Chemistry 1B
General Chemistry

Laboratory Manual
Spring 2011

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California State University, Sacramento
Department of Chemistry
Laboratory Policies

I. SAFETY

a. Familiarize yourself with the location and use of all safety equipment and emergency exits in the laboratory.

b. Eating and drinking are not allowed in the laboratory at any time.

c. Visitors are not allowed in the laboratory; leave the room for the duration of the visit.

d. **YOU MUST:**
  - Wear department approved safety goggles at all times when in lab. Shields are never allowed!
  - Wear shoes that completely cover your foot when in lab.
  - Wear appropriate clothing that covers your skin or wear a lab coat when in lab.
  - Long hair must be restrained to prevent fire hazard.

e. For chemical spills
  - On your skin rinse the area thoroughly for at least 15 min and report incident to your instructor and the stockroom.
  - For splashes into the eyes rinse using an eyewash for at least 15 minutes, and notify your instructor and the stockroom.

f. Working in laboratories outside of the regularly scheduled periods is strongly discouraged. When such work is necessary, the written permission of both instructors is **REQUIRED**.

g. Students in lower division laboratories are not to work in the laboratory unless an instructor is immediately available (i.e. in the lab).

h. Students in upper division laboratories are not to work in the laboratory unless an instructor is available in the vicinity (i.e. on the floor).

i. Experiments using utilities such as gas, water, steam, heat, etc. are not to be left unattended. If it is necessary to use these utilities overnight, you must attach a card signed by your instructor to the apparatus and notify the Chemistry Stockroom.

j. Broken glassware must be placed in the "glass disposal boxes" provided.

k. Unauthorized experimentation is prohibited!

l. **NO CHEMICALS, SUPPLIES, OR EQUIPMENT ARE TO BE REMOVED FROM THE LABORATORY WITHOUT THE WRITTEN PERMISSION OF THE INSTRUCTOR AND THE STOCKROOM SUPERVISOR**.

II. PREGNANCY

a. Women that are, or may become pregnant should carefully determine, upon consultation with your personal physician or the Student Health Service Center, if it is advisable for them to participate in the laboratory program. If you are pregnant or are planning to become pregnant please inform your instructor.

III. CHEMICALS

    a. Treat all chemicals as if they were hazardous.

    b. It is the student's responsibility to know the hazards of the chemicals used in the lab. This information is located in the chemical's MSDS (material safety data sheet), which can be obtained from the kiosks at the north end of the 4th and 5th floors of Sequoia Hall.

    c. Students are encouraged to practice good chemical hygiene by washing their hands after lab, and before eating, drinking or smoking.

    d. Never put chemical waste down drains or in the trash receptacles. Use appropriately labeled waste containers.

    e. If a chemical waste container is almost full, immediately notify your instructor or the Stockroom. **DO NOT OVERFLOW THE WASTE CONTAINER!**

    f. Never put anything (i.e. spatulas, pipets, fingers, etc.) into a reagent bottle. Place any unused reagents in the appropriate waste container; **DO NOT** return it to the bottle.

    g. Always return chemicals to their appropriate location.

    h. **NEVER** remove or borrow chemicals from another laboratory.

    i. If a required chemical is not available or needs to be refilled, notify your instructor.

    j. If chemicals are spilled, clean up the mess immediately. This especially includes spill on or around balances and other equipment. If you are unsure of how to clean up a spill, seek assistance from your instructor or the Stockroom.

IV. EQUIPMENT

    a. **DO NOT** use any equipment until you have been properly instructed in its use.

    b. **DO NOT** move **ANY** piece of equipment without the permission of your instructor.

    c. **DO NOT** attempt to alter or repair any piece of equipment. If it is not in proper working order, inform your instructor.

    d. Clean all equipment immediately after you have finished using it, and if it was borrowed or checked out, return it immediately.

    e. Because of the limited number of certain items. Special equipment issued by the Stockroom must be returned the same day or a fine of $5.00 will be assessed.

V. STOCKROOM

    a. The Chemistry Stockroom staff **WILL NOT** issue chemicals or equipment (other than those specifically listed for an experiment, student locker or instructional laboratory) without the consent of the instructor.

    b. The Stockroom staff **WILL NOT** set-up labs after they have been taken down. It is best not to miss your regularly scheduled lab time.

VI. EMERGENCIES

    a. In the event of **ANY EMERGENCY**, notify your instructor, and the Stockroom personnel immediately! Dial 911 for emergencies, or 8-6851 to reach campus police on any campus phone. Emergency phones are located in the lobbies of each floor in Sequoia Hall.

**Failure to follow these policies will result in your removal from lab!

Safety Contract

I HAVE READ ALL OF THE ABOVE, AND I AGREE TO CONFORM TO ITS CONTENTS.

Name: _____   Course:_____

Student ID:_____   Section:_____

Signature: _____   Room: _____

Date: _____

Lab Instructor: _____

Laboratory Regulations

1.   Safety is a prime requisite for laboratory work. Eye protection is required at all times unless explicitly stated otherwise. You can not work without appropriate eye protection. A lab apron or coat will prove a good investment for protecting clothing. Learn the location of the safety equipment: fire extinguisher, safety shower, and eye wash fountain. Injuries/accidents should be immediately reported to your instructor.

2. Lab work is to be done on an individual basis unless you are instructed otherwise. Prepare for lab by reading the experiment, preparing tables in your lab notebook for collecting data, and completing the prelaboratory assignment.

3. Record your results immediately and directly into your notebook. Record observations in detail. ***Do not write on scratch paper, only write in your laboratory notebook.***

4. The most productive research demands original work, and this is strongly encouraged. However, for safety reasons this may be done only with the approval and supervision of the instructor. Unauthorized experiments are strictly forbidden.

5. Students are allowed in the laboratories only during regularly scheduled class periods. Make-up labs must be approved by the lab instructor and must be completed within one week of the missed laboratory experiment. Approval is usually only given for medical reasons. You may not work in another lab without written permission from your laboratory instructor and the laboratory instructor in charge.

6. Keep your lab area clean. Wipe up in a safe and approved manner spilled materials. Only soluble, harmless materials should be put in the sink, and these should be washed down with plenty of water. Your instructor will advise you when it is permissible to dispose of chemicals in the sink. Unless otherwise instructed insoluble or toxic materials should be put in the containers provided for chemical wastes in the hood. If in doubt, do not pour a substance down the drain; it will soon be carried to a water-treatment plant and possibly pass through into a stream. Heed the warnings on the reagent bottles. If in doubt ask your instructor.

7. Balances and other delicate instruments require special care. Follow carefully the directions for their use.

Laboratory Notebook Requirements

You must have a notebook for recording laboratory data that meets one of the two following formats: A lab notebook containing bound pages for original recording of data followed by another page that has a carbon to make a copy (our bookstore sells the most convenient type).

Always begin an experiment on a new page. **Each page** of an experiment must show the following at the top of the page: (1) **Title of experiment**; (2) your name; (3) date of activity; and (4) name of partner, if an experiment is done with one.

The **first item of a new laboratory experiment is a statement of the objective or purpose** of the experiment (one or two sentences).
This is **immediately followed by a reference to procedures** by referencing page numbers in the lab manual.

The second item contains **answers to the pre-lab** section. **Identify this section**. You must **clearly** answer questions, provide explanations for your answers and include units in all steps of calculations.

The major section after pre-lab material contains the observations or results for the experiment. This section includes documentation of all observations of results associated with each procedure, tables, drawings, and anything else related to the experiment. It is a key part of the laboratory report and a lack of organization, details, vagueness, etc. will result in low lab scores.

All entries in the notebook ***must be in ink.*** Record data as you gather them directly into the notebook. ***Never record data on loose slips of paper*** (e.g. paper towels, scrap paper, etc.) for later transfer to the notebook. Should a correction be necessary, draw a single, light line through the erroneous value and enter the correct value (~~example~~.) The original value must remain legible (you may later decide to use it). Wherever possible, **tables of data are preferred** to isolate values; in either case, **all values must be clearly labeled** so that your notebook is comprehensible to someone with training comparable to you own.

Data should be neatly organized. Record the measurements at the time you make them. If repeated trials are made, list repetitive measurements in parallel columns. For example:

Title of Table (Descriptive)

Description of what is being recorded	Trial 1 (units)	Trial 2 (units)	Trial 3 (units)

Be sure to include _units_ with all measured numbers. Units are shown in the columns with their labels and not with the number.
Bring your laboratory notebook and laboratory syllabus to each class period unless otherwise stated.

Tips for Successful Report Writing
Chem 1B

Each experiment that you perform will have its own list of information that needs to be organized into the report you will turn in to your laboratory instructor. This information is found at the end of each experiment in the section labeled Laboratory Report.

General Requirements for each report:

All reports are computer processed.

- **Title page**: Your title page is always to be **typed**. Any additional information listed in the Laboratory Report section for Title Page should also be included. For example, your partner's name (if any), the identity of an unknown, etc. Title page should always **include experiment number, title, your name, section number, and date**.

- **Tables**: Any tables that are mentioned in the Laboratory Report section should be **computer processed**. There may be an example shown of how that table should look, if not you should create one of your own to display the values or data that is requested. Generally speaking, re-typing of data collected in lab in not necessary unless specifically requested the Laboratory Report section. Tables should be formatted in a way that the data/values are clearly presented. This may mean that you have to print them in landscape orientation rather than portrait. It depends on the size of the table, use your judgment and resize columns as necessary. The sample tables below show you an acceptable table with proper sizing and super and subscripts. The second table shows improper column sizing and font formatting.

Acceptable:

K_a (exp) H_3PO_4
1.79×10^{-5}

Not Acceptable:

Ka (exp) H3PO4
1.79 x 10^-5

Your tables should not be split in half; one page and a couple orphaned rows on the next page. Reformat your page size (margins) so that it all appears on one page. If a table is too large to appear on one page, the column headings should be repeated on the second

page where the table continues. *An unacceptable* table is shown below and continues onto the next page without proper column headings:

Acid	pH obs	pH theo	% Diss	K_a exp	K_a theo	pK_a obs	pK_a theo	% Error

---------------------------------- PAGE BREAK ---

HCl	#.##	#.##	###	------	large	-----	-------	-------
NH4Cl	#.##	#.##	#.##	#.##	#.##	#.##	#.##	#.##

Sample Calculations: (hand write)

- **Sample Calculations**: Many tables that you prepare will be filled with values that you have calculated. See hypothetical table above. You do not need to type a sample calculations. *Neatly* hand writing that calculation *under the table* is sufficient. **Remember that if we can't read it, we can't grade it**. The sample calculations should always be shown under the table that displays those values. **If those calculations cannot be written under the table, clearly list (by giving the page number) where those calculations can be found and number the pages of your report (by hand) so that finding them is clearly mapped out**. Most students, however, turn in *all* their calculations so that simple math mistakes can be tracked easily and fewer points taken off for those mistakes.

