Dye absorption spectrum

Select a dye solution from the reagent shelf. If working in groups, your instructor will instruct you as to whether each student should select a different dye solution. or whether the same dye solution will be used by each member of the group. Record the name of the dye (if it is provided) and the visible color exhibited by the solution. Fill a clean cuvette half full with the dye solution, and fill a second cuvette with deionized water to use as a blank or reference solution.

With the Spectronic 20 cell compartment empty and closed (and the instrument turned on and, warmed up), set the wavelength dial to the desired starting wavelength (i.e., 400 nm). Adjust the left control to place the meter needle or digital display exactly on 0% T. Place the blank solution in the cell compartment, close the cover and adjust the right control to set the needle or digital display to 100% T. Each time the wavelength is changed, this standardization procedure must he carried out.

Replace the blank solution with the dye solution, close the cover, and observe the needle position on the meter scale or digital readout. Record the experimental percent transmittance and absorbance, making sure to read the scales correctly. Since the transmittance scale is linear and the absorbance scale is exponential, it is better practice to record both experimental %T and A values, and then use the %T value to calculate a more precise value for absorbance, using the equation: $A = 2 - \log \%T$.

Complete Table II entries at each wavelength from 400 nm to 625 nm, using wavelength increments of 25nm to cover the spectral range. Remember to zero the instrument with the blank solution at each new wavelength. Allow each member of the group to read and record experimental % T and A values for his or her indicator solution before changing the wavelength.

Table II

λ, nm	Experimental A	Experimental %T	Calculated A

Data treatment and report

A three-page report must be submitted by each student. Each page must contain a complete heading, listing: experiment title, student name, names of members in the group, instructor's name, class number and section number, and date on which the report was submitted.

The first page of the report will contain a neat, complete titled, copy of the data given in Table I. All information taken in the laboratory procedure must be included, using a format identical to that of Table I.

The second page of the report will consist of a titled copy of Table II, giving all data recorded in lab. In addition, the specific name of the dye must be reported if known. The information should he examined determine the light colors and wavelengths which are best transmitted by the dye solution as well as the colors and wavelengths which are best absorbed. Conclusions about the regions of transmittance and absorption should be expressed in a summary statement.

The third and final page of the report will consist of the absorption and transmittance spectra of the indicator solution. On the same sheet of graph paper (18 x 24 cm), make two separate plots, one of % T vs. λ and a second of calculated A vs. λ. The following specifications and instructions must be obeyed in performing the graphical data treatment.

The long axis must be used as the abscissa (horizontal axis), upon which the wavelength (in nm's) is scaled in increasing values from left to right. The left ordinate (vertical axis) is to be used for the calculated absorbance values, while the right ordinate (vertical axis) will be the % T axis.

Use independent linear scales for each axis, and maximize the scale values to use most of the graph paper. The % T axis should be scaled to go from a starting value of 0% T to an upper value of 100% T. The A axis should begin at 0, but the upper value should he chosen to expand the data points over most of the graph sheet.

Connect the data points of each curve in a smooth, continuous line. Do not make connect-a-dot curves. Include a plot title and complete heading on the graph page, and make sure to identify the specific dye used in the spectroscopic measurement.

Experiment 6: Equilibrium and Le Châtelier's Principle

Objective: The objective of this experiment is to examine equilibrium systems and the effects of stresses placed on those systems.

Background: Not all reactions go to completion, or use up all of one of the reactants. In some chemical reactions there is always some amount of products and some reactants present. In these chemical systems two competing processes are occurring, the forward reaction and the reverse reaction of that system. Both the forward and the reverse reactions are taking place simultaneously. When the rate of the forward reaction equals the rate of the reverse reaction, the system is at **equilibrium**. The concentrations of the products and reactants remain constant. That is not to say that the system is static. Both reactions are occurring and are doing so at the same rate, so there is no net change in the concentrations of the reactants or of the products. When writing an equation for a reaction at equilibrium a double headed arrow (↔) or double arrows pointing in opposite directions (⇄) is used. These designations indicate that both the forward and reverse reactions are occurring at the same time.

Any system at equilibrium will remain at equilibrium unless the conditions of the system change. **Le Châtelier's principle** states that a system at equilibrium will respond to a stress on the system in such a way so as to relieve the stress and establish a new equilibrium. The system will have one reaction dominate until the offsetting changes allow the rates of the forward and reverse reactions to be equal again (reestablishing equilibrium). If the forward reaction dominates in order to offset the changes, we say the system "shifts to the right" or "shifts toward products" in order to reestablish equilibrium conditions. This will increase the concentration of the products and decrease the concentration of the reactants. However, if the reverse reaction dominates in order to offset the changes, we say the system "shifts to the left" or "shifts toward reactants" to reestablish equilibrium conditions. This will increase the concentrations of the reactants and decrease the concentrations of the products. The changes will not return the system to the original conditions, but to a new set of conditions that establish equilibrium.

For endothermic reactions, heat can be considered a reactant, since heat is absorbed by the system from the surroundings. When heat is added to an endothermic reaction, the system will shift toward the products. For exothermic reactions, heat can be considered a product, since heat is released from the system to the surroundings. When heat is added to an exothermic reaction, the system will shift toward the reactants.

In this experiment, you will analyze two equilibrium systems. The reaction for the first system is shown below and produces one colored complex ion.

$$Fe^{3+}_{(aq)} + 6\ SCN^{-}_{(aq)} \rightleftarrows [Fe(SCN)_6]^{3-}_{(aq)} \qquad \text{Eq 1}$$

The $[Fe(SCN)_6]^{3-}$ complex ion forms a blood-red solution. We can induce a shift in this equilibrium, and in so doing induce a color change in the solution, which we can monitor visually and by determining the absorbance of our system using the Spec 20.

The reaction for the second system is shown below and has two colored complex ions.

$$[CoCl_4]^{2-}_{(alc)} + 6\ H_2O_{(l)} \rightleftarrows [Co(H_2O)_6]^{2+}_{(alc)} + 4\ Cl^-_{(alc)} \qquad \text{Eq 2}$$

The $[CoCl_4]^{2-}$ complex ion produces a brilliant blue color while the $[Co(H_2O)_6]^{2+}$ ion produces a rose-pink color. Again by observing changes in the color and by monitoring the absorbance of the system resulting from placing a stress on the system we can monitor the equilibrium of the system. For each of the two systems you will make observations of the results from stresses placed on each system, and use the information you collect to determine whether the reaction in each system is endothermic or exothermic.

Procedure: Begin by setting up a hot water bath using a 250 mL beaker. The water does not have to reach boiling, but it should be hot. Set up an ice water bath in a 150 mL beaker by filling the beaker about 2/3 full with ice and adding about 25 mL water. *For each experiment (Part I and Part II), each group of students working together should assemble 6 clean test tubes (15 × 125 mm) and 2 clean Spec- 20 cuvettes.*

Part I: Fe(NO3)3 + KSCN Equilibrium

1. Using a 100 mL graduated cylinder, transfer 50 mL of 0.002 M KSCN into a clean 100 or 150 mL beaker. Observe any color in the solution. Using a disposable pipet, add 4 drops of 0.2 M $Fe(NO_3)_3$ to the solution in the beaker and mix well. Observe the color of the solution. This is your equilibrium solution as described by eq. 1 above.

2. Prepare 6 clean, dry small to medium size test tubes. Add approximately equal amounts of the equilibrium solution prepared in step 1 above to each test tube and label them 1-6. It is important that you use all 50 mL of the equilibrium solution divided into 6 approximately equal parts so that when each is poured into a cuvette, it will cover the entire beam of light in the Spec 20. The first test tube is your control or reference test tube.

