CHEMISTRY 1010
Lab Manual

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

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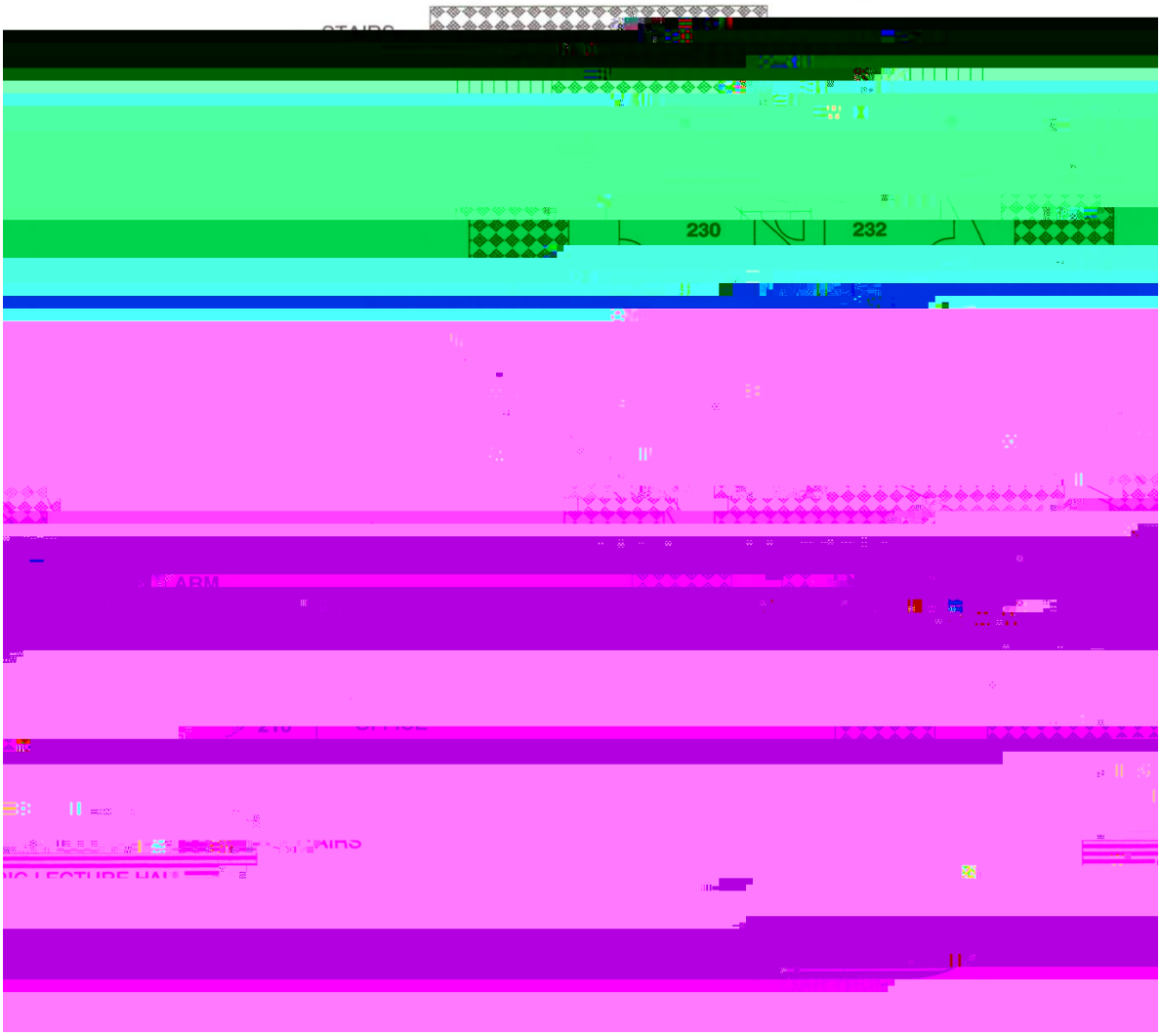
Exp/o 0ents

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

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

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 1.7×10^{-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.

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

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

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).

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

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

The rules above deal qualitatively with solubi[illegible]of[illegible]erated wat[illegible]s you may realize, there are ways (we're particularly int[illegible]n two) by [illegible] a third [illegible]ponent in [illegible]olution can change the apparent solubility of a salt. T[illegible]o categories o[illegible]t intere[illegible]this cou[illegible]re 1) strong acids and 2) complexing agents.