- **Questions and Error Analysis**: Many experiments you perform this semester will include a few questions to be answered. **These questions should be typed**. Make sure you write in complete sentences. Hint: students often misread or misunderstand the question being asked. Always re-read what the question is asking you to answer. A common, yet ***unacceptable*** answer is shown below:

  Will the calculated value of K be too high or too low if:
          1) the original solution was supersaturated?
  Student answer: if the solution was supersaturated then that means there was too much of the solid in the solution. Our calculated value of K will be off a lot because we can't account for this amount.

  Student did not answer the question that was asked. "Our calculations will be off" is obvious and true for all error analyses yet it does not answer the question asked. Make sure you answer the question you are asked.

- **Conclusions**: *Some* experiments ask you to reflect and make conclusions at the end about what you have done. Conclusions should be typed. A one sentence conclusion is never sufficient however a full page is rarely needed either. Generally a paragraph is all that is needed to accurately describe your conclusions.

- **Pre-Lab Assignment**: Always include your prelab assignment (yellow copies unless unreadable). You can put your prelab with all corrections made at the beginning of the report or at the end. Corrections can be made in your lab notebook or on a separate piece of paper, it is your choice. As always, please make those corrections easy to read and **reference where those corrections can be found** (by page # in report) if they are placed elsewhere in the report.

   Data Pages: yellow copy pages unless unreadable, inwhich case you should make photocopies to attach.

- **Thank you**: We know how hard you work in this class, thank you for all your hard work! ☺

Nomenclature of Acids, Bases and Salts
Review

I. Objective: To review the rules for naming common inorganic acids, bases and salt.

II. Principles: The rules of nomenclature are the rules published by the International Union of Pure and Applied Chemistry (IUPAC). Compounds are still named by these rules; however, others are still named by their historical names (common names). The rules in this section are used by chemists in naming acids, bases and simple salts derived from acids and bases.

I. <u>Binary Compounds</u>.

A binary compound contains only two elements. In general, a binary compound is named by first stating the name of the more electropositive element, followed by the name of the more electronegative element (usually a nonmetal), changing its stem to <u>-ide.</u>

A. Acids: Binary acids in aqueous solution are named differently than in the gas phase. Refer to the examples below to see the differences.

Examples:	Aqueous Solution	Gas Phase
HCl	hydrochloric acid	hydrogen chloride
HBr	hydrobromic acid	hydrogen bromide
H_2S	hydrosulfuric acid	hydrogen sulfide
HCN	hydrocyanic acid	hydrogen cyanide
HI	hydroiodic acid	hydrogen iodide

Note: CN^- is treated as if it were a single element.

B. Bases: The OH^- ion is considered as a single element, therefore all compounds containing OH^- are called hydroxides.

Example:	$Ca(OH)_2$	calcium hydroxide
	NaOH	sodium hydroxide
	NH_3	ammonia (common name)

C. Salts: If the metallic element has more than one valence, the oxidation number is designated by a Roman numeral: Fe(II) and Fe(III), for example. Group IA and IIA cations have only one valence; thus there is no need for a Roman numeral.

D. Binary compounds containing two *nonmetallic* elements are usually named in the following manner:
The number of atoms each element in a chemical formula are indicated by numerical prefixes: mono (1), di (2), tri (3), tetra (4), penta (5), hexa (6), hepta (7), octa (8).
Examples: N_2O dinitrogen monoxide
P_2S_5 diphosphorous pentasulfide.

II. Ternary Compounds

    Ternary compounds contain three elements.

A. Acids: Most common ternary acids (also called oxyacids) contain hydrogen, oxygen, and another element.

    1. The most common acid consisting of this combination of elements is named by adding *-ic* to the nonmetallic element.

        Examples: H_2SO_4 sulfuric acid H_3BO_3 boric acid

                     $HClO_3$ chloric acid H_2CO_3 carbonic acid

                     HNO_3 nitric acid H_3PO_4 phosphoric acid

    2. For an acid containing one less oxygen atom than that in (1), the suffix -ic changes from *-ic* to *-ous.*

        Examples: H_2SO_3 sulfurous acid $HClO_2$ chlorous acid

                     HNO_2 nitrous acid H_3PO_3 phosphorous acid

    3. For acids containing one less oxygen atom than in (2), the suffix remains the same but the prefix *hypo-* is added.

        Example: $HClO$ hypochlorous acid

    4. For acids containing one more oxygen atom than the most common acid with a suffix of *–ic* is named by adding the prefix *per-* to the name.

        Example: $HClO_4$ perchloric acid

    5. A table has been prepared for you on the following page to help summarize the nomenclature rules for naming oxy-acids and oxy-anions. This table is not a complete listing of all ternary compounds but it is a more visual summary of these types of compounds and their corresponding names. The authors of this lab manual urge you to use it and expand it as necessary for your own needs.

<p align="center">Oxy-Anions</p>

Prefix	Suffix						
hypo-	-ite		ClO^-	BrO^-			
	-ite	NO_2^-	ClO_2^-	BrO_2^-		SO_3^{2-}	PO_3^{3-}
	-ate	NO_3^-	ClO_3^-	BrO_3^-	CO_3^-	SO_4^{2-}	PO_4^{3-}
per-	-ate		ClO_4^-	BrO_4^-			

Notice the shaded row. All of those anions are named using the –ate suffix only. If you memorize those anions only, and know the nomenclature rules when oxygens are added or removed, you will automatically know how to name them correctly without actually having to memorize them. A few examples are shown below.

Anion	Name
NO_2^-	Nitrite ion
NO_3^-	Nitrate ion
ClO_3^-	Chlorate ion
ClO^-	Hypochlorate ion
CO_3^-	Carbonate ion
SO_3^{2-}	Sulfite ion

<p align="center">Oxy-Acids</p>

Prefix	Suffix						
hypo-	-ous		$HClO$	$HBrO$			
	-ous	HNO_2	$HClO_2$	$HBrO_2$		H_2SO_3	H_3PO_3
	-ic	HNO_3	$HClO_3$	$HBrO_3$	H_2CO_3	H_2SO_4	H_3PO_4
per-	-ic		$HClO_4$	$HBrO_4$			

Examples:

Acid	Name
HNO_2	Nitric acid
HNO_3	Nitrous acid
$HClO_3$	Chloric acid
$HClO$	Hypochlorous acid
H_2CO_3	Carbonic acid
H_2SO_3	Sulfurous acid

Remember: Learn the "-ates" for both categories (how many oxygens and the charge of the ion) and you will be able to name all the rest by only having to know the prefix and suffix.

6. **There are six strong acids that you need to memorize.** This list can also be found in your current text book as well. Assume all other acids are weak acids.

Strong acid	Name
HCl	Hydrochloric acid
HBr	Hydrobromic acid
HI	Hydroiodic acid
HNO_3	Nitric acid
$HClO_4$	Perchloric acid
H_2SO_4	Sulfuric acid

B. Salts:

1. Anions of salts derived from the ic acids, with all hydrogens removed, are named by changing ic to ate.

   Example: H_2SO_4 sulfuric acid Na_2SO_4 sodium sulfate.

2. Anions of salts formed from acids containing an ous suffix are named by changing ous to ite.

   Example: $HClO_2$ chlorous acid $NaClO_2$ sodium chlorite

3. Anions of salts of hypo ...ous acids retain the prefix hypo but ous is changed to ite.

   Example: HClO hypochlorous acid   NaClO sodium hypochorite
4. Anions of salts from a per...ic acid retain the prefix per and ate is substituted for ic.

   Example: $HClO_4$ perchloric acid $KClO_4$ sodium perchlorate.

5. Some salts contains anions that contain hydrogen, e.g. KHS and $NaHSO_4$. These anions are derived from acids which are not completely neutralized. The name of the anion is formed by adding the word "hydrogen" with a numerical prefix where necessary, to indicate the number of replaceable hydrogens. The word hydrogen occurs first.

   Examples: $NaHSO_4$ sodium hydrogen sulfate
   $Al(HSO_4)_3$ aluminum hydrogen sulfate
   NaH_2PO_4 sodium dihydrogen phosphate
   $Ca(H_2PO_4)_2$ calcium dihydrogen phosphate

   The prefix "mono" is not necessary to indicate one hydrogen.

Appendix 1 has many practice problems for you to work.

Experiment 1
Chemical Reactions and Net Ionic Equations

I. Objective:

To predict the products of some displacement reactions and write net ionic equations.
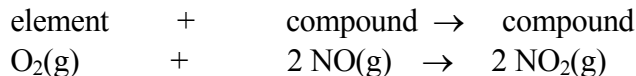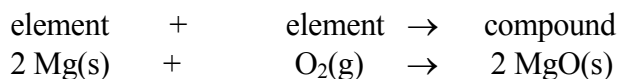
II. Chemical Principles:
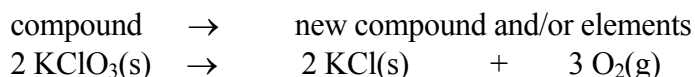
A. Reaction Types.

Chemical reactions can be classified into several different categories. The common classifications are as follows:

Note: For ease of production in this syllabus (aq) has been eliminated from all equations while (s), (l) and (g) have been used to represent phases. ***When you write chemical reactions in your lab reports you must show all phases including (aq).***
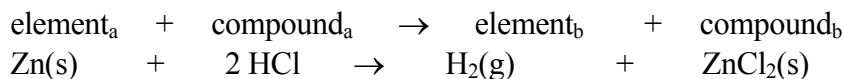
1. __Combination__. This reaction type involves the combining of elements and/or compounds to form a new compound.
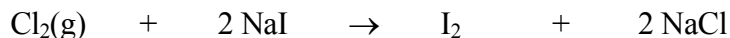
element   +   element →   compound
$2 Mg(s)$ + $O_2(g)$ → $2 MgO(s)$

element   +   compound →   compound
$O_2(g)$ + $2 NO(g)$ → $2 NO_2(g)$

compound   +   compound →   compound
$NH_3(g)$ + $HBr(g)$ → $NH_4Br(s)$

2. __Decomposition.__ This reaction type involves the splitting apart of a single compound to form new compounds or elements.

compound   →   new compound and/or elements
$2 KClO_3(s)$ → $2 KCl(s)$ + $3 O_2(g)$

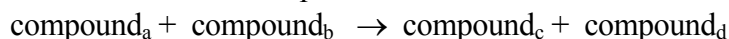$CaCO_3(s)$ → $CaO(s)$ + $CO_2(g)$

3. __Single Replacement.__ This reaction type involves an element displacing another element or ion in a compound, or a chemical compound displacing an element or ion from another compound.
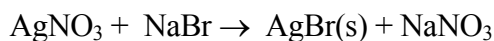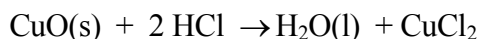
element$_a$ +   compound$_a$ →   element$_b$ +   compound$_b$
$Zn(s)$ + $2 HCl$ → $H_2(g)$ + $ZnCl_2(s)$

$$Cl_2(g) \quad + \quad 2\,NaI \quad \rightarrow \quad I_2 \quad + \quad 2\,NaCl$$

4. <u>Double Displacement (Metathesis).</u>   This reaction type involves the exchange of elements or ions in two compounds.