3. Add two drops of 0.2 M KSCN solution, side shelf, to test tube 2 and mix well. Observe color changes.

4. Add one drop of 0.2 M $Fe(NO_3)_3$ solution, side shelf, to test tube 3 and mix well. Observe color changes.

5. Add a pinch of solid NaF, side shelf, to test tube 4 and mix well. Observe color changes. Fluoride reacts and coordinates with Fe^{3+}, thus removing it from participating in the equilibrium reaction.

$$Fe^{3+}_{(aq)} + 6\ F^-_{(aq)} \rightarrow [FeF_6]^{-3}_{(aq)} \qquad \text{Eq 3}$$

6. Place test tube 5 in the hot water bath. Place test tube 6 in the ice water bath. After about 5 minutes observe color changes for both.

7. Next, you will use a Spec 20 to measure and record the absorbance of each solution you prepared. The Spec 20 instrument should be set to the desired wavelength (475 nm) and with the cell compartment empty the left control dial should be adjusted to read 0%T. With DI H_2O in your cuvette, place the cuvette in the cell compartment and adjust the right control dial to read 100%T. Remember to make sure the filter lever, front left bottom, is set appropriately for the wavelength you are using.

8. Record the absorbance of the solution in each of the 6 test tubes at 475 nm. Each solution was mixed in a test tube, but should be poured into a cuvette before placing in the Spec 20 for the absorbance measurement. Do not place test tubes in the sample compartment of the Spec 20 even if the tubes fit. The optical quality of the cuvettes is higher and more consistent than that of test tubes. For tubes 5 and 6, record the absorbance immediately after removing them from their respective water bath.

9. When your work is complete pour all solutions into the waste container under the fume hood.

Part II: $[CoCl_4]^{2-}_{(alc)}$/ $[Co(H_2O)_6]^{2+}_{(alc)}$ Equilibrium

10. Using a clean, dry 100 mL graduated cylinder, transfer 40 mL of 0.01 M $[CoCl_4]^{2-}$ in alcohol to a clean, dry 100 or 150 mL beaker. **(The beaker and the graduated cylinder must be clean and DRY!!!!)** Observe the color of the solution. Using a disposable pipet, add 30 drops DI water to the solution in the beaker and mix well. Observe the color of the solution. This is your equilibrium solution.

11. Prepare 6 clean, dry small to medium size test tubes. **(Again, the test tubes must be DRY!!)** Add approximately equal amounts of the equilibrium solution prepared in step 9 above to each test tube and label them 1-6. It is important that you use all 40 mL of the equilibrium solution divided into 6 approximately equal parts so that when each is poured into a cuvette and placed in the Spec 20, it will cover the entire beam of light in the instrument.The first test tube is your control or reference test tube.

12. Add one drop of concentrated HCl to test tube 2 and mix well. Observe color changes.

13. Add 3-4 drops DI H_2O to test tube 3 and mix well. Observe color changes. Since ethanol is the solvent, water would be considered a reactant and not a solvent.

14. Add one drop 0.02 M $AgNO_3$ to test tube 4 and mix well. Ag^+ in solution reacts with Cl^- to precipitate as AgCl according to the following equation:

$$Ag^+_{(alc)} + Cl^-_{(alc)} \rightarrow AgCl_{(s)} \qquad \text{Eq 4}$$

After a couple of minutes, centrifuge for about 2 minutes and observe color changes in the supernanant.

15. Place test tube 5 in the hot water bath. Place test tube 6 in the ice water bath. After about 5 minutes observe color changes for both. Be sure to turn off the bunsen-burner flame when test tube 5 is placed in the hot water because it might ignite the escaping alcohol vapors.

16. Next, you will use a Spec 20 to measure and record the absorbance of each solution you prepared. The Spec 20 instrument should be set to the desired wavelength (655 nm) and with the cell compartment empty the left control dial should be adjusted to read 0%T. With alcohol in your cuvette, place the cuvette in the cell compartment and adjust the right control dial to read 100%T. Remember to make sure the filter lever, front left bottom, is set appropriately for the wavelength you are using.

17. Record the absorbance of the solution in each of the 6 test tubes at 655 nm. A wavelength of 655 nm is used because this wavelength gives us the greatest differences in the absorbances for the solutions you are preparing. Remember, mixing of solutions is done in test tubes: absorbance measurements are done in cuvettes. For tubes 5 and 6, record the absorbance immediately after removing them from their respective water bath.

18. When your work is complete pour all solutions into the waste container under the fume hood.

19. Fill in the information in the tables of the Data Report in preparation for your lab report and make sure you answer the questions.

Data Report:

Name:_____ Partner:_____

Part I:

Test Tube	Absorbance, 475 nm	Color observations	Shift from Equilibrium, toward reactants or toward products
1			
2			
3			
4			
5			
6			

Part II:

Test Tube	Absorbance, 655 nm	Color observations	Shift from Equilibrium, toward reactants or toward products
1			
2			
3			
4			
5			
6			

Questions:

As part of your lab report answer each question below for both Part I and Part II above:
1. Explain how each change affected the equilibrium in terms of Le Châtelier's principle.
2. Is the forward reaction endothermic or exothermic?

Experiment # 7: Quantitative Absorption Spectroscopy

When radiant energy passes through a solution containing an appropriate absorbing species, some of the EMR is absorbed. Absorption of energy in this manner has been recognized for more than two centuries and accounts for the fact that colorimetric and spectrophotometric methods are the most prevalent analytical techniques. Colorimetry refers to determinations which employ only visible light, while photometry implies the use of photoelectric instruments. Spectrophotometric methods often utilize radiation outside the visible region, particularly EMR in the infrared and ultraviolet ranges.

Two elementary laws make up the basic foundations of quantitative absorption spectroscopy. The first law was formulated by Bouguer in l729 (and later restated by Lambert in 1760). It says: each absorbing substance layer of the same thickness absorbs an equal fraction of the EMR passing through it. In mathematical terms, absorption increases exponentially with the thickness of the absorbing species.

The second basic law is that of Beer: the absorption of a monochromatic EMR beam increases exponentially with the concentration of the absorbing species. Both laws state the same fundamental aspect of absorption spectroscopy: namely, that absorption is proportionate to the number of absorbing species with which the EMR beam comes in contact. Thus, neither law is functionally complete without the other. No deviations from Bouguer's Law are known, however, deviations from Beer's law are fairly common.

The two laws are usually combined into a single relationship commonly referred to as "Beer's Law" and are expressed in the following mathematical relationships.

$$- \text{Log } (P/P_o) = - \text{Log } (T) = a\ b\ C = A,$$

where "P" is the emergent EMR intensity passing through the absorbing medium, "P_o" is the incident EMR intensity going into the absorbing medium, "T" is defined as transmittance, "a" is the absorptivity constant whose value depends upon the EMR wavelength and the chemical nature of the absorbing species, "b" is the cell width or length of the light path though the absorbing medium, "C" is the concentration of the absorbing species in the medium, and "A" is defined as absorbance.

It should be obvious from the above relationships that if all variables except absorber concentration are held constant (i.e., the same wavelength, cell length, light source, etc., is used in all measurements), the absorbances of a solution series will be directly related to the absorber concentrations of the solutions. Thus, absorption spectroscopy is a direct quantitative analysis method for materials which obey Beer's Law within acceptable limits.

The divalent copper cation, Cu^{2+}, forms a coordinate covalent complex with ammonia, as: $Cu(NH_3)_4^{2+}$. This complex species absorbs strongly in the visible region of the EMR spectrum from 550—650 nm. The wavelength of maximum absorption lies between 600—620 nm, nominally at 610 nm. However, the strongly absorbing species is formed only in an excess of the complexing agent, NH_3. If an excess of ammonia is not present in the solution, non-absorbing complexes may be formed instead of the tetraamminecopper (II) species, and the Beer's Law relationships will not be observed.

Preparation of standard copper complex series

A 1.000 mg Cu^{2+} /mL standard solution is prepared by dissolving 3.928 grams of $CuSO_4 \cdot 5H_2O$ to 1.000-liter with deionized water. The copper standard and a 7.5 N $NH_{3\,(aq)}$ solution are provided in labeled bottles on the reagent table. Burets will be used to deliver measured portions of these two reagents as well as deionized water (from the large storage bottle on the lab benchtop).