In the first case insoluble salts of weak acids [illegible]ly show increas[illegible]lubilit[illegible]metime[illegible]matic increases, if strong acids (high [H^+] concentra[illegible] are added. The[illegible]lt is fo[illegible]on of t[illegible]eak acid, usually quite soluble itself, with the release o[illegible]ation. Such a[illegible]

$$ZnS_{(s)} + 2\,HCl_{(aq)} \rightarrow [illegible]^{2+}_{(aq)} [illegible]_{(aq)} + H_2S_{(aq)}$$

This is, of course, a chemical reaction, not jus[illegible]mply ZnS dissolving. Nevertheless, we could now discern the presence of zinc ion and hydroge[illegible]ide for that matter, in the solution.
Another important case is where insoluble sa[illegible]e '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

$$HC67[illegible]aq8$$

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.

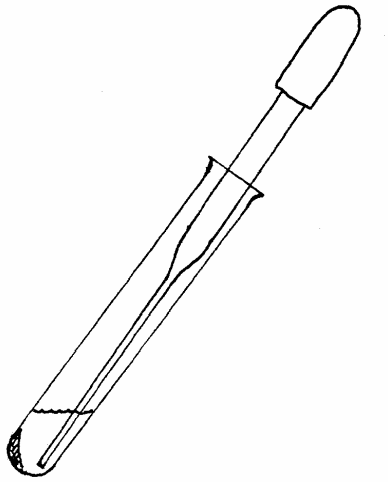


Figure 1

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

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 plotte

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 **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.

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

Rearranging Eq 2 gives

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

Now substituting Eq 3 into the unit definition of molality yields

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

And substituting Eq 4 into Eq 1 gives

$$\Delta T_f = (k$$

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.

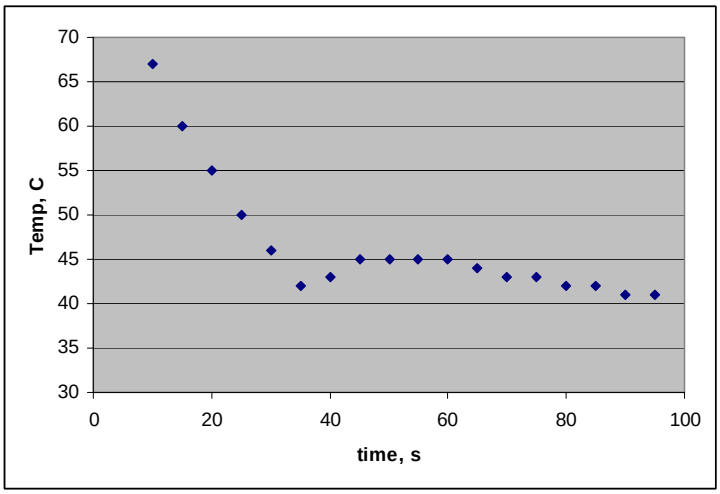


Figure 1: Cooling curve for a pure solvent.

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.

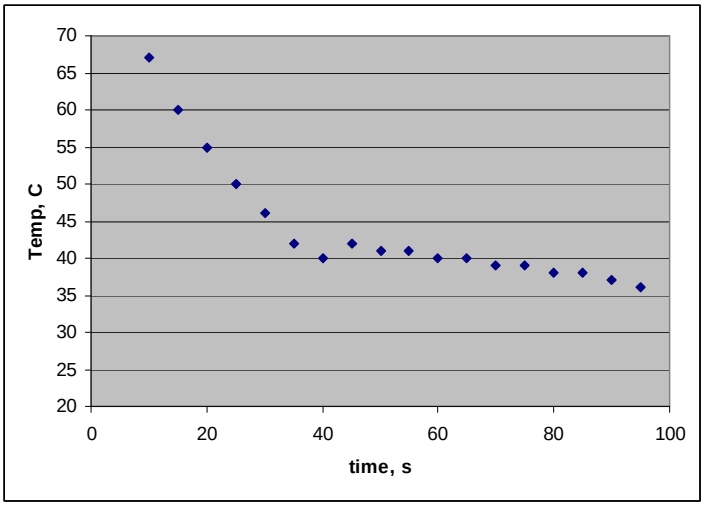


Figure 2: Cooling curve for a solution.

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.