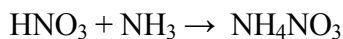$$compound_a + compound_b \;\rightarrow\; compound_c + compound_d$$

a. precipitation:

$$AgNO_3 + \; NaBr \rightarrow \; AgBr(s) + NaNO_3$$

b. dissolution

$$CuO(s) \; + \; 2\,HCl \;\rightarrow H_2O(l) \; + CuCl_2$$

c. neutralization

$$HNO_3 + NH_3 \rightarrow \; NH_4NO_3$$
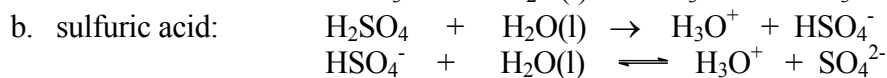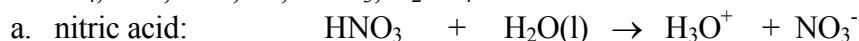
5. <u>Acid-Base Reactions.</u>   These reactions are commonly displacement reactions. To be able to predict such a reaction, you must know the identity and properties of a few specific acids and bases.

<u>Acids</u>
1. *Strong Acids.* All strong acids completely dissociate in water, for example:
$HClO_4$, HCl, HBr, HI, HNO_3, H_2SO_4

a. nitric acid: $\qquad\qquad\quad HNO_3 \quad + \quad H_2O(l) \;\rightarrow\; H_3O^+ \; + NO_3^-$
b. sulfuric acid: $\qquad\qquad H_2SO_4 \quad + \quad H_2O(l) \;\rightarrow\; H_3O^+ + HSO_4^-$
$\qquad\qquad\qquad\qquad\qquad\quad HSO_4^- \quad + \quad H_2O(l) \;\rightleftharpoons\; H_3O^+ \; + SO_4^{2-}$

The first ionization step for sulfuric acid is 100%, however the second step is an equilibrium situation and ionization is only partial.

Note: Molecules of strong acids such as $HClO_4$ and H_2SO_4 do not exist in solution because we treat them as ionizing 100 %, that is as strong electrolytes. $H^+(aq)$ can be written in place of H_3O^+, the hydronium ion.

2. _Weak Acids._ These acids react only slightly with water to produce the hydronium ion. They, however, will react completely with a strong base.

Acid	Reaction	Extent of Reaction
acetic acid	$HC_2H_3O_2 + H_2O(l) \rightleftharpoons H_3O^+ + C_2H_3O_2^-$	0.42%
carbonic acid	$H_2CO_3 + H_2O(l) \rightleftharpoons H_3O^+ + HCO_3^-$ $HCO_3^- + H_2O(l) \rightleftharpoons H_3O^+ + CO_3^{2-}$	0.065%
ammonium ion	$NH_4^+ + H_2O(l) \rightleftharpoons H_3O^+ + NH_3$	0.0024%

Bases

1. _Strong bases:_ dissociate completely in water.
   a. Soluble metal hydroxides. $MOH \rightarrow M^+ + OH^-$
   b. Insoluble metal hydroxides. All insoluble metal hydroxide dissolve to a very limited extent to form metal ions and hydroxide ions. Because the dissolved form of the insoluble metal hydroxide dissociates completely it is considered a strong electrolyte and thus it is a strong base. The OH⁻ ion is the strongest base that exists in water.   For example, calcium hydroxide is said to be insoluble, but the reality is that some calcium and hydroxide ions exist in solution and therefore the solution is basic. $Ca(OH)_2(s) \rightleftharpoons Ca^{2+} + 2 OH^-$
   **Moderately soluble bases are strong bases because what does dissolve, dissociates 100%.**
2. _Weak bases:_ These substances react slightly with water to produce OH⁻ and are weak electrolytes.

Base	Reaction	Extent of reaction*
ammonia	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.3%
acetate ion	$C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^-$	0.42%
carbonate ion	$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$	0.0024%
fluoride ion	$F^- + H_2O \rightleftharpoons HF + OH^-$	0.00039%

* 1.0 M solution

Salts:

Salts contain a metal ion and a nonmetal or polyatomic anion. Salts can be formed by a neutralization reaction: a reaction between an acid and a base producing a salt and water. For example:

$NaOH + HF \rightarrow NaF + H_2O(l)$

$Ba(OH)_2 + H_2SO_4 \rightarrow BaSO_4(s) + 2H_2O(l)$
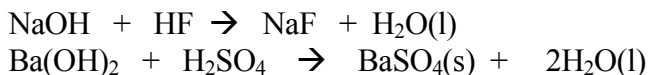
Some salts, such as sodium fluoride, are very soluble in water, therefore a change is not observed upon reaction. However, some salts such as barium sulfate are quite insoluble in water and a precipitate will be observed when formed as a product in a reaction.

B. Predicting Products of Displacement Reactions and Writing Net Ionic Equations.

To predict if a displacement reaction will occur, you must become familiar with the conditions required before a reaction takes place. Rules have been developed to assist you with predicting the products of displacement reactions and for writing the net ionic equations associated with these reactions.

You first determine if a displacement reaction can occur when you have two salts or an acid and base or a salt and acid/base reacting. Assume that a single or double displacement is responsible for causing a reaction. Carry out the single or double displacement reaction and focus on the predicted products. A product of a reaction having one of the characteristics in Table I supports the occurrence of a displacement reaction.

Table I. Observations of a Chemical Reaction

1.A A solid (precipitate) forms. This requires that you know the solubility rules.
2.A A new weak electrolyte or a compound with a new covalent bond forms. For example; formation of water, acetic acid, or carbon dioxide.
3.A A new gas forms. For example; the formation of gaseous water, carbon dioxide, hydrogen sulfide, hydrogen, or ammonia.
4.A A new element forms.   Zn, Pb, H_2, O_2 etc.
5.A A precipitate dissolves. A colored, or clear, solution may result.

Unless a precipitate forms, a gas evolves, or a colored ion forms, it may be difficult to determine with your senses if a displacement reaction has taken place. Examples of physical evidence that sometime accompany a displacement reaction and which may indicate their occurrences are:

- change in acidity or basicity of the product compared to the reactants.
- evolution or absorption of heat, other than heat of solution.
- solid reactant disappears.

- change in the color of the solution.
- precipitate forms in a solution.

To apply these rules (1A -5A) you need to know which substances are strong and weak electrolytes and which substances are soluble and insoluble and what is the limit of solubility of a compound in aqueous solution. Some rules are given in the following Tables.

Table II. Strong and Weak Electrolytes

1.B *Strong electrolytes* include all ionic substances except the halides and cyanides of Hg_2^{2+}, Cd^{2+}, Zn^{2+}, and Ag^+. Strong acids, strong bases and many salts are strong electrolytes.[*]
2.B   *Weak electrolytes* include weak acids, weak bases and many organic compounds. Only a few ions will be produced in aqueous solution.
3.B   *Nonelectrolytes* include pure water and many organic compounds, including sugar, for example. These are normally molecular compounds.

* Many salts are insoluble in water, however, what limited quantity that does dissolve in water, dissociates 100%.   Salts, soluble or insoluble (except for those identified in 1B) will be treated as strong electrolytes. The terms strong electrolyte and solubility are not equivalent.

Table III. Solubility Rules for Salts.

1.C   All alkali metal and ammonium compounds are soluble. $KClO_4$ is slightly soluble.
2.C   All nitrates are soluble.
3.C   All acetate salts are soluble. $AgC_2H_3O_2$ is slightly soluble.
4.C   All sulfate salts are soluble except $BaSO_4$, $PbSO_4$, and Hg_2SO_4. Slightly soluble salts include $CaSO_4$, and $SrSO_4$.
5.C   All salts of chloride, bromide, and iodide are soluble except those of Ag^+, Pb^{2+}, and Hg_2^{2+}.
6. C   All hydroxides, phosphates, carbonates, chromates, oxalates and sulfides are insoluble except those of the alkali metals and ammonium ion. $Ba(OH)_2$, $Ca(OH)_2$, and $Sr(OH)_2$ are moderately soluble.
7.C   All oxides are quite insoluble.
Note: If a compound is slightly soluble, usually it can be considered insoluble.
It is necessary to know the *solubility limit* of a particular compound.

Solubility is defined as the maximum amount of substance that dissolves in a given amount of solvent at a given temperature . The solubility limit of many compounds can be found in the Handbook. of Chemistry and Physics.

C. Rules for Writing Net Ionic Equations

1. Write the overall balanced "molecular" equation.

2. Rewrite the molecular equation so that only soluble, strong electrolytes are separated into their ions.

3. Eliminate all species common to the reactants and products (spectator ions).

4. The resultant equation is the net ionic equation.

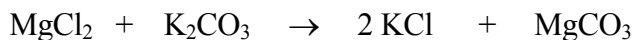5. There is no net ionic equation if there is no reaction.

D. Application of Net Ionic Equation Rules.

Example 1: (Production of a **solid**)
Predict the outcome of the following reaction and write the net ionic equation,

$$MgCl_2 + K_2CO_3 \rightarrow \quad ?$$

a. Complete the equation by carrying out a double replacement reaction (exchange partners)

$$MgCl_2 + K_2CO_3 \rightarrow 2\,KCl + MgCO_3$$

b. Use rules 1.A - 6.A, 1.B - 3.B, and 1.C - 7.C to determine if a reaction occurred. According to 6.C, $MgCO_3$ is insoluble and will precipitate. According to 1.A, a reaction occurs.

c. Write the molecular equation and then apply rules given above to separate strong electrolytes into their ion forms and identify magnesium carbonate as an insoluble substance.

$$MgCl_2 + K_2CO_3 \rightarrow 2\,KCl + MgCO_3(s)$$

$$Mg^{2+} + 2Cl^- + 2K^+ + CO_3^{2-} \rightarrow 2K^+ + 2Cl^- + MgCO_3(s)$$
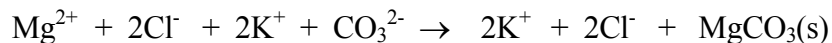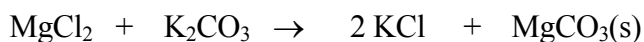
d. Eliminate ions common to reactants and products and the result is the net ionic equation:

$$Mg^{2+} + CO_3^{2-} \rightarrow MgCO_3(s)$$
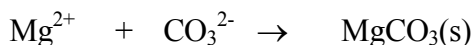
Example 2: (Production of a **Gas)**
Predict the outcome of the reaction of hydrochloric acid with $MgCO_3(s)$.

a. Complete the double displacement reaction.

$MgCO_3(s)\ +2HCl\ \rightarrow\ MgCl_2\ +\ H_2CO_3 \xrightarrow{Heat} MgCl_2 + H_2O(l) +\ CO_2(g)$

Note: H_2CO_3 is a weak acid that in the presence of heat decomposes to $H_2O(l)$ and $CO_2(g)$, We normally show carbonic acid in the decomposed form.

b. Use the rules to determine if a reaction has occurred. A reaction occurs because carbonic acid forms and it is a weak acid and weak electrolyte.

c. Separate the soluble and strong electrolytes into ions.