Each group of students working together should assemble six clean test tubes (15 x 125 mm) and two clean Spectronic 20 cuvettes. Using the burets, each filled with the proper reagent, prepare the solution mixtures listed in Table I. Run the specified volume of each reagent into a labeled test tube, cap the tube with a rubber stopper, and thoroughly mix the solutions. Rinse a cuvette with the copper complex standard, and then fill the cuvette about half-full with the solution. Standard sample #6 will be used as the blank or reference solution to calibrate the Spectronic 20 to read 100%T at 610 nm.

Table I

Sample #	mL Cu^{2+} standard	mL deionized H_2O	mL 7.5 M $NH_{3\,(aq)}$
1	9.00	0.00	1.00
2	7.00	2.00	1.00
3	5.00	4.00	1.00
4	3.00	6.00	1.00
5	1.00	8.00	1.00
6	0.00	9.00	1.00

Note that 1.00-mL of the 7.5 M $NH_{3\,(aq)}$ is used in each of the solutions: this provides an excess of ammonia to insure that all complexes are forced into the $Cu(NH_3)_4^{2+}$ species. Also, the total volume of each solution is 10.00mL.

Calculate the theoretical concentration of the copper-ammonia complex, using the simple dilution equation:

$$C_{STD}(\text{mg Cu/mL}) = C_{STOCK\ STD}(\text{mg Cu/mL}) \times \frac{\text{mL } Cu^{2+} \text{ Stock Std.}}{10.00 \text{ mL}}$$

Record the complex concentration of each solution in Table II.

Preparation of unknown copper complex solution

Several soluble copper (II) salts are provided in numbered bottles on the reagent shelf. Your instructor will tell you whether each member of a group should analyze a different salt to determine the copper content, or whether only one salt will be analyzed by the group. When selecting an unknown solid, record the unknown # written on the container for later inclusion in the experiment report.

Using the technique of weighing-by-difference (as explained by the lab instructor), accurately weigh out 0.4-0.6 grams of an unknown copper (II) salt into a clean beaker (150-mL or larger). Record the sample mass as precisely as the balance is capable of measuring, that is, to the third decimal place.

Add about 100 mL of deionized water to the solid in the beaker, and make sure the copper salt dissolves completely. Transfer the salt solution into a clean, 250.00-mL volumetric flask. Rinse the beaker with several portions of deionized water, collecting the washings in the flask. These rinses are made to insure quantitative transference of the copper solution to the volumetric flask. Add deionized water to the flask until the solution level reaches the calibration mark on the flask neck. Stopper the flask, and mix the solution thoroughly.

Note: Since this procedure prepares 250 mL of unknown copper solution, you may be asked to provide unknown solution for other students in other groups, or you may be asked to acquire unknown solution from another group. This determination will be made by the lab instructor.

Each group will need three test tubes for the copper unknown. Pour a small amount of the unknown copper solution into a clean buret in order to rinse it, then fill the buret with the unknown copper solution. Withdraw three 9.00-mL samples of the copper salt solution each into three clean, dry test tubes. Add 1.00-mL of the 7.5 M $NH_{3\,(aq)}$ solution (measured from a buret) to each of the test tubes cap with stoppers, and mix the solutions thoroughly. The resulting copper-ammonia complex solution is now ready for use in the spectroscopic analysis.

Spectroscopic measurements for Beer s Law plot

If the Spectronic 20 is not already turned on, using the left control to turn it on and allow at least five minutes for it to warm up. Adjust the wavelength dial to 610 nm. With the cell compartment empty and closed, adjust the left control to set the meter needle (or digital display) at 0% T.

Place the cuvette containing the blank/reference solution (standard sample # 6) into the cell compartment, close the cover, and adjust the right control to position the meter needle (or digital display) at 100% T. The instrument is now calibrated at the wavelength setting of 610 nm.

Working in groups of no more than three students, place each copper complex standard in turn into the cell compartment. Read and record the values in terms of % T and A values, listing the data in Table II. It is good practice to measure experimental values for each solution at least twice to insure that no errors are made. Such readings should show reproducibility to within ± 0.2 %T. After all the standard solutions have been measured, each group should read/record the %T and A values of his/her unknown copper samples, listing the data in Table II. Theoretical values for A should be calculated, using the equation: $A = 2 - \log \%T$.

Table II

Sample	CSTD (mg Cu/mL)	Measured A	Measured %T	Calculated A

On an 18 x 24 cm sheet of graph paper, plot C_{STD} (mg Cu/mL) for the standard series on the abscissa (long, horizontal axis) versus calculated A on the ordinate (short, vertical axis). Select the axis scales to maximize use of the graph paper for the actual data points recorded starting both axes at zero. Use a ruler to draw the best straight line through the plotted data points.

Calculate an average A value for the three unknown sample readings, and determine the concentration of copper complex in the unknown solution by a graphical interpretation of the Beer's Law plot. Mark the position of the average unknown A value on the ordinate, draw a horizontal straight line to intersect the Beer's Law plot, and drop a perpendicular to the abscissa to determine unknown copper complex-concentration, C_{UNK}(mg Cu/mL). Record the numerical value of the unknown complex concentration on the graph paper beside the perpendicular line which intersects the abscissa.

Since 9.00mL of the unknown copper solution in the volumetric flask is diluted by the addition of 1.00 mL of the 7.5 M NH_3 solution (which provides an excess of ammonia to complex all the copper as the tetraammine species), the corrected complex concentration necessary to give the true copper concentration in the volumetric flask is given by the dilution equation:

$$C_{FLASK}\ (\text{mg Cu/mL}) = C_{UNK}\ (\text{mg Cu/mL}) \times \frac{10.00\ \text{mL}}{9.00\ \text{mL}}$$

Using this corrected concentration of copper in the original 250.00 mL solution, the mass of copper, in grams, in the salt sample is given by:

$$\text{grams } Cu^{2+} = C_{FLASK}\ (\text{mg Cu/mL}) \times (250.0\ \text{mL}) \times (0.001\ \text{g/mg})$$

Thus, the percent copper in the soluble copper (II) salt equals:

$$\%\ Cu = \frac{\text{grams } Cu^{2+}}{\text{grams salt}} \times 100\%$$

Each student will submit a two-page report, each page containing a complete heading. The first page should include a neat, titled, completed copy of—Table II. Additional information to be listed are: the unknown number on the copper (II) salt container, the mass of the salt in grams, the concentration of the stock copper standard solution, absorbances of the three unknown complex solutions and the average A value, the unknown copper complex concentration from the Beer's Law plot, the corrected concentration of copper in the flask, the calculated mass in grams of copper in the salt sample, and the calculated percent copper in the salt sample.

The second page should consist of a neat, complete Beer's law plot on the proper type of graph paper. The graph should have a title and a complete heading. The axes should be properly labeled and scaled, and the best straight line should be drawn through the data points of the standard concentration series. All specific instructions must be carried out in the interpretations and operations performed on the experimental data.

Experiment # 8: Qualitative pH titration curves

Procedures involving pH measurements are among the most common analytical techniques. The acidic or basic properties of a compound are important characteristics of the substance and may influence the kinetics or equilibrium systems of chemical and/or physical reactions. Solution pH and pH changes are routinely measured by one of two methods: visual indicators or pH meters. Since most indicator color change intervals cover 2 pH units or more, pH meter (i.e., potentiometric) measurements are inherently more precise and accurate. In addition, it may not be possible to obtain an appropriate indicator, making it necessary to measure pH by potentiometric methods.