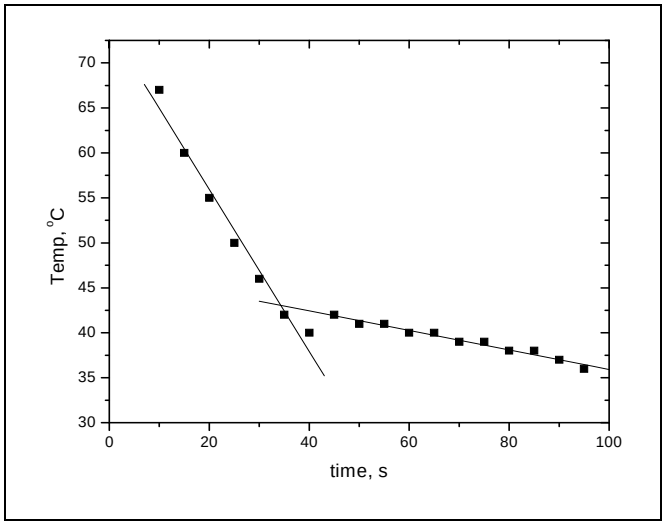


Figure 3: Solution cooling curve
showing best fit straight lines through the two portions of the curve discussed in the text.

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

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

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 sampp

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, **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,

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

or alternately written in ionic form as

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

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:

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

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

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

$$Pb^{2+} + 4Cl^{-} \leftrightarrow \quad {}^{2-}_{4Cl}$$

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.

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

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

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

$Ag(NH_3)_2^+$

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.

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

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^+.

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

$$+ \qquad \rightarrow \qquad ^+ + \qquad ^-$$

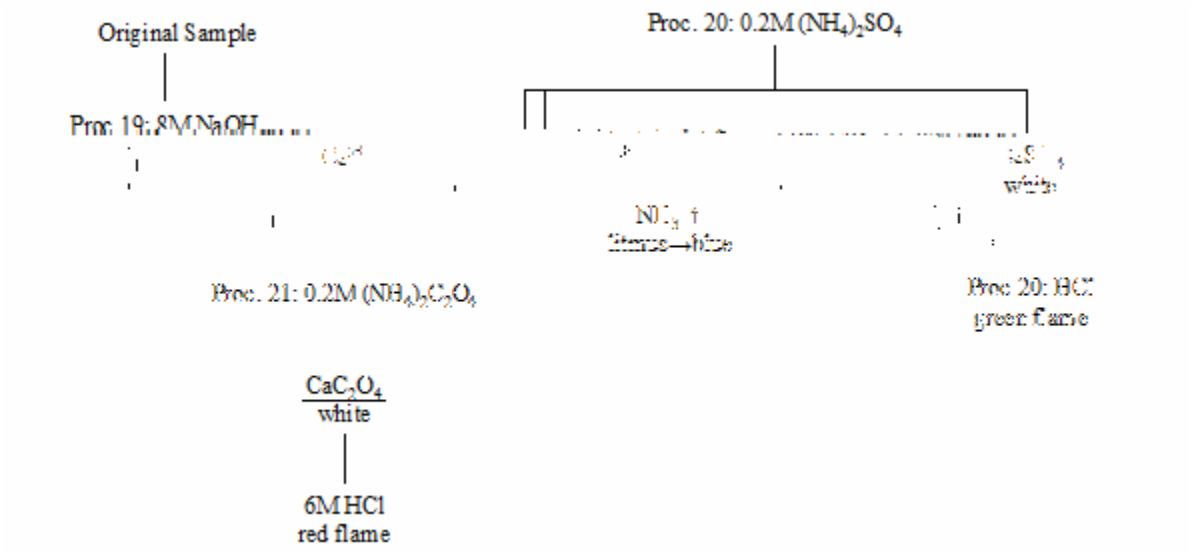
repeatedly. After several tries, barium (probably as the oxide) often tends to build up on the wire making the test easier to see.

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

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.