$MgCO_3(s)\ +2H^+\ +\ 2Cl^-\ \rightarrow\ Mg^{2+}\ +\ 2Cl^-\ +\ H_2O(l) +\ CO_2(g)$

d. Eliminate the common ions and the result is the net ionic equation.
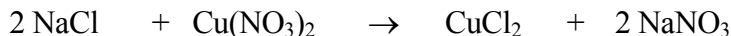
$MgCO_3(s)\ +2H^+\ \rightarrow\ Mg^{2+}\ +\ H_2O(l) +\ CO_2(g)$

Example 3: (No observed reaction)
Predict the result of the following reaction and write the net ionic equation.
$NaCl\ +\ Cu(NO_3)_2\ \rightarrow\ $?
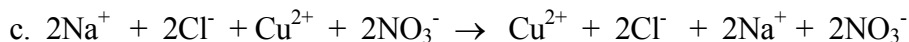
a. Complete the equation by carrying out a double displacement reaction.
$2\,NaCl\ \ \ +\ Cu(NO_3)_2\ \ \ \rightarrow\ \ \ CuCl_2\ \ \ +\ \ 2\,NaNO_3$

b. Use the rules to determine if a reaction has occurred.
Both $CuCl_2$ (5.C) and $NaNO_3$ (2.C) are soluble and strong electrolytes. Thus no reaction can occur as the requirements of Rules 1.A - 5.A are not met.

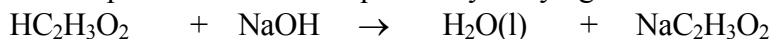c. $2Na^+\ +\ 2Cl^-\ +Cu^{2+}\ +\ 2NO_3^-\ \rightarrow\ Cu^{2+}\ +\ 2Cl^-\ +\ 2Na^+ +\ 2NO_3^-$

d. All the ions cancel and thus there is no net ionic equation.

Example 4: (Acid - base reaction)
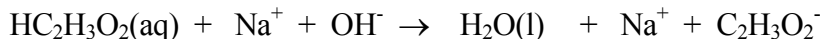Predict the outcome of the following reaction and write the net ionic equation.
$HC_2H_3O_2\ +\ NaOH\ \rightarrow$

a. Complete the balanced equation by carrying out a double displacement reaction.
$HC_2H_3O_2\ \ \ +\ NaOH\ \ \ \rightarrow\ \ \ H_2O(l)\ \ \ +\ \ \ NaC_2H_3O_2$

b. Has a reaction occurred?
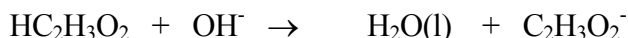Water is a new covalent substance (2.A), so a reaction has occurred.

c. Separate all strong electrolytes into ions.

$$HC_2H_3O_2(aq) + Na^+ + OH^- \rightarrow H_2O(l) + Na^+ + C_2H_3O_2^-$$

Note: $HC_2H_3O_2$ is a weak electrolyte and therefore it written as a molecule.

d. Eliminate the spectator ion and the result is the net ionic equation.

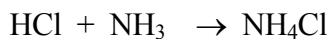$$HC_2H_3O_2 + OH^- \rightarrow H_2O(l) + C_2H_3O_2^-$$

Example 5 (Acid-base reaction):
Predict the outcome of the following reaction and write the net ionic equation.
$$HCl + NH_3 \rightarrow$$

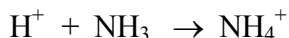a. Complete the equation by carrying out a single displacement reaction.

$$HCl + NH_3 \rightarrow NH_4Cl$$

b. This is a strong acid reacting with a weak base. A weaker acid (a new covalent substance), H_2O, is produced therefore a reaction occurs.

c. $H^+ + Cl^- + NH_3 \rightarrow NH_4^+ + Cl^-$

d. Eliminating chloride ion, the spectator ion, gives the net ionic equation.

$$H^+ + NH_3 \rightarrow NH_4^+$$

B. Procedues: Solubilities and Primary Species of Substances in Water and Acid.

Experimental Procedures for Table II:

Slowly add, with a spatula, a very *tiny* amount (big enough to see how it will behave in water, but not so much to exceed the capacity of your solvent) of each compound to about 1 mL (approximately 20 drops) of water in a test tube. Note any change in the solubility. Do not add too much compound to the water as the volume is small and only a small amount of compound is required. Add extra water if needed.

Waste Disposal for Table II:

Your laboratory instructor has already shown you where the waste disposal bottles are in the back fume hood. The following compounds need to be placed in the correct waste bottle for safety reasons as well to reduce fees incurred by cross contamination.
The following compounds need to be disposed of in the Metal Salts container:
- $BaSO_4$, $Ca(NO_3)_2$, $Ca_3(PO_4)_2$, $(NH_4)_2SO_4$, $PbCO_3$, $AgC_2H_3O_2$, Hg_2Cl_2,
- Cu_2O, $NaHSO_4$, KI, $BaCl$.

Use the Organic Waste container for the following compounds:

- $C_6H_{12}O_6$
- benzoic acid, C_6H_5COOH

Table II Solubility of Compounds in Water

	Solid compound	Name of compound	Strong, Weak, Nonelectrolyte	Primary species in H_2O	Predicted Solubility in H_2O	Solubility in 100mL H_2O (Handbook)	Predicted Solubility in HNO_3	Laboratory Observations
1a	$BaSO_4$	Barium sulphate	Strong	$BaSO_4$	insoluble	0.2 mg		
1b	$BaSO_4$							
2a	$Ca_3(PO_4)_2$							
2b	$Ca_3(PO_4)_2$							
3	$(NH_4)_2SO_4$							
4a	$PbCO_3$							
4b	$PbCO_3$							
5a	$AgC_2H_3O_2$							
5b	$AgC_2H_3O_2$							
6	Hg_2Cl_2	Mercury(I) chloride	Strong	$Hg_2Cl_2(s)$	Insoluble	0.2 mg		
7a	Cu_2O							
7b	Cu_2O							
8	Glucose $C_6H_{12}O_6$							
9	$NaHSO_4$							
10	KI							
11	benzoic acid, C_6H_5COOH							
12	$BaCl_2$	Barium chloride	Strong	Ba^{2+} and Cl^- ions	soluble	37.5 g		

Note: Shaded boxes indicate that no data will be collected. Don't fill in the shaded boxes. You will test the solubility of compounds 1b, 2b, 4b, 5b, and 7b in HNO₃ only. You will have the solubility of those same compounds in water just above the "b" series.
Write Net Ionic Equations for the "b" series compounds with HNO₃ below or on a clearly labeled separate sheet of paper.

Table III: Electrolytes

Compound	Primary Species in H_2O	Acid, Base, Salt, Organic	Strong, Weak, Nonelectrolyte	Observation in the laboratory
HNO_3				
$HC_2H_3O_2$	$HC_2H_3O_2$	Weak acid	Weak electrolyte	
NH_3				
$NaOH$				
$Ca(OH)_2$				
$PbCO_3$				
K_2CO_3	$2K^+$, CO_3^{2-}	salt and weak base (CO_3^{2-})	strong electrolyte	
$PbCl_2$				
$NiCl_2$				
$MgCl_2$				
$Zn(NO_3)_2$				
$Cu(NO_3)_2$				
C_2H_5OH (ethanol)				
$C_6H_{12}O_6$ (sugar)				

Experimental Procedures: Place each compound in the first column in a well of a spot plate. If a compound is a solid and not a liquid, add a small amount of water to it and stir. Use a conductivity device to determine if the substance is conducting or not. Record the relative brightness of the light or absence of light. A bright light only indicates more ions are in solution compared to a dim light, not whether it is a strong or weak electrolyte. The concentration of ions must be known to make a more definitive conclusion. The absence of a light indicates that ions are not present. Only the ends of the two copper probes of the device should be in the solution. Your instructor will demonstrate the use of the conductivity device.

Table IV. Net Ionic Reactions

	Reactants (A)	Net Ionic Equations (B)	Predicted Observation (C)	Experimental Observations (D)
1a	$Ba(NO_3)_2 + K_2SO_4$			
1b	$BaSO_{4(s)} + HCl(12M)$			
2a	$NiCl_2 + Na_2CO_3$			
2b	$NiCO_{3(s)} + HCl (12M)$			
3a	$CoCl_2 + KOH (6M)$			
3b	$Co(OH)_{2(s)} + HCl(12M)$			
4a	$Na_3PO_4 + ZnSO_4$			
4b	$Zn_3(PO_4)_{2(s)} + HCl(12M)$			
5	$KCl + Cu(NO_3)_2$			
6a	$Na_2S + Cu(NO_3)_2$			
6b	$CuS_{(s)} + HCl (12M)$			
7	$Na_2CO_3(sat'd) + HCl (12 M)$			
8	$(NH_4)_2SO_4(sat'd) + NaOH (6M)$			
9	$Cu(NO_3)_2 + NH_3 (12M)$			
10a	$AgNO_3 + NaCl$			
10b	$AgCl_{(s)} + NH_3 (12M)$			
11	$CaCl_2 + NH_3(aq)$			
12	$CaCl_2 + NaOH$			
13	$Ca(OH)_2(aq)(sat'd) + NH_4Cl$			
14	$NH_4Cl + NaOH$			

Experimental Procedure: Add approximately 2 drops of each pair of reactants in the first column to a test tube or the well of a spot plate. Use 0.1 M solutions for all reactants except when noted differently. Record your observations in column D. Be sure to note the formation of a precipitate, any color change, color of precipitate, evolution of a gas, etc. **For a "b" reaction**, remove the excess solution from the product of the "a" reaction by gently drawing the solution off the top with a Pasteur pipet. Add 6 drops of the indicated reagent to the precipitate that is left in the well plate to determine if it dissolves in the reagent. Record your observations in column D.

Waste Disposal:

Place all waste in the Metal Salts container.

D. Prelaboratory Assignment: You will not be allowed to perform the experiment if the prelaboratory assignment is not completed when you come to lab.

Day 1: (continues on next page)

- If you do not have the lab manual, print out entire experiment.
- Read pages 14-23.
- Using WORD, construct and Print out tables (Prelab Table I-Table III). For future experiments, you will be required to construct tables in your notebook.
- **Prelab Table I**: Using the solubility rules on page 18 or your text book, fill in the predicted results for each pair of ions. Write the formula of the compound that would result for each pair and indicate an I for insoluble, or S for soluble. Two examples have been done for you. You should print this table (and all other tables) on separate pages and make them larger at your convenience.

Table I : Prediction of Solubility of Salts in water.