A pH meter is actually a high-impedance voltmeter which measures the potential difference between two electrodes or half-cells: a reference electrode (of saturated calomel or Ag/AgCl) of constant potential and a pH indicator electrode (usually having a special glass membrane sensitive to hydrogen ions). The potential of the indicator electrode varies according to the Nernst equation, as:

$$E_{ind} = E^{\circ}_{ind} - 0.059 \log (1/ [H^{+}]) = E^{\circ}_{ind} - 0.059 \text{ pH}.$$

Thus, changes in pH are represented by the changes in the potential of the glass electrode. A recent design innovation has resulted in the combination electrode, a one-piece unit containing both the indicator and reference electrodes in a single structure. (Read about the “glass pH electrode” in the lecture text.)

Graphical methods are used to achieve maximum useful pH data for the investigated chemical system. In an acid-base neutralization titration, the solution pH is plotted against the volume of added titrant. The titration curve of a strong or monoprotic weak acid titrated with a strong base is S-shaped, having two horizontal regions at different levels joined by a vertical section. The first horizontal section represents the slowly decreasing analyte concentration, the vertical region follows the change-over from analyte to titrant control of solution pH, and the latter horizontal portion shows the steadily increasing titrant concentration. The equivalence point is interpreted as that point on the curve at which the rate of change in pH is at a maximum. This point is usually midway along the vertical portion most nearly parallel to the pH axis.

In a potentiometric acid-base neutralization titration, the analyte may be either a strong or weak species (the titrant must be a strong species). If a strong analyte is used, the analysis provides mainly quantitative information based on the equivalent mass relationships. More extensive information is obtained from a potentiometric analysis of a weak species.

A pure weak acid, for example, can often be identified by its equivalent mass and the pH values of the half-neutralized solutions. The pH of the solution at 50% neutralization equals the pKa for the dissociation process: [acid] $\leftrightarrow$ [H^{+}] + [base]. The equilibrium constant for the above reaction is called the acid dissociation constant, K_a, and the equilibrium concentration relationships are given by:

$$K_a = \frac{[H+]\,[base]}{[acid]} \quad \text{or} \quad pK_a = pH - \log \frac{[base]}{[acid]}$$

At 50% neutralization, the conjugate pair concentrations are equal (that is, [base] = [acid]), and the above equation reduces to:

$$K_a = pH + \log (1) \text{ or } pK_a = pH + 0 = pH_{50\%}.$$

If the unknown acid is monoprotic; data analyses are simple and direct. Polyprotic weak acids can be investigated in a similar manner, although the data interpretations are more complicated.

In conventional potentiometric titrations, the analysis is an exact quantitative one involving accurate measurements of reagent volumes, and the concentrations of all reagent solutions are exactly known. Measurements are typically taken to at least four significant figures. The experiment to be performed in the lab will be performed at a less-sophisticated level. Reagent solutions of approximately known concentrations will be used, however, titrant volumes (in milliliters) and pH values will be read to the nearest hundredth of a unit.

Qualitative pH titration curves will be constructed from the experimental data. A strong acid and a weak acid will be investigated to determine their equivalence volumes and relative pK_a values (in the case of the weak acid). These acids will exhibit different pH titration curves.

Calibration of pH Meter

The pH meters in use in the freshman lab have digital output and three adjustments. Start by setting the temperature at room temperature, usually about 25 °C, by pressing the °C key and adjusting the 'Temperature' knob. Next, press the pH key on the meter and immerse the glass combination electrode in standard pH = 7 buffer. After a couple of minutes, adjust the 'OFFSET ' knob until the display reads 7.00. Rinse the electrode with deionized water and blot dry with tissue (not paper towels) and place the electrode in standard pH = 4 buffer. After a couple of minutes, adjust the digital meter to read 4.00 with the 'SLOPE' knob. Be patient with this setting and allow the signal to settle in before your final adjustment.

Measurement of pH titration curve

Obtain a 50.00-mL buret from under the hood. Fill the buret with the 0.10 M NaOH from the solution bottle on the storage shelf. This stock base is prepared by dissolving 4.00 grams of NaOH per liter of deionized water. Make sure the base solution meniscus lies exactly on the 0.0-mL mark on the buret. Place the buret in a clamp above the solution.

Select the weak mono-protic acid solution provided and record the name and pertinent information in Table I as Acid 1. Use a l00-mL graduated cylinder to measure 25.0 mL of the acid solution into a clean l50-mL beaker, and then add a 25.0-mL portion of deionized water. Mix the solution, and place a clean magnetic stir-bar in the beaker. Place the beaker and solution on the magnetic stirrer unit. Note: If magnetic stirrers are not available, you will have to stir with a glass stirring rod.

Insert the calibrated pH meter electrode into the acid solution, and press the pH key on the pH meter control panel. Leave the pH meter control on "pH" throughout the entire titration of the acid. Turn on the magnetic stirrer (if available), and adjust the stir-bar rotation rate to an appropriate level. Record the initial pH of the weak acid solution (and the corresponding titrant volume of 0.0 mL) in Table I.

Position the tip of the buret at the height of the beaker lip. Open the buret stopcock, run in a portion of base, and close the stopcock. Allow the solution to mix for a few seconds while stirring, and then record the solution pH as read on the pH meter scale. For the first 10 mL of added titrant, add the base in l.0-mL portions. Thereafter, use 0.5 mL base additions to obtain enough data points to define the titration curve. Portions smaller than 0.5 mL will not appreciably improve the pH curve, except in the region very near the equivalence point.

Continue adding titrant until the solution pH is above 11. Go to a final titrant volume of at least 2.5 times the equivalence volume (for example, if the equivalence volume is 16.0 mL, add titrant to a total volume of at least 40.0 mL). Addition of this much titrant is routinely done to insure that the acid does not have a second equivalence point. Your acids (both weak and strong) will be mono-protic. When one acid has been analyzed, turn the pH meter off and then remove and clean the electrode (and stir-bar if present).

Select the strong mono-protic acid solution provided and record the name and pertinent information in Table I as Acid 2. Measure the pH titration curve for this strong acid as analyte versus aqueous sodium hydroxide as titrant using the same procedure that was followed for the weak acid.

Students should work in groups of two or three as specified by the instructor. Group size may be dictated by the number of pH meters available for use. Each student in the group should rotate through the experimental duties of operating the buret while stirring, reading the pH meter, and recording the pH vs. mL titrant.

Table 1 has three columns for data entry , one for Acid 1 and one for Acid 2. The third column is included in case your instructor wants you to titrate another weak acid (Acid 3).

Table I

Acid 1:_____ Acid 2:_____

Base:_____

mL Base	pH	mL Base	pH	mL Base	pH

Data treatment and report

This experiment will require a three-page report. The first page should include a complete heading and a full, neat copy of the pH vs. mL base data from Table I. Be sure to report the particular acids for which the data were taken. The second page of the report will be a neat, well-prepared pH titration curve of the strong acid, including a complete heading and title. Page three is to be the pH titration curve for the weak acid.

The scales of the axes of the pH titration curve should be chosen to use the entire graph page for the actua1 pH vs. mL titrant data sets. Plot pH on the ordinate (short, vertical axis), using a scale which ranges from just below the minimum pH reading to just above the maximum pH reading. Plot mL of base titrant on the abscissa (long, horizontal axis), using a scale ranging from 0.0 mL to a value slightly larger than the maximum or total volume of the last pH reading.

Draw a smooth curve through the data points: do not play connect-a-dot. It is not necessary that every data point lie on the line. For all weak acids titrated with a strong base, the equivalence point should lie at a pH above 7 (due to the equilibrium reactions of the conjugate pair). Determine the pH of the equivalence point of the titration curve in the vertical region midway between the two horizontal regions. Visual inspection or graphical interpretation methods are both appropriate. Write the value of the equivalence point pH on the graph to the right of the equivalence point.

The half-equivalence point (at 50% neutralization) occurs at the titrant volume half-way between 0.0 mL and the equivalence volume (that is, for a titration with an equivalence volume of 16.0 mL, the 50% point will be at 8.0 mL). The pH on the titration curve at the 50% neutralization point equals the pK_a of the weak acid.