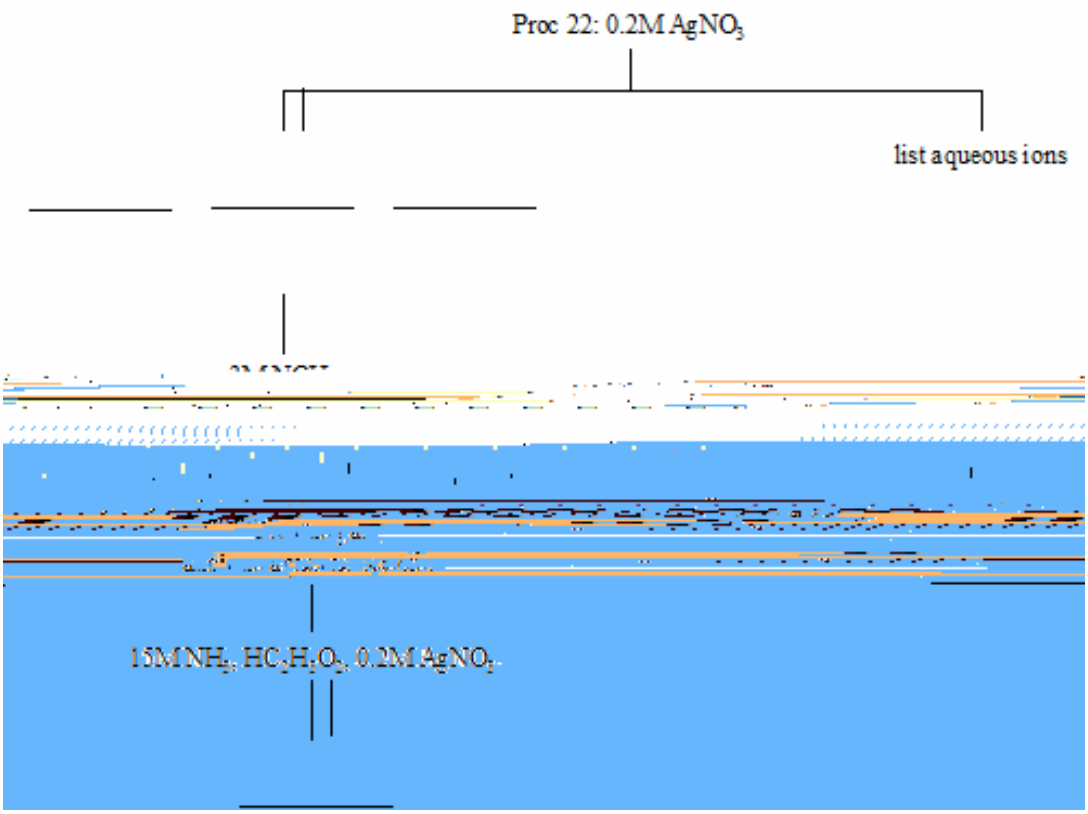
Experiment 1 (Essentially Procedure 22)

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:

$$Cl^-(aq) \; + \; 0.2M \;\; AgNO_3 \;\; \rightarrow \text{o}$$

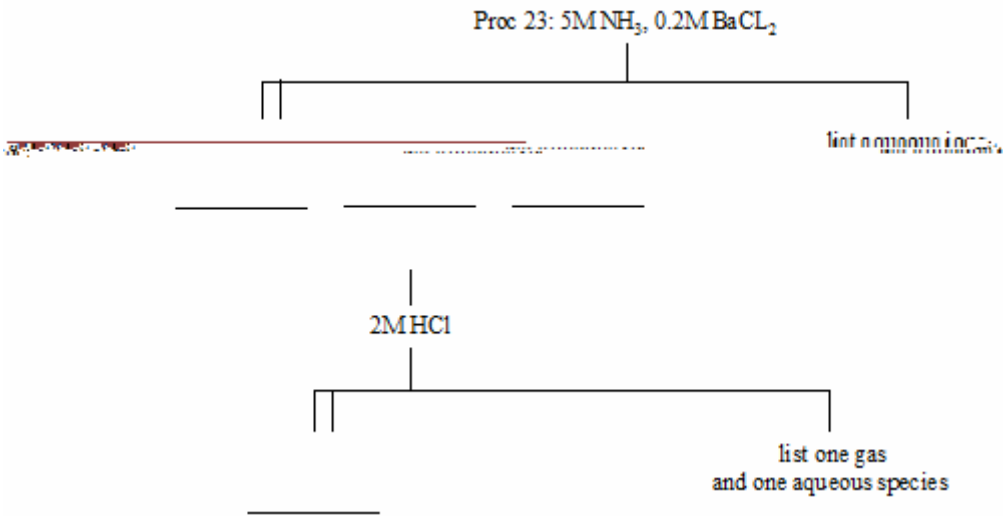
Anion Experiment One Diagram

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



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

$$+ \quad {}^{+} + \quad CH\ OH \quad \rightarrow$$

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 2.0431(u6)-.11dure 27e1.00118 7.7(s12.0436 0 0 12.22)Tj-4008 Twns

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.

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

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

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

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

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.

$$Fe^{3+}_{(aq)}$$

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.

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.

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 absorb

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 we1dh8(h)8 382.92 T

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 vol

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 dissocia

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.

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.

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:

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

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 i7af3ek of

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:

Table I

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			

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:

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

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

12A Experiment

1. Rinse your burette and fill it with standardized $Na_2EDTA•2H_2O$ solution
2. (7.445 g Na_2EDTA • 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. _____