	Cl^-	Br^-	I^-	SO_4^{2-}	PO_4^{3-}	OH^-	CO_3^{2-}	$C_2H_3O_2^-$	S^{2-}	CrO_4^{2-}
Na^+	NaCl S									
K^+										
NH_4^+										
Ca^{2+}										
Mg^{2+}										
Ba^{2+}										
Cr^{3+}										
Fe^{2+}										
Co^{2+}										
Ni^{2+}							$NiCO_3$ I			
Cu^{2+}										
Ag^+										
Pb^{2+}										

Day 1 Continued:

- **Table II**: Once prepared in WORD, fill in all columns (typed) EXCEPT the one labeled Laboratory Observations. Laboratory Observations column will be done in lab. Write net ionic equations for the "b" series compounds from that table.
- In the column labeled "**primary species in water**" you are to type the primary form of each substance when it is present in water. If it is insoluble or a weak electrolyte, you are to type it in a "molecular" form with its phase. If it is soluble and a strong electrolyte, you type it in the ion form. In the column labeled "**solubility in 100 mL of water"**, look up the solubility of each compound in 100 mL of water in the Handbook of Chemistry and Physics or find it in a reliable source from the internet. A copy of Handbook of Chemistry and Physics is in Sequoia 502. Organic compounds may not have solubility data. Two examples are shown.

- **Table III**: Print out Table III. Fill in all columns (typed) EXCEPT the one labeled Laboratory Observations. Just like for Table II, you will fill in that column during lab.

Day 2 Prelab:

- Print out **Table IV** as shown on page 24. Print in "landscape mode. Type in all columns EXCEPT column D. You will record your observations in column D during lab.
- Column C: Type in whether you think a soluble or insoluble product will form.

E. Laboratory Report:

1. Printed Title page
2. Laboratory data pages containing your instructor's signature. These are the same tables that you printed out for your prelab assignment. If your instructor has indicated errors on these pages, correct those on a separate sheet of paper and attached it after the table.
3. Table IV: Since you have already typed this table, print out a new copy of it containing your typed corrections where needed.
4. Once your report has been assembled, write the page number in the upper right corner for each page. An example layout is shown below.

Title Page Your name Experiment #	Prelab Table I	Table II (signed copy)	Table II (reprinted with corrections)	Table III (signed copy)
Table III (reprinted with corrections)	Table IV (signed copy)	Table IV (reprinted with corrections)		

Experiment 2
Standardization of Sodium Hydroxide Solution

I. <u>Objective:</u>

To prepare and determine the concentration of a standard sodium hydroxide solution. The solution that you prepare in this lab will be used in subsequent experiments.

II. <u>Chemical Principles:</u>

In the next experiments you will be required to use a sodium hydroxide solution whose concentration is accurately known. This is called a standard solution. The preparation of a standard solution is normally done by first preparing a saturated solution of NaOH and letting it stand for about a week. An aliquot (portion) of the saturated solution is added to deionized water to form a NaOH solution of approximate concentration desired. This solution is then titrated against a primary standard and, once its concentration is accurately determined, it becomes a standard solution.

The NaOH solution is kept isolated from air to ensure that CO_2 does not dissolve in it. If CO_2 dissolves, $NaHCO_3$ forms and this causes errors in the process of determining the concentration of a solution. In this experiment you will be provided a 6.0 M NaOH solution which is relatively free if dissolved carbon dioxide. You will take a small aliquot of this solution and add it to approximately one liter of deionized water in a polyethylene bottle. The desired concentration of the final NaOH solution is approximately 0.1 M. However, at this point, the exact concentration is not known.

To determine the exact concentration of the NaOH solution you will titrate a solution of ***potassium hydrogen phthalate, KHC<u>$_8$</u>H<u>$_4$</u>O<u>$_4$</u>***, to the equivalence point. **The abbreviation, KHP, is often given to this compound and it does <u>not</u> refer to potassium, hydrogen, and phosphorus**. KHP is one of the common primary standards for NaOH standardization. The compound is a potassium salt of phthalic acid, $H_2C_8H_4O_4$. Only one proton per empirical formula unit of KHP is acidic and reacts with NaOH. KHP reacts with NaOH according to the following equation:

$$HC_8H_4O_4^- \text{ (aq)} + OH^- \text{ (aq)} \rightarrow H_2O\text{(l)} + C_8H_4O_4^{2-} \text{ (aq)}$$
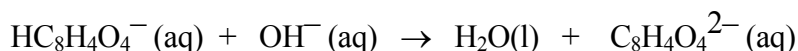
The net ionic equation shows that at the equivalence point of the titration, the <u>number of moles of NaOH equals the number of moles of KHP</u>. From the mass of the KHP the number of moles can be calculated. The molarity of the NaOH solution can be calculated from the following:

$$M_B V_B = \text{moles of KHP}$$

where M_B is the molarity of the NaOH to be calculated and V_B is the volume of the NaOH used to titrate a primary standard KHP solution.

In this experiment, precision is important. Precision is the reproducibility, or closeness, of replicate measurements. High precision in titrations means that your next measurements will be close to the average of those already done. A large uncertainty is reflected in low precision.

For purposes of this experiment, precision is measured by the relative standard deviation, (D), where

$$D = \frac{\bar{d}}{\bar{x}}(1000) \quad or \quad D = \frac{\bar{s}}{\bar{x}}(1000)$$

$\bar{d}$, or $\bar{s}$, is the standard deviation and is calculated from the expression:

$$\bar{d} = \bar{s} = \sqrt{\frac{\sum_{i=1}^{n}\left(x_i - \bar{x}\right)^2}{n-1}}$$

where i represents a single value, $\sum$ means to sum the values in the expression, n = number of data points and $\bar{x}$ = average of all values.

Example: A student determines the molarity of a base solution in four separate titrations:

$$0.2041 \text{ M, } 0.2049 \text{ M, } 0.2041 \text{ M, } 0.2043 \text{ M.}$$

$$\bar{x} = average = \frac{0.2041 + 0.2049 + 0.2041 + 0.2043}{4} \approx 0.2043$$

$$\bar{d} = \sqrt{\frac{(0.2041-0.2043)^2 + (0.2049-0.2043)^2 + (0.2041-0.2043)^2 + (0.2043-0.2043)^2}{3}}$$

$$\bar{d} = \bar{s} = \sqrt{\frac{4.0x10^{-8} + 3.6x10^{-8} + 4.0x10^{-8} + 0.0}{3}} = 3.8 \times 10^{-4}.$$

Relative standard deviation $= D = \frac{\bar{d}}{\bar{x}}(1000) = \frac{3.8x10^{-4}}{0.2043} \times 1000 = 1.9 \text{ ppt}$

where ppt = parts per thousand. Note the number of significant figures in each step of the calculation.

The smaller the value of relative standard deviation, the better the precision. If you calibrate your glassware, you should obtain a relative standard deviation of <2 ppt. In this experiment you do not calibrate your glassware; therefore you should obtain a precision <4 ppt. If your precision is greater than 4 ppt, run additional samples to reduce uncertainty.

III. **Experimental Procedures:**

        *   Some semesters the service center will provide the NaOH solution. In that case your instructor will tell you to clean and rinse a 1 L polyethylene bottle to be filled with the "stock" solution. You MUST RECORD the concentration of the solution you are using. **If** you use the stock solution provided you do NOT do steps 1 and 2.

1. *   Clean a 1 L polyethylene bottle and rinse thoroughly. Add approximately one liter of deionized water and cap the bottle.

2. *   In a clean graduated cylinder that is rinsed several times with small quantities of the 6M NaOH solution provided in the laboratory, measure the volume of NaOH that was calculated in the pre-lab exercise. Transfer this volume of 6M NaOH to the water in the polyethylene bottle. Do not do this until your pre-lab calculation is approved by your instructor. Cap the bottle securely. Shake (swirl) carefully for at least 15 min to insure complete dissolving and mixing. The solution must be thoroughly mixed.

3. While you are occasionally shaking the NaOH bottle, clean three 125 Erlenmeyer flasks. Rinse several times with deionized water. Remove excess water by shaking the flask but do not dry with air lines or paper. Turn upside down on top of a paper towel to store until the next step.

4. To avoid long lines in the balance room, start by weighing two samples and return later to weigh out more. Weigh out <u>accurately</u> 700 to 800 mg of KHP into each of the three Erlenmeyer flasks. Record all digits displayed on balance, which will give you four significant figures. Be sure to label the flasks with the appropriate weight of sample. The KHP has been dried to remove any hydroscopic water. A sample of KHP is weighed either on weighing paper or in a dry container and the mass recorded. Then the KHP is carefully transferred to one of the Erlenmeyer flasks. Do this for all three samples. Be careful not to spill any KHP or let air currents blow it off your weighing paper or from the flasks. Avoid any contamination. Record in your laboratory notebook, which is taken to the balance room (not scratch paper), all mass measurements made with the balance. Be sure to properly identify all measurements and show units.

5. Dissolve each sample of KHP in about 50 mL of deionized water, warming **slightly** if necessary (Do NOT boil!). Rinse any solid KHP down the sides of the flask. You should now have three samples of the primary standard KHP dissolved in about 50 mL of water.

6. Clean a buret and then rinse several times with small quantities (5-10 mL) of the standard NaOH solution that you have prepared. It is very important that all water be

removed and that only the standard solution be present. Carefully add the 0.1 M NaOH to the buret. Use a small filter funnel inserted into the buret to assist with the transfer. Be sure the filter funnel is also clean and rinsed with the 0.1 M NaOH solution before using it. Fill the buret to **about** the 0 mL mark. Release some of the solution into an empty beaker. There should be no air bubbles in the tip of the buret. When this is completed, be sure to record the starting volume of the solution in the buret. The initial reading will not be 0.0. When you record volume of a liquid in a 50 mL buret, be sure to record **two digits to the right of the decimal point**. The last digit is estimated.

7. **In your data book** prepare the following table (Give a title to the table). With any measured value you must show its units with the column heading. Use a ruler to prepare the lines for the table.

Title

Titration #	KHP (g)	V_{final} (mL)	$V_{initial}$ (mL)	V_{total} NaOH (mL)
1				
2				
3				

Proper reading of your buret:
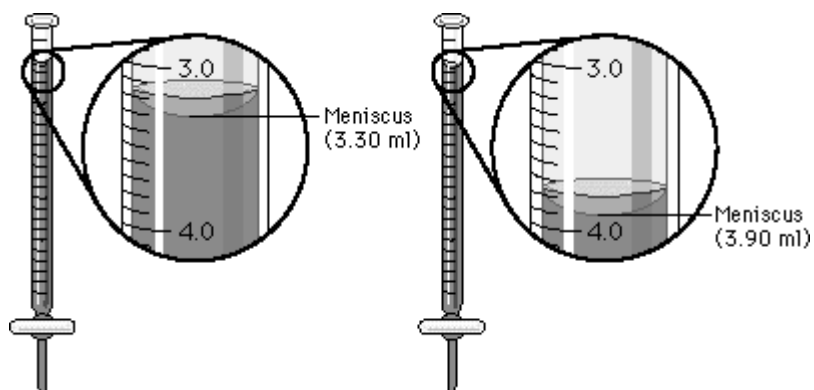
Assume that the buret is filled to the point indicated in the figure at the left. You would record the initial point as 3.30 ml; the ending point would be 3.90 ml. Therefore, the titration would have required 0.60 ml. Remember that you should read the number that is at the bottom of the meniscus. 3.90 – 3.30 = 0.60 mL

Your buret volume readings for this example would be entered on your table as follows:

Titration #	KHP (g)	V_{final} (mL)	$V_{initial}$ (mL)	V_{total} NaOH (mL)
1		3.90	3.30	0.60
2				
3				

7. Add **3 drops** of phenolphthalein indicator and a clean magnetic stirring bar to the first flask and titrate using the standard NaOH to the first faint pink end point that persists for 20 sec. Depending on the quantity of KHP, this should take between 25 - 45 mL. Titrate drop wise near the end point, splitting drops at the equivalence point to obtain the most accurate volume possible. When this is completed, be sure to record the ending volume of the NaOH solution in the buret. If necessary, adjust the number of drops of phenolphthalein indicator and add to the other two flasks. Titrate them using the same procedures. You should try to obtains the same intensity of pink color for each titration to insure reproducibility.
When you have completed three titrations you are NOT done. Do not clean up until you have **completed** step 8 and you instructor has okayed your results.