Draw a vertical line from the 50% neutralization point volume on the abscissa to the titration curve, and then draw a horizontal line from the curve to the pH axis to determine the pK_a value. Write the value of the $pH_{50\%} = pK_a$ on the graph above the horizontal line and next to the pH axis.

Record the name, concentration, and other pertinent information about the acids on the pH titration curve graph and on the first page of the report. Also, record the equivalence volumes and pK_a values on both pages of the report.

Experiment # 9: The Henderson-Hasselbalch Equation

A buffer is commonly defined as a solution that resists changes in pH when a small amount of acid or base is added or when the solution is diluted with pure solvent. This property is extremely useful in maintaining the pH of a chemical system at an optimum value to appropriately influence the reaction kinetics or equilibrium processes. A buffer solution actually is a mixture of a weak acid and its conjugate base or a mixture of a weak base and its conjugate acid. The conjugate forms are commonly referred to as "salts".

For a typical weak acid, the dissociation equilibrium is represented as:

$$\text{Acid} \rightleftharpoons H^+ + \text{Base}; \quad K_a = \frac{[H^+]\,[\text{Base}]}{[\text{Acid}]}$$

according to the Bronsted-Lowry concept. If a pure weak acid is dissolved in a pure solvent the concentrations of H^+ and conjugate Base will be equal, neglecting autoprotolysis of the solvent. Rearranging the dissociation constant equation and solving for $[H^+]$ gives: $[H^+] = [K_a\,(\text{Acid})]^{1/2}$. If other factors governing conjugate base concentration are present in the system (either as added salt of the weak acid or as added base to partially neutralize the acid), the concentrations of H^+ and conjugate Base will no longer be the same. Under these conditions, the equation for $[H^+]$ becomes:

$$[H^+] = K_a\,[\text{Acid}]/[\text{Base}] = K\,[\text{Acid}]/[\text{Base}].$$

Taking negative logarithms of both sides of the above equation gives:

$$-\log([H^+]) = -\log(K_a) - \log([\text{Acid}]/[\text{Salt}])$$
$$\text{or } pH = pK_a - \log([\text{Acid}]/[\text{Salt}]).$$

Upon inversion of the argument the last log term becomes positive, as:

$$pH = pK_a + \log([\text{Salt}]/[\text{Acid}]).$$

This form of the ionization or dissociation constant expression is called the Henderson-Hasselbalch equation. This equation is very useful in calculating the pH of a solution containing a weak acid and its conjugate base (or salt). A comparable equation is obtained for a buffer solution consisting of a mixture of a weak base and its salt, namely:

$$pOH = pK_b + \log([\text{Salt}]/[\text{Base}]).$$

Solutions of a weak acid and its salt (conjugate base) may be obtained by mixing an excess of weak acid with some strong base to produce the salt by partial neutralization. A similar mixture can be obtained by mixing an excess of salt with a strong acid to produce the weak acid component. Most often, however, a weak acid-conjugate base buffer is prepared by a direct mixing of the weak acid with

its salt. This third method allows an accurate control of the concentrations of both the weak acid and conjugate base species.

The buffering mechanism of a mixture of a weak acid and its salt can be explained as follows. The buffer pH is governed by the logarithm of the ratio of the salt and acid concentrations, as: pH = constant + log ([Salt]/[Acid]), where the constant is the pK_a of the particular weak acid used in the buffer. If the buffer solution is diluted with pure solvent, the common volume of the salt and acid components is increased, but the amounts of each are unchanged. Consequently, the ratio remains constant, and the solution pH does not change. (In actuality, the pH increases slightly due to an increase in the activity coefficient of the salt resulting from the decrease in ionic strength. But for practical purposes, the pH does not change significantly)

If a small amount of a strong acid is added to the buffer, the strong acid will combine with an equivalent amount of the conjugate base, converting it to the weak acid form. Thus, [Salt] decreases and [Acid] increases, but the logarithm of the overall ratio does not change significantly. A comparable affect is seen if a small amount of strong base is added to the buffer; the [Salt] increases slightly as the [Acid] decreases accordingly, but the logarithm of the ratio changes only slightly.

The amount of acid or base that can be added without causing a large change in pH is governed by the buffering capacity of the solution. This property is determined by the relative concentrations of acid and salt. The higher their concentrations, the more acid or base the solution can accommodate before the relative acid/salt ratio is changed. The buffering capacity is also controlled by the ratio of acid to salt. The capacity is at a maximum when the ratio is unity, that is, when the $pH = pK_a$. In general, the buffering capacity is satisfactory over a pH range of $pK_a \pm 1$.

A buffer solution of a given pH can be prepared by choosing a weak acid (or a weak base) and its conjugate salt that has a pK_a value near the pH (or pOH) that is desired. There are a number of such weak acids and bases, and any pH region can be buffered by a proper choice of components. The salt does not react with water (or other solvent) to ionize as an acid or base due to the presence of the acid or base in the mixture. The presence of appreciable amounts of acid will suppress the ionization of the salt to the acid form (and similarly for a weak base/salt buffer system).

In this experiment, the dissociation constant, K_a, of a weak acid will be determined by a technique based on the Henderson-Hasselbalch relationship. Specifically, standard solutions (equimolar) of a weak acid and its conjugate base (or salt) will be mixed in a standard series. For this system, it may be considered that negligible reaction occurs, since transferring a proton between the species in a conjugate acid-base pair changes nothing, and the relative concentrations of the conjugate pair species in the mixture will be the same as that in the proportionate volumes of standard solutions.

Plots of measured mixture pH versus various functions of the conjugate pair concentrations will be made in order to demonstrate the usefulness of the Henderson-Hasselbalch equation in determining the acid strength (i.e., K_a) of the weak acid in the buffer. The functions of conjugate pair concentrations to be examined with respect to mixture pH include: volumes of acid (or salt), ratio of volumes of salt and acid, and logarithm of the ratio of volumes of salt and acid.

Interpretations of the resulting plots should show that the Henderson-Hasselbalch equation gives an accurate description of the variation of pH in mixtures of conjugate pairs or buffers. If such a plot of pH versus log ratio salt/acid results in a straight line, the intercept should measure the acid dissociation

constant, K_a. Being assured that the relationship is valid allows the preparation of a buffer of desired pH by a simple mixing of the acid and its salt in the ratio indicated by the equation for the desired pH.

Preparation of buffer mixtures

Students will work in groups of no more than three students. One or more buret stations will be set up. Each will consist of a buret stand and clamp supporting a pair of 50.00-mL burets. The number of such stands and the responsibility for setting them up will be determined by the lab instructor. Those responsible will clean the burets, and rinse each with one of the standard equimolar solutions of acid or salt provided on the storage table. The weak acid is a 0.100 M acetic acid solution; the salt or conjugate base is a 0.100 M sodium acetate solution. Fill each of the burets with the standard solution used as that burets final rinse, either acid or salt.

Collect a set of fourteen clean, labeled, dry test-tubes (15 x 125 mm), following the specified volumes of acid and salt listed in Table I, prepare a standard mixture series of buffers. Note that the total volume of each mixture is 10.0 mL. Be sure that all acid-salt mixtures are well mixed, and do not get the test tubes out of order. An easy check is to remember that the pH should increase steadily as the salt content is increased. If a mixture does not fit into the trend when the pH is measured, discard the buffer, and prepare a new mixture of the appropriate volumes of acid and salt solutions.

Measurement of buffer mixture pH's

Use standard buffers of pH = 7 and pH = 4 to calibrate a pH meter, as described in Experiment 8. In these measurements of pH, the combination electrode will be inserted into each of the test tubes, and the solution stirred to take a pH reading. Rinse the electrode with deionized water after the calibration (making sure to turn the pH meter control to "standby" whenever the electrode is removed from solution), and dry the outside/bottom with tissue paper before immersion into the test samples. Measure the pH of each of the twelve buffer mixtures and the two solutions of pure acid and salt. Record the experimentally determined pH of each mixture in Table I, reading the pH value to the second decimal place. Check to see that the pH values follow the expected trend of increasing with salt content. When the pH of each buffer mixture has been determined, discard the solutions, and clean the test tubes.

Data treatment and report

A three-page report will be required for this experiment. On the first page, make a complete, titled, copy of the data in Table I, including a heading and all pertinent information about the acid and salt solutions. The remaining two pages of the report will be graphs of measured pH versus functions of acid and salt concentrations.

The second page should include two half-page plots, one for pH versus volume of acid and the other for pH versus salt/acid ratio. Since the acid and salt standard solutions are equimolar (each is 0.100M), the resulting concentrations can be expressed in terms of the number of mL's of each solution in the mixture. For the two plots, the scales should be chosen such that one-half of the graph page is used for each plot. The ordinates should be appropriately scaled to present the graphs as large as feasible. The abscissa should be mL's of acid or ratio of salt/acid with a range of mL's 0 to 10.0 or ratio's 0 to 5. In each plot, connect the experimental data points in a smooth curve, and do not attempt to force a straight line unless the actual points call for one.

On the third page, make a single plot of pH (ordinate) versus log ratio salt/acid (abscissa), using appropriate large scales. Since the log of ratio values will range from negative to positive numbers, set the ordinate origin in the center of the long side of the papers and place negative log values on the left side and positive log terms on the right side. Select a pH scale such that the experimental data points cover the full graph page.

Table I

Sample #	mL acid	mL salt	Salt/acid ratio	Log ratio	pH
1	10.00	0.00			
2	8.00	2.00			
3	7.50	2.50			
4	7.00	3.00			
5	6.50	3.50			
6	6.00	4.00			
7	5.50	4.50			
8	4.50	5.50			
9	4.00	6.00			
10	3.50	6.50			
11	3.00	7.00			
12	2.50	7.50			
13	2.00	8.00			
14	0.00	10.00			

Draw the best straight line through the data points, assuming that the Henderson-Hasselbalch equation is valid: $pH = pK_a + \log([salt]/[acid])$. Determine the value of the pH at the intersection of the data point line through the ordinate axis; this value of pH equals the pK_a of the weak acid. Write the value on the graph beside the point of intersection, and label it as pK_a .

Look up the literature value for the pK_a of acetic acid, and record this as the "literature" value on the first page of the report, citing the source. Record the experimental value of pK_a for acetic acid, labeling it "Henderson-Hasselbalch" value.

Experiment # 10: Solubility Product Determination

When a chemical species is classified as "insoluble", this does not mean that none of the compound dissolves in the given solvent or solution system. In reality, a measurable level of material does go into solution, but it is sometimes considered negligible relative to the total amount of the chemical. perhaps a better name for such salts is "sparingly soluble." The dissolving of a solid monovalent-monovalent salt, represented as MX, in an appropriate solvent is represented by the general equation:

$$MX_{(s)} \rightleftharpoons M^{+}_{(aq)} + X^{-}_{(aq)}.$$

where the subscripts "(s)" and "(aq)" represent the solid and aqueous solution physical states, respectively. For a set of given conditions, the precipitate has a definite solubility (or maximum amount that will dissolve) expressed in units of grams/liter or moles/liter.

An equilibrium constant expression can be written for the above reaction, as: $K_{eq} = [M^{+}][X^{-}]/[MX]$. The "concentration" of any solid material, such as MX, is proportional to its density and is constant. Thus, the term [MX] is usually combined into the K_{eq} value, giving: $K_{eq}[MX] = [M^{+}][X^{-}] = K_{sp}$, where "$K_{sp}$ is called the "solubility product" constant. Note: Square brackets indicate saturation or equilibrium molarities.

The ideal or thermodynamic solubility product expression is written in terms of the "activities" or "effective concentrations" of all species, rather than in actual mass/volume or mole/volume concentrations. In solutions of low concentrations, the activity coefficients are near unity, and the simplification of terms is appropriate for equilibrium systems for most reactions.

For a given chemical species and solvent system, the main factor which affects the value of K_{sp} is the temperature. Most often, an increase in the temperature causes an increase in the solubility and value. However, there are some exceptions, as in the case of a salt which dissolves with a loss of energy (i.e., an exothermic dissolution). For a given temperature and set of experimental conditions, there are often kinetic limitations as to how fast crystalline solids form. Thus, sufficient time should be allowed for the system to come to a true state of equilibrium.

The amount of a slightly soluble salt that dissolves does not depend on the amount of the solid in equilibrium with the solution, so long as there is enough to saturate the solution. A non-symmetric salt, such as lead iodide or PbI_2, would have a reaction as:

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^{-}(aq), \text{ with } K_{sp} = [Pb^{2+}][I^{-}]^2$$

As with any equilibrium constant, the K_{sp} value holds under all conditions at the specified temperature. If there is an excess of one ion over the other, the concentration of the second is suppressed (due to the common-ion effect), and the solubility of the precipitate is decreased. Because the solubility product value always holds constant, precipitation will not occur unless the product of $[M^{+}]$ and $[X^{-}]$ exceeds the value of K_{sp}. If the product of the ion concentrations is just equal to K_{sp}, all the M^{+} and X^{-}would remain in the solution (i.e., no precipitate or solid forms).

In this experiment, the relative solubility (and an approximate value of the K_{sp}) of lead iodide will be determined by direct observation. The procedure calls for the mixing of two standard solutions (one of a soluble lead salt, and a second of a soluble iodide salt) in different proportions and allowing time for the resulting mixture to come to equilibrium. In some of the mixtures, the solubility product constant for lead iodide will be exceeded, and precipitation of PbI_2 crystals will occur. In other mixtures, the final concentrations of lead and iodide ions will be such that precipitation does not occur.

A simple product function "Q," called the Ion Product will be defined so that:

$$Q = \{\text{lead ion}\} \times \{\text{iodide ion}\}^2 = \{Pb^{2+}\}\{I^-\}^2,$$

where curly brackets indicate prepared molarities before precipitation occurs (if it does occur). An experimental value of "Q" will be calculated for each mixture, based on the total amount of lead ion and iodide ion added in each solution. Clearly, the formation of solid crystals of PbI_2 will occur when the value of "Q" exceeds the solubility product value of lead iodide (i.e., when $Q > K_{sp}$). Similarly, precipitation will not occur when the value of $K_{sp} > Q$.

Thus, in this experimental procedure, if some sample mixtures form PbI_2 crystals and other solutions do not, the value of the solubility product constant lies between Q values with precipitates and Q values without precipitates. The most precise value for K_{sp} is given as:

$$Q_{minimum} \text{ with } PbI_2 > K_{sp} > Q_{maximum} \text{ without } PbI_2$$

The value for K_{sp} is determined with an uncertainty level equal to the difference of the two Q values. In order for a more precise determination of K_{sp}, the solution mixtures are designed such that the various Q values are rather close together.

Caution: lead salts are toxic, so be careful handling the solutions, and make sure to wash your hands after you complete the experimental work.

Preparation of lead iodide mixtures

Equimolar standard solutions of lead and iodide compounds are provided on the reagent shelf. A 1.00 x 10^{-2} M Pb^{2+}solution is prepared by dissolving 3.312 grams of Pb $(NO_3)_2$ in 1.00 liter of deionized water, while a solution of 1.00 x 10^{-2} M I^- is prepared by dissolving 1.660 grams of KI in 1.00 liter of deionized water.