8. After you complete all three titrations determine the precision of your results. For each titration, calculate the molarity of the solution. Be sure to determine the correct number of significant figures. Determine the precision of the calculated molarities for the three titrations. If your molarities do not agree with a precision of 4 ppt or lower, you must do additional titrations until you have three values that show this precision. If you run out of time, you will have to choose the two results that give you the best precision. This may result in less accurate results in the next experiments and affect how your instructor grades these laboratory reports. Show your calculations to your lab instructor and have him/her sign your laboratory notebook.

9. When finished, dilute all acid and base solutions and then you may dispose of them in the sink. ***Do not dispose of the standard NaOH solution in the polyethylene bottle***. Be sure it is labeled with your name, date, the average concentration. Securely cap it and place it in your locker. You will use it in future experiments.

10. Rinse the buret with deionized water several times and fill with water. Store in the cabinet provided.

11. **IV. Laboratory Report:** (Parts 1, 4, and 5 are word processed.)

1. Title page including the **average** calculated value of molarity of NaOH and the precision of the titrations.
2. Laboratory notebook pages containing Pre-lab with corrections to pre-lab.
3. Laboratory notebook pages containing procedures, observations, data and calculation of precision.
4. Prepare a table summarizing each titration, including average molarity and precision.

<div align="center">Title</div>

Titration	M_{NaOH} (mol/L)	$M_{average}$ NaOH
1		
2		
3		Precision:

5. Will the calculated Molarity of NaOH be too high or too low if the following happen. Assume the error was not corrected. For each case give an explanation for your conclusion. In your discussion consider how the situation affects the calculation of molarity of NaOH and moles NaOH, which is calculated from the mass of KHP. (see (e) below for example.)

    a) KHP is wet when you weigh it.
    b) The buret has water in it when you add the NaOH.
    c) You exceed the equivalence point by one milliliter.
    d) You add the weighed KHP to a flask containing a small amount of distilled water.
    e) You splash some KHP solution from the flask before you titrate the solution. (you do not have to answer this question, see answer below)
Example answer to e:
        The weight of KHP written in the data book before any was lost is now higher than was actually used. Since moles of NaOH is calculated from recorded weight of KHP this gives a high value of moles of NaOH. Also since we actually titrate less KHP we use less volume of NaOH. Our calculation becomes:

$$\text{Molarity of NaOH} = \frac{\text{high moles}}{\text{low volume}} = \text{molarity too high.}$$

.

V. <u>Pre-Lab:</u>   This and all other prelabs are handwritten in the data book. See page 6.

1. Define the following terms: equivalence point, end point, indicator, titration, molarity, meniscus, precision, and accuracy.

2. How many milliliters of 6.0 M NaOH must be used to prepare 1.0 liter of 0.10 M solution?   Show units in each step of your calculation (Required for all calculations).

3. A student titrates 15.00 mL aliquots (a portion taken from a larger volume) of an unknown KOH solution with 0.2000 M HCl. The volumes of the HCL solution at the three equivalence points are 30.00 mL, 29.76 mL, and 29.92 mL.   Calculate the three molarities.   What is the average molarity of the KOH solution? What is the relative average deviation of molarities? Is the data within the precision standard? Should another experiment be done? Explain.

4. What is the average number of moles of KOH in 15.00 mL of the unknown solution in (3)?

5. What is the molar mass of potassium hydrogen phthalate, KHP?

6. If it took 25.00 mL of a monoprotic base to titrate 730.0 mg of KHP, what is the molarity of the base? Show clearly all steps in your calculation. Write a generalized chemical reaction.

7. Water is added to the weighed KHP to make a solution. Does it make a difference in the titration if 25 or 50 mL of water is added?   Explain

.

Experiment 3
Acid- Base Titration

I. **Objective:**

To obtain titration data that provides information to develop three titration curves : strong acid with a strong base; weak acid with a strong base; and a weak base with a strong acid. From this information the K values for the weak acids and weak bases are determined.

II. **Chemical Principles:**

. pH, Percent Reaction and Equilibrium Constants of Acids and Bases

Acids in aqueous solution are simply compounds that increase $[H_3O^+]$ above 10^{-7} M; conversely, bases cause $[H_3O^+]$ to be less than 10^{-7} M. The extra H_3O^+ created by acids can either come from the acid itself, as in the case of HCl, H_2SO_4, or NH_4^+, or can come from a reaction of a metal ion with water to form hydrogen ions (or hydronium ions, H_3O^+). An example of this is dissolved $Fe(NO_3)_3$ forming hydronium ions in water.

$$[Fe(H_2O)_6]^{3+}_{(aq)} + H_2O \leftrightarrow [Fe(H_2O)_5(OH)]^{2+}_{(aq)} + H_3O^+ \quad K_a = 6.3 \text{ x } 10^{-3}$$
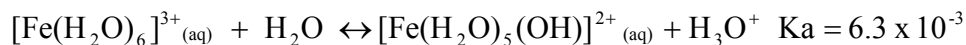
Metal hydroxides produce hydroxide ions (OH^-) by dissociating in water. Two examples are NaOH and $Ba(OH)_2$. Basic solutions are also formed when a weak base, such as ammonia, or the anion of a weak acid reacts with water to form hydroxide ions.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^-$$
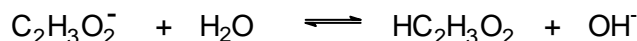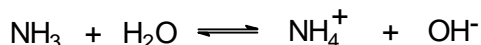
In all aqueous system we observe that when [OH^-] increases, [H_3O^+] decreases, and vice versa, because water undergoes an auto-ionization equilibrium:

$$2 H_2O(l) \leftrightarrow H_3O^+ + OH^-$$
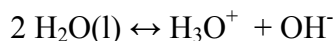
$$K_w = [H_3O^+][OH^-] = 1.0 \text{ x } 10^{-14} \text{ at } 25^o \text{ C in } H_2O.$$

For weak acids, the percent ionization of HX is the concentration of H_3O^+ from pH divided by the initial concentration of the weak acid, multiplied by 100.

$$\% \text{ Dissociation} = \frac{[H_3O^+]_{Measured}}{[HX]_{initial \text{ concentration}}} \text{ x } 100$$

For an anion or weak base that reacts with water to form a basic solution, the percent of the reaction that occurs is

$$\% \text{ Reaction} = \frac{[OH^-]_{\text{Measured}}}{[\text{Base}]_{\text{initial concentration of weak base}}} \text{ x } 100$$

The reaction of an ion with water is sometimes called hydrolysis.

Both hydrochloric acid and acetic acid contain one ionizable hydrogen and are therefore called monoprotic acids. If the monoprotic acid is titrated with a strong base, such as NaOH, the pH at the equivalence point for a strong acid is 7, whereas for the titration of a weak acid it is greater than 7. When a weak base is titrated with a strong acid the pH at the equivalence point is less than 7.

A. Strong Acid-Base:

A strong acid does not have a K_a and a strong base does not have a K_b because both are strong electrolytes. When they react together they form a salt and water. The salt contains a metal ion and a nonmetal anion, neither of which has acidic or basic properties. At the equivalence point only the salt and water exist. Thus, at this point in the titration the pH is 7. For example:

$$HCl + NaOH \xrightarrow{100\%} NaCl + H_2O(l)$$
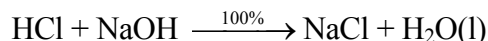
NaCl has ions that do *not* further react with water to form an acidic or basic solution.

B. Weak Acid:

The titration of a weak acid with a strong base forms a salt and water, as occurs with a strong acid. However, the anion of the salt is a weak base. The anion reacts further with water to form a basic solution at the equivalence point.

The equilibrium constant, K_a, for a weak monoprotic acid can be determined by two different experimental methods. These are described in the following.

Method 1: Using Initial Concentrations and pH

Consider the equilibrium for acetic acid (1):
$$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^- \quad (1)$$
An equilibrium expression (2) can be written for it.
$$K_a = ([H_3O^+][C_2H_3O_2^-])/[HC_2H_3O_2] \quad (2)$$

If the initial concentration of the acid, $HC_2H_3O_2$, is known and we measure the pH of the solution we can determine $[H_3O^+]$ and K_a.

* From the pH we can calculate the hydrogen ion concentration.

*At equilibrium, based on the stoichiometry, we can write: $[H_3O^+] = [C_2H_3O_2^-]$, Thus, from the pH, we know both concentrations at equilibrium.

*The equilibrium concentration of acetic acid is not the initial concentration. However, if we subtract the hydrogen ion concentration from the initial concentration, we calculate the equilibrium concentration of acetic acid. The hydrogen ion concentration represents the amount of weak acid ionized.

* We now know all three concentrations in the K_a expression and we can calculate its value.

Method 2: Using the Midpoint of the Titration

The net ionic equation for the titration of $HC_2H_3O_2$ with NaOH is

$$HC_2H_3O_2 + OH^- \rightarrow H_2O(l) + C_2H_3O_2^-. \qquad (3)$$
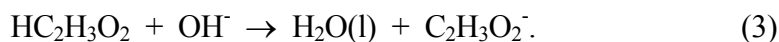
***At the midpoint of the titration**, half of the original acetic acid, $[HC_2H_3O_2]$, has been neutralized. Therefore at the half-way point: $[HC_2H_3O_2] = [C_2H_3O_2^-]$.

*The ratio of the two species, the acid and its conjugate base, is always one because they have the same concentrations:

$$[C_2H_3O_2^-]/[HC_2H_3O_2] = 1 \qquad (4)$$

*Inserting the value of one into the K_a expression for this ratio gives:

$$K_a = [H_3O^+]. \qquad (5)$$

*Taking the $-$ log of each side of this equation gives

$$\mathbf{pK_a = pH} \qquad (6)$$

C. Weak Base:

The titration of a weak base with a strong acid forms a salt and water. However, the cation of the salt is a weak acid. The cation reacts further with water to form an acidic solution at the equivalence point.