Each student or group of students should assemble a set of nine clean, dry test-tubes (15 x 125 mm). A number (to be determined by the lab instructor) of buret stations will be set up in the laboratory. Each station will consist three delivery burets, one buret for each of the stock solutions and a third for deionized water. Following the specifications listed in Table I, prepare a mixture series of the lead and iodide stock solutions. To avoid 1ocal, temporary supersaturation, always mix the water first. Note that the total volume of each mixture solution is 10.0 mL. Be sure that the solutions are mixed thoroughly, and do not get the test tubes out of order. An easy check is to observe that the Q values progressively decrease from #1 to #9 samples.

After preparing the solutions, allow each mixture to set for at least 30 minutes before checking for precipitation. During this equilibration period, calculate the theoretical or maximum concentration of each ion in the mixture, using the equation:

$$[\text{Ion}]_{\text{mixture}} = [\text{Ion}]_{\text{standard}} \text{ x } \frac{\text{mL's ion in solution}}{\text{mL's total mixture}}$$

Use these concentration values to calculate the "Q" value for each mixture, and record the data in Table I. Colorless clarity (clearness) of solution indicates no precipitate. Golden cloudiness (lack of clarity) indicates formation of a precipitate.

After the equilibration period is completed record under the "PbI_2?" column whether or not a precipitate has formed in each test tube. If all goes well, the mixtures of higher Q values will contain shiny, golden crystals of lead iodide, while the tubes of lower Q values will have no solid.

Table I

#	mL Pb^{2+}	mL I^-	mL H_20	[Pb^{2+}]	[I^-]	Q	PbI_2?
1	4.00	5.00	1.00				
2	3.00	5.00	2.00				
3	2.00	5.00	3.00				
4	1.00	5.00	4.00				
5	2.50	2.00	5.50				
6	1.20	2.50	6.30				
7	1.25	2.00	6.75				
8	2.50	1.00	6.50				
9	1.00	1.00	8.00				

Data treatment and report

A single-page report will be submitted for this experiment. Under a full heading, recreate the completed data entries of Table I. Be sure to indicate which test tubes contain precipitates of lead iodide. Identify the smallest value mixture containing a precipitate and the largest Q value test tube which has no solid crystals. The K_{sp} for lead iodide should lie within these two Q values, so report the experimental value of K_{sp} within this range, as:

$$Q_{\text{minimum}} \text{ with } PbI_2 > K_{sp} > Q_{\text{maximum}} \text{ without } PbI_2$$

Look up the actual K_{sp} for lead iodide in a textbook or other reference book, list this value as "literature K_{sp}" in the report, and cite your source.

Experiment # 11: Spectroscopic determination of indicator pKa

pH indicators may be defined as highly colored Bronsted-Lowry acid-base conjugate pairs. Used in low concentrations, these compounds signal pH changes within a specific range determined by the particular indicator in use. This color change range depends upon the relative acid strength (or pK_a) of the conjugate acid form of the indicator. In many indicator systems, both conjugate species are colored, and, within the pH transition range, the observed color is really a mixture of the colors of the two forms.

The ratio of concentrations of the conjugate acid and base forms is controlled by the pH of the solution, as indicated by the same equation as that used for determining buffer pH's, namely, the Henderson-Hasselbalch equation:

$$\log\left(\frac{[\text{conjugate base}]}{[\text{conjugate acid}]}\right) = \log\left(\frac{[Ind^-]}{[HInd]}\right) = pH - pK_a$$

where HInd and Ind^- represent the acidic and anionic (or basic) forms of the indicator, respectively.

The indicator concentration ratio is controlled by the pH of the solution, whereas the buffer concentration ratio controls the solution pH. At first glance, this statement seems contradictory. In reality, however, it is simply a matter of relative concentrations. The buffer components are present in high concentrations, so they control the pH of the buffer solution via the conventional acid-base reactions. On the other hand, the indicator species are present in low, even negligible, amounts relative to the other acid-base systems in the solution. In terms of visible absorption, however, the indicator species predominate over the buffer components (most of which are colorless).

Procedures for determining solution pH using a short range of visual comparisons of indicator colors can usually distinguish 0.2 pH unit differences over a pH range of 2.0 units. This analytical approach is improved if a spectroscopic instrument is used to accurately measure absorbance of one or both of the indicator forms. To adequately interpret such data, knowledge of the value of the indicator pK_a is essential.

In the present experimental procedure, previously obtained knowledge of the acetate buffer system and the Henderson-Hasselbalch equation will be used to determine pK_a values of various indicators. As in the earlier buffer experiment, standard solutions of 1.0 M acetic acid and 1.0 M sodium acetate will be mixed to produce buffer solutions of various pH's. This time, however, the buffer pH will be calculated from the Henderson-Hasselbalch equation, using the previously determined pK_a value for the acetic acid-acetate ion system.

An additional modification of the procedure is that a constant total concentration of indicator will be added to each buffer mixture. This operation involves the most critical measurement of the experiment; unless equal total amounts of indicator are present in all buffers, the spectroscopic measurements will be meaningless. A number of indicators are provided for analysis, as listed in Table I (along with pertinent spectroscopic information).

Table I

Indicator (concentration)	acid form (λ_{max})	base form (λ_{max})
Bromocresol green (67 mg/l)	yellow (453 nm)	blue (610 nm)
Chlorophenol red (33 mg/l)	yellow (433 nm)	magenta (575 nm)
Bromocresol purple (40 mg/l)	yellow (432 nm)	purple (590 nm)

To simplify calculations, all spectroscopic measurements will be made at the wavelength of maximum absorbance, λ max, of the base form of the indicator. Each student (or group of students) will make three determinations of the pK_a of one of the indicators, each determination to be made with a different buffer mixture (and buffer pH value). The absorbance of the indicator in unmixed (or pure 1.0 M) acid solution will be measured to determine the minimum absorbance level of the base form, designated "A_a ", and the absorbance of indicator in unmixed (or pure 1.0 M) salt solution is measured as the maximum absorbance of the base form, designated "A_b".

The spectroscopic determination of indicator pK_a, involves calculations based on the following argument. The total indicator concentration is the same for all buffer mixtures and is proportional to the value (A_b - A_a) if all measurements are made at the λ max of the base form. In each buffer, the indicator is distributed between two forms, acid and base, the relative amounts of each determined by the buffer solution pH. The concentration of the base form, [Ind^-], is proportional to (A_i - A_a) where "A_i" is the absorbance of the particular buffer sample under study.

The indicator acid form concentration, [HInd], is then proportionate to that part of the total amount not in the base form. Thus, the [HInd] is given by the relationship:
(A_b - A_a) - (A_i - A_a) = (A_b - A_i). Since the proportionality constant for these concentration relationships is the same, it cancels out when a ratio is made of the concentration terms. Thus, neither total indicator concentration nor any "ab" term from absorbance values appears in the calculations. The ratio [Ind^-]/(HInd] equals the ratio of absorbance terms or
(A_i - A_a)/(A_b — A_i).

The indicator pK_a is calculated by substituting the absorbance ratio term (for the ratio of salt/acid) and a theoretical buffer pH value into a modification of the Henderson - Hasselbalch equation, as:

$$pK_a = pH - \log\left(\frac{[A_i - A_a]}{[A_b - A_i]}\right),$$

Preparation of indicator/buffer mixtures

Working in groups of not more than three students, prepare the indicator/buffer mixtures in the familiar manner. Three burets will be involved in the operation: the first contains 1.0 M acetic acid, the second 1.0 M sodium acetate, and the third the indicator of choice.

Mix the reagents as specified in Table II. Note that 2.00 mL of indicator is added to each solution (buffer mixtures, pure acid, and pure salt alike).

Table II

sample #	mL Hind	mL salt	mL acid	salt/acid ratio	log ratio	buffer pH
1	2.00	0.00	8.00	--------	-------	----
2	2.00	2.00	6.00			
3	2.00	4.00	4.00			
4	2 00	6.00	2.00			
5	2.00	8.00	0.00	--------	-------	

Calculate the pH of each buffer mixture using the original Henderson-Hasselbalch equation: $pH = pK_a + \log([salt] / [acid])$. The pK_a in this equation is for the dissociation of acetic acid as determined in a previous experiment (it should have a value of about 4.62). Notice that the dilution effect from adding the indicator cancels in the buffer salt/acid ratio.

Measurement of indicator/buffer absorbances

Turn on a Spectronic 20, and allow the instrument to warm-up. Set the wavelength dial to λ max for the base form of the indicator chosen for study. Place each of the indicator/buffer solutions in a clean, dry, or properly rinsed cuvette. Use deionized water in a sixth cuvette to calibrate the spectrometer to read 100% T.

Record the observed %T (to ±0.1 %) and A for each of the samples in data Table III, and calculate A_{calc} using the equation: $A = 2 - \log \%T$

Table III

Sample #	%T.	A_{meas}	A_{calc}
1			$= A_a$
2			
3			
4			
5			$= A_b$

Note the designations given to the absorbance values for Samples #1 and #5. The value for Sample #1 is A_a, the minimum absorbance measured at λ max for the base form of the indicator (since the indicator is in a solution of pure 1.0 M acetic acid). Correspondingly, the absorbance of sample #5 is A_b, the maximum absorbance of the base form (since the indicator is in 1.0 M salt solution).

Determination of indicator pKa

Use the absorbance values recorded in Table III to calculate the indicator pK_a's for the buffer mixtures (Samples #2, #3, and #4). Complete the entry columns in Table IV, and calculate the indicator pK_a for the modified Henderson-Hasselbalch equation:

$$pK_a = pH - \log\left(\frac{[A_i - A_a]}{[A_b - A_i]}\right),$$

Table IV

Sample #	(A_i-A_a)	(A_b-A_i)	$\frac{[A_i - A_a]}{[A_b - A_i]}$	Log ratio	Hind pK_a
2					
3					
4					

Data treatment and report

A two-page report is required for this experiment. On the first page, under appropriate headings, make complete copies of Tables II, III, and IV. List the name (and pertinent spectroscopic data) of the indicator used in the experiment, and then give the calculated pK_a for the indicator system.

On the second page of the reports answer the following questions, giving a clearly thought-out explanation of each answer.

1) What single error would have the greatest effect on the accuracy of the experimental results?

2) All indicator pK_a values in this experiment are within 2 units of the pK_a of acetic acid. Is this necessary to the method, or can any indicator pK_a be determined in acetate buffer solutions?

Experiment 12: Make-Up Experiment
Copper Analysis by Complexometric Titration

A quantitative analysis of copper in a soluble copper salt will by performed by complexometric titration. The complexing agent will be ethylenediaminetetraacetic acid (EDTA) in the form of its disodium dihydrate salt ($Na_2C_{10}H_{18}N_2O_{10}$), with a molar mass of 372.24 g mol^{-1}. Since EDTA forms complexes with many metal ions, this particular method can only be used in the absence of such ions as Ca^{2+}, Ni^{2+}, etc. The reaction of complexation is:

$$Cu^{2+}_{(aq)} + (EDTA)^{2-}_{(aq)} \rightarrow Cu(EDTA)^{2-}_{(aq)} + 2H^{+}_{(aq)}$$

The stoichiometry is one metal cation to one EDTA anion. However, for Cu^{2+} (since it has lost 2 electrons), the equivalent mass is 63.546/2 = 31.773 g eq^{-1}, and since $(EDTA)^{2-}$ is a dianion its equivalent mass is 372.24/2 = 186.12 g eq^{-1} (for the disodium dihydrate salt). The equation above represents two equivalents reacting with two equivalents. The complex dianion is formed with the release of two moles of H^+ from EDTA, with the indicator being released from the copper ion.

The complex dianion has the structure shown in Figure 13.1. Note that the anion completely surrounds the cation, forming six coordinate covalent bonds to copper and a very stable complex. The bonding to the copper ion is nearly octahedral.

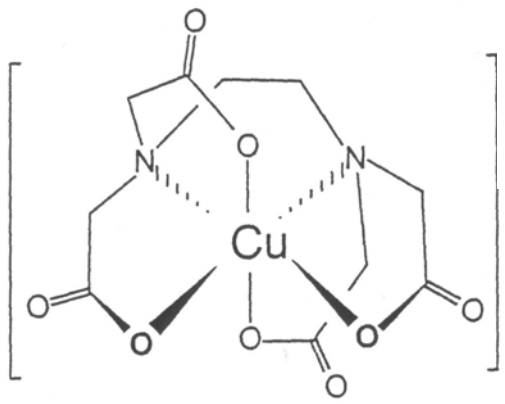


Figure 13.1
Structure of Cu^{2+}— EDTA dianion

The indicator used for the titration is called murexide. This indicator is highly colored and will complex with the copper ion to give a different colored species. During the titration, the $EDTA^{2-}$ forms a more stable complex and frees the indicator, which then displays its original color. The appearance of the free indicator means that all metal ions have been complexed by $EDTA^{2-}$, which signals the end point. At the end point, the following equation applies:

$$N_{EDTA}V_{EDTA} = N_{Cu(II)}V_{Cu(II)} = \#eq\ Cu(II), \text{ if V is given in L}$$
$$= \#meq\ Cu(II), \text{ if V is given in mL}$$

The mass of Cu equals (#eq Cu(II)) × (equivalent mass of Cu(II)), and

$$\frac{\text{mass Cu(II)}}{\text{mass Cu(II) salt}} \times 100 = \%\ Cu$$

12A Experiment

1. Rinse your burette and fill it with standardized $Na_2EDTA•2H_2O$ solution
2. (7.445 g $Na_2EDTA \cdot 2\ H_2O$ per liter of water).
3. Weigh accurately three approximately 0.1 g samples of the copper salt, reported to three decimal places. Your instructor may specify that each sample be > 0.08 g and < 0.1 g. If so, remember that this will limit your final results to two significant figures.
4. Dissolve each sample in 50 mL of de-ionized water.
5. Add *exactly* the same amount of indicator to each sample, three to five drops to start off with. If the indicator solution is not strong enough, add more but always the same for all samples. (The indicator's concentration should be 100 mg/100 mL H_2O)
6. Titrate each sample with the standardized EDTA. The light yellow solution turns green near the end point, then suddenly purplish blue at the end point. This end point is fairly hard to see, so put a white sheet of paper under your beaker and watch carefully. The distinctly purplish hue, due to free murexide, is the key to observing the end point. Look for the complete absence of green.
7. For each titration, calculate the number of equivalents or (milliequivalents) of Cu(II) found.
8. For each titrated sample, calculate the mass of copper in that sample.
9. For each titration, calculate the % copper content in the sample, then average them.

	Sample 1	**Sample 2**	**Sample 3**	
(a) Normality of EDTA				
(b) grams of Cu(II) sample				
(c) mL of EDTA solution				**Average % copper content**
(d) eq (or meq) of Cu(II)				
(e) mass of copper				
(f) % copper content				

12B Exercise

Copper(II) sulfate forms a hydrate which contains 36.1% by mass water. Since the only component (other than H_2O and Cu^{2+}) is the sulfate ion, SO_4^{2-}, we can now determine the complete formula of the hydrated copper(II) sulfate. Do this determination.

NOTE Solutions preparation:
Either weigh the EDTA analytically or standardize the solution. Label the bottles with the normality of EDTA. Use deionized water. About 1 liter will be used by 20 students, 10 groups. Make these solutions up fresh, including the murexide solution.

Report Form 12: Copper Analysis by Complexometric Titration

Name:_____ Partner:_____

12A Experiment

	Sample 1	Sample 2	Sample 3	
(g) Normality of EDTA				
(h) grams of Cu(II) sample				
(i) mL of EDTA solution				**Average % copper content**
(j) eq (or meq) of Cu(II)				
(k) mass of copper				
(l) % copper content				

12B Exercise

Complete formula of hydrated copper(II) sulfate. _____