Both Methods 1 and 2 described above can be used to determine K_b for a weak base. Method 2 applied to a weak base is illustrated in the following example.

Consider the titration of ammonia with a strong acid. Before the titration begins, ammonia is in equilibrium with water according to:

$$NH_3 + H_2O(l) \rightleftharpoons NH_4^+ + OH^- \qquad (7)$$

and the equilibrium constant expression is:

$$K_b = ([NH_4^+][OH^-])/[NH_3] \qquad\qquad (8)$$

The net ionic equation describing the reaction for the titration of ammonia with a strong acid is

$$NH_3 + H^+ \rightarrow NH_4^+ \qquad\qquad (9)$$

* From the pH of the solution at the half-way point in the titration we can determine pOH and $[OH^-]$:

$$pOH + pH = 14 \qquad\qquad (10)$$

__At the midpoint of the titration, 50% (half) of the original amount of ammonia is titrated and forms ammonium ion.__ Therefore, the following quantities are equal: $[NH_4^+]$ and $[NH_3]$. Thus, by cancellation of these two quantities in the K_b expression gives:

$$K_b = [OH^-] \qquad\qquad (12)$$

*At half-way point in the titration we can also write:

$$\mathbf{pK_b = pOH}. \qquad\qquad (13)$$

III. Experimental Procedure (Reminder: Record all procedures with details as you do them, including data with units and observations for all steps in the experiment):

A. Before beginning any of the titrations, record using pH paper and again with a pH meter, the pHs of 25 mL solutions of the following: deionized water, 0.10 M NaCl, 0.1 M $NaC_2H_3O_2$, 0.1 M NH_4Cl, 0.1M $NH_4C_2H_3O_2$, and 0.1 M $Fe(NO_3)_3$.

Prepare tables, with titles, similar to the ones below to record your data in your lab notebook. For any solution that is not neutral, write a net ionic equation that explains the observed pH.

Title:

Substance	pH using pH paper	Equilibrium expression
H_2O		

You may observe for water a pH that is slightly acidic. This occurs for two reasons: (1) carbon dioxide dissolves in water and forms carbonic acid, a weak acid; (2) and pH electrodes do not measure accurate pHs unless there are a reasonable quantity of ions present in solution.

Title:

Compound	pH of 0.1 M solutions using pH paper	pH of 0.1 M solution using meter	N.I.E. Explains observed pH
NaCl			
NaC$_2$H$_3$O$_2$			
NH$_4$Cl			
NH$_4$ C$_2$H$_3$O$_2$			
Fe(NO$_3$)$_3$			

You may observe for water a pH that is slightly acidic. This occurs for two reasons: (1) carbon dioxide dissolves in water and forms carbonic acid, a weak acid; (2) and pH electrodes do not measure accurate pHs unless there are a reasonable quantity of ions present in solution.

B. **Two people will work together on this experiment.**

Assemble the following glassware and other apparatus as shown below:
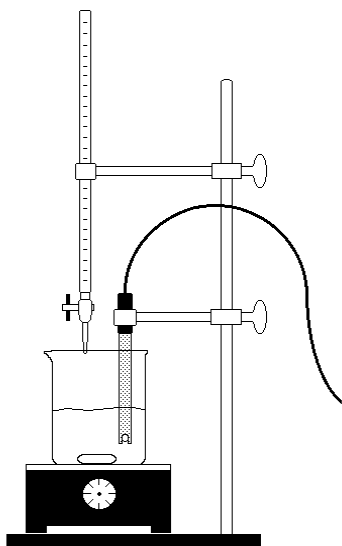
1. General overview:

   (a) Each student will titrate the unknown HCl solution in a dispensing bottle with the NaOH he/she prepared (or used) in Experiment #2.
   (b) Student 1 will titrate the unknown HC$_2$H$_3$O$_2$ solution with NaOH,
   (c) Student 2 will titrate the unknown NH$_3$ solution with HCl.
   (d) Each student will complete at least two titrations for each set.
   (e) Students will record lab data for their two sets of titrations. The information for the titration done by one student is then shared with his/her partner. Before you leave the lab be sure to arrange with your partner how you plan to share the data.
   (f) You will determine the unknown concentrations and prepare titration curves.
   (g) Each student will individually prepare their own lab report and titration curves.

2. Record the concentration of the base you prepared in Experiment 2. Place this value in a table or box with title for clarity.   The concentration of hydrochloric acid used is approximately 0.10 M, however you will determine the exact concentration to four significant figures using your titration data.

3. Clean your buret using several rinses with your standard NaOH solution.

4. Calibrate your pH meter at three different known pHs. Your instructor will demonstrate, however you have in your appendix the instructions for calibration.

5.   (a) Pipet 25.00 mL of the unknown HCl solution into a clean 100 mL beaker using a 25.00 mL volumetric pipet. Assume the pipet dispenses exactly 25.00 mL. Do not use your mouth to fill the pipet with solution. Add a clean magnetic stirring bar to this solution.
     (b) Arrange a buret so it is firmly attached to a support pole and fill it carefully with the NaOH solution. The position of the buret should make it accessible to the pH meter and a magnetic stirring/hot plate. The 100 mL beaker sits on top of the magnetic stirring/hot plate and the pH electrode is inserted into the solution so no part of it touches the glass of the beaker or magnetic stirrer. (See picture on previous page.)
     (c) Turn on the magnetic stirring/hot plate until the magnetic stirring bar turns slowly. The magnetic stirring bar should not touch the sides of the beaker or electrode.
     (d) To record the pH data during the titration prepare a table with a ruler in your lab notebook that permits easy recording of the data and is explanatory. Various formats can be used, but here is one example having only three data points shown for the HCl and NaOH titration. You will need **many more** rows of data because you will be reading data at each mL added. (See Experiment 2 for reading the buret)

Add an appropriate Title:

Titration	V_{final} (mL) NaOH	$V_{initial}$ (mL) NaOH	V_{total} NaOH (mL)	pH
HCl				

     (e) Do a rough titration first. Record the initial volume of the standard NaOH solution. Do not start at 0 mL, but at a point slightly larger than this value. Record the volume in the buret to two digits to the right of the decimal point, for example, 13.43 mL. The last digit is estimated. If a value is exactly 12, write 12.00 mL, not simply 12 mL. Add approximately 1.00 mL of NaOH, let the system equilibrate, and read the pH meter. Continue adding incrementally NaOH and recording pHs until you have passed the equivalence point and obtain a pH of approximately 10-12 and when the pH levels off.

(f) Plot a rough titration curve in your notebook using this data.   Do not draw a small graph. Discuss the graph with your instructor who will also sign it. Determine where the approximate equivalence and half-way points are in the titration curve. Determine whether the titration curve gives you sufficient information to do a final, accurate titration.

(g) Repeat the procedures, but add smaller increments of NaOH when you are near the equivalence and ½ equivalence points in the titration. For example, begin the second titration by adding 1 mL of NaOH at a time. When you are within 2 mL *before* the half-way point (the ½ equivalence point), take readings at 0.10 mL increments until you are 2 mL beyond the ½ equivalence point. When you are **2 mL before the equivalence point** reduce the volume of added NaOH to approximately 0.10 mL until you are 2 mL **beyond** the equivalence point. Continue adding NaOH for another 5 readings at 1 mL each.

6. Student 1: Repeat all procedures described in (6) using 25.00 mL of acetic acid instead of HCl. Use the NaOH solution you prepared in Experiment 2.

7. Student 2: Repeat all procedures described in (6) using 25.00 mL of ammonia as the unknown. *However*, you will fill the buret with the unknown HCl solution. Note: You will need eventually to calculate the concentration of the unknown HCl solution from your titration data in procedure (1).   Keep in mind that you can perform the titration and find the equivalence point before calculating the concentration of HCl.

IV. **Laboratory Report:**

You will need to obtain the lab data and titration curve for the titration you did not perform from your partner. Reminder: each person does his/her own calculations, preparation of titration curves (except for the one done by partner), analysis and writing of lab report.

1. Title page with partner's name, and concentration of unknown HCl solution. Your unknown score for this experiment is based on how close your value is to the true one, as determined by the service center.
2. Pre-lab and all corrections to pre-lab.   Copies of all data pages, including partner's.
3. Attach two computer generated graphs for each of the three titrations. These graphs should be generated from the best set of data. Use a scatter graph with a smooth line connecting data points as shown in appendix 3. Label graph and axes. One of the two graphs is used to show how you determined the equivalence point for the titration and therefore the equivalence point volume of NaOH. Your instructor will demonstrate in lab how this is done. Also show at the half-way point in the titration the pH and the volume of NaOH. The other titration curve is a clean copy.
4. Prepare typed tables (all information in tables is typed) and **hand write sample calculations** below the tables with the following information:

a. **Table I:** For each titration the initial pH of the solution, the pH and volume of NaOH at the half-way point, and the pH and volume of NaOH at the equivalence point. The pH of   the solutions and volumes of NaOH at the half-way and equivalence points

are found using a two- step process: (1) First obtain the best numbers from the titration curves and (2) refine the numbers by looking at the closest pHs and volumes of NaOH in your tables of titration data. Ask your laboratory instructor assistance if you have questions about this process.

   b. **Table II:** The concentrations of the three unknown solutions and the known NaOH solution. Under the table, show neat hand written sample calculations for determining the concentrations for *one* of the acids and for ammonia. Show all steps of you calculations in a step-wise format, with units shown with all measured numbers in each step.

   c. **Table III:** Show K values for the weak acid and the weak base using **both** Method 1 and Method 2 (see intro.) , K's from tables in text, and percent error of experimental values compared to table values. Under this table, hand write sample calculations with method used. Show all steps of calculations in a step-wise format, with units shown with all measured numbers in each step.

   d. **Table IV: From the initial pH values:** The percent ionization of hydrochloric acid, acetic acid and ammonia. Explain how the data helps you determine if each is a strong or weak electrolyte. Also, under this table show sample calculations with method used. Show all steps of calculations in a step-wise format, with units shown with all measured numbers in each step.

V. Pre-Lab (Show all steps in a calculation with units):

1. Write the net ionic equations for (a) the titration of HCl with NaOH, (b) $HC_2H_3O_2$ with NaOH, and (b) NH_3 with HCl. Include phases with all substances.

   a. $HCl_{(aq)} + NaOH_{(aq)} \rightarrow$?
   b. $HC_2H_3O_{2(aq)} + NaOH_{(aq)} \rightarrow$?
   c. $NH_{3(aq)} + HCl_{(aq)} \rightarrow$?
   d. Write the reaction that occurs at the equivalence point for the acid/base pairs shown above in a-c. Indicate whether the pH at the equivalence point would be acidic, basic, or neutral.

2. Calculate the pH of (a) 50.00 mL of 0.01000M HCl; (b) 50.00 mL of 0.01000 M NaOH.

3. If 50.00 mL of 0.01000 M HCl is titrated with 0.02500 M NaOH, how much base is required to reach the equivalence point?

4. What is the pH at the equivalence point for the titration in (3)?

5. Calculate the initial pH of 50.00 mL of a 0.025000 M ammonia solution. [$K_b = 1.8 \times 10^{-5}$].

6. (a) Calculate the pH at the half-way point for the titration of 25.00 mL of 0.01000 M $HC_2H_3O_2$ with 0.02000 M NaOH. (b) Calculate the pH at the half-way point for the titration of 50.00 mL of 0.01000 M acetic acid with 0.01000 M NaOH. (c) Explain any differences or similarities of your answers given the different conditions. For $HC_2H_3O_2$ $K_a = 1.8 \times 10^{-5}$.

7. (a) In a solution of 0.1 M HCl, which is the primary species present: HCl or H^+ or OH^-? (b) In a solution of 0.1 M HCN, which is the primary species present: HCN, or CN^- or H^+ or OH^-? Explain for each case.

Experiment 4
Titration Curves for Polyprotic Acids

I. Objective:

To construct titration curves for a known weak acid, weak base, and strong acid. You will also learn to predict whether an acid is monoprotic or diprotic by using its titration curve. To determine the identity of an unknown organic acid, appropriate equilibrium constants and molar mass will be determined.
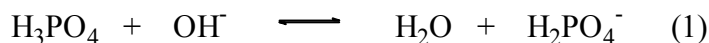
II. Chemical Principles:

A. Titrations

The titration curve of a weak monoprotic acid was prepared in Experiment 3. One equivalence point is observed. Titration curves for polyprotic acids are more complex. An observable end point corresponding to the first equivalence point is seen only when $K_1/K_2 > 10^4$. Consequently, for a diprotic acid, two distinct equivalent points should be observed, however, often only one will be observed. The other can be calculated as described in this experiment.

The pK_a of a weak monoprotic acid may be determined from the pH at the halfway point as described in Experiment 3. At the halfway point, the weak acid is half consumed and the conjugate base is half produced therefore for the acid HX,

$[HX] = [X^-]$, $K_a = [H_3O^+]$, and $pK_a = pH$.

Three consecutive end points are anticipated for the titration of the three phosphate species containing hydrogen in the titration of H_3PO_4.

$$H_3PO_4 \ + \ OH^- \ \longrightarrow \ H_2O \ + \ H_2PO_4^- \quad (1)$$

$$H_2PO_4^- \ + \ OH^- \ \longrightarrow \ H_2O \ + \ HPO_4^{-2} \quad (2)$$

$$HPO_4^{-2} \ + \ OH^- \ \longrightarrow \ H_2O \ + \ PO_4^{-3} \quad (3)$$

The equilibrium constant for (3) is so small, however, that no end point is observed. As in the case of a monoprotic acid, each pK_a can be determined from the pH for the titration at halfway point of each equivalence point.

Just as with monoprotic acids, at the first halfway point

$$[H_3PO_4] \text{ remaining} = [H_2PO_4^-] \text{ produced.} \quad (4)$$

$$\text{Therefore, } K_1 = [H_3O^+] \text{ and } pK_1 = pH. \quad (5)$$

Similar relationships hold true at the next two halfway points, although the third is not observed.

The three literature values for phosphoric acid are:

$$pK_{a1} = 2.12 \qquad K_{a1} = 7.6 \times 10^{-3} \qquad (6)$$

$$pK_{a2} = 7.21 \qquad K_{a2} = 6.2 \times 10^{-8} \qquad (7)$$

$$pK_{a3} = 12.38 \qquad K_{a3} = 4.2 \times 10^{-13} \qquad (8)$$

In a diprotic acid titration, frequently the <u>first</u> end point is sometimes not observed, or it not very pronounced. Nevertheless, close examination of the titration curve can reveal whether the acid is monoprotic or diprotic and the approximate pK values can be determined. Using a the acid's titration curve, one can perform a simple calculation to reveal whether it is monoprotic or diprotic by finding the pH at the ¾ equivalent point and subtracting from it the pH at the ¼ equivalence point. $\Delta pH = pH_{3/4} - pH_{1/4}$. For derivation, see Appendix IV.

For a <u>weak</u> acid, if ΔpH between the ¼ and ¾ points is ≤ 0.954 then the acid is <u>monoprotic</u>.

If the acid is diprotic, the final equivalence point is always easy to find, but the first one is frequently obscured, or not clearly defined. However, ΔpH between the 1/4 and 3/4 points in the titration curve for a <u>diprotic</u> acid will always be <u>larger than 0.954</u> pH units.

Thus you can determine whether or not your weak acid unknown is mono or diprotic by determining the ΔpH.

Look at the graph below:
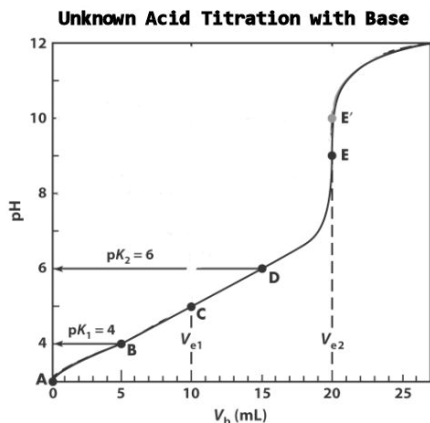
| Point	Eq. Pt	pH
A	0	3.5
B	¼	4.0
C	½	5.0
D	¾	6.0
E	1	9.0

$\Delta pH = pH_{3/4} - pH_{1/4} = ?$
$\Delta pH = 6 - 4 = 2$
Since $2 > 0.954$ this acid must be diprotic.

B. Determination of Molecular Weight of an Unknown Acid.

Titration of a weighed sample of an unknown solid acid permits determination of its molecular weight (molar mass). It is helpful to compare the titration of a monoprotic and a diprotic acid. In either case the molar mass (MM) of the acid is given by grams/mole.

Monoprotic: The net ionic equation for the titration of a weak monoprotic acid is

$$HX \; + \; OH^- \; \rightleftharpoons \; H_2O \; + \; X^- \qquad (9)$$
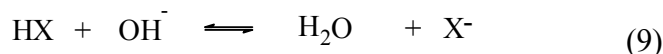
The moles of base at the equivalence point is known from the volume of titrant, V_B, and the molarity of the standard base, M_B: $n_B = M_B V_B$.

At the equivalence point of the titration, according to the stoichiometry of the titration the moles of acid equals the moles of base,

$$n_A = n_B \qquad\qquad (10)$$

Therefore the molar mass of acid, MM_A, can be determined from the mass of the acid in the solution titrated and the calculated value of n_A .

$$MM_A = \frac{g_A}{n_A} . \qquad\qquad (11)$$

Diprotic: The net ionic equation for the titration of a weak diprotic acid is

$$H_2Y \; + \; 2OH^- \; \rightleftharpoons \; 2H_2O \; + \; Y^{-2} \qquad (12)$$
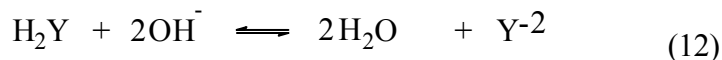
At the equivalence point of the complete titration diprotic acid, the number of moles of acid used is still: $n_B = M_B V_B$. Since each mole of acid requires 2 moles of base at the equivalence point as shown by the stoichiometry of the reaction, the number of moles of acid is one-half that of the total number of moles of base:

$$n_A = n_B/2 \qquad\qquad (13)$$

Again, the MM_A of the acid can be calculated knowing the grams of acid in the solution titrated and the calculated value of $n_A.$

For this experiment, it is convenient to weigh all of your unknown acid sample into a   100.00 mL volumetric flask. If a 25.00 mL aliquot of the acid solution is titrated, remember that the mass of acid used in each aliquot is 25/100 or 1/4 of the original mass.

III. Experimental Procedures:

B. Underline Acid.   Record your unknown number.

1. Determine two times the capillary melting point of your sample: one is a rough measurement and the other is an accurate measurement of capillary melting point. Your instructor will demonstrate the use of the melting point apparatus and how to fill a capillary tube. You will use a tiny amount of your solid.   **You do not need to find the M.P. of your unknown acid before you titrate, however you need to fill your capillary tubes before step 2 or reserve a small amount of your sample to fill capillary tubes at another time.   Since we are limited in M.P. apparatus, just watch for a convenient time to do your M.P.**

2. Accurately weigh and record the remaining unknown sample of your weak acid. Quantitatively transfer the solid into a 100 mL volumetric flask make up 100.00 mL of solution by first using about **20 mL of ethanol** to dissolve most of the sample. Slowly add small amounts of water (just a mL or so) and watch to see if the sample begins to precipitate out of the solution. If you see a milky white color form in the solution, or if it starts to precipitate, switch back to ethanol and use it exclusively to make up the rest of the 100.00 mL. Do not pass the 100.00 mL line on the volumetric flask. Mix,cap, label and store.

3. After leaving the solution to sit for at least 30 minutes and mixing one more time, you may start your titrations. Pour ~ 30 mL of the unknown acid solution into a beaker. Transfer 25.00 mL of your unknown acid solution to a beaker using your 25.00 mL pipet.   Add 75 mL of deionized water (**or ethanol if your acid required mostly ethanol to dissolve**) and titrate with NaOH. As with Experiment 3, run a quick titration at 1 mL additions. Make a rough plot of your data in your notebook. Determine the volumes at which you observe the 1/4, 1/2, 3/4, and equivalence points. Have your instructor initial the graph. Then perform a careful titration. Starting about 2 mL before each of the points until 1mL past the point, add 0.10 mL to 0.20 mL increments of NaOH.

IV. Laboratory Report (Summary tables and data within are to be typed):

1. Typed Title page including **the unknown number and the name of the unknown acid**.
2. Pre-lab and corrections to pre-lab
3. Copy of laboratory data
4. Computer generated titration curve of Unknown acid. Follow the standards for preparing these graphs found in the previous experiment and appendix 3.
5. Type summary tables I –III and answer questions throughout next few pages:

Table I.
Summary of Titration Data for Unknown Acid.

Titration Point	pH	Volume of NaOH added.
Initial		
¼		
½		
¾		
Equivalence		

Table II.
Summary of Equilibrium Data for Unknown Acid

K_1 Experimental	pK_1 Experimental	pK_1 Literature	% Error	K_2 Experimental	pK_2 Experimental	pK_2 Literature	% Error

If you have a monoprotic acid, report only K_1 and other associated values. Show all calculations under the table (hand write them).

6. Table III: Summary of data for Unknown acid: Unknown number _____

	Literature Value	Experimental	%Error
Name of Acid			
Mono or Di			
Solubility in water			
Formula, and structural formula of acid			
Melting Point			
Molar Mass			

*TOXICITY & DISPOSAL: _____

Show all calculations for the molar mass under the table III.

You can find toxicity, disposal, and solubility information in the MSDS (Material Safety Data Sheet) for your acid (found on the Internet). How should you dispose of your acid solution when you are finished with the experiment according to the MSDS ?

Look up the **structural formula** of the acid in an organic chemistry reference textbook or online.   A structural formula might look like this for benzoic acid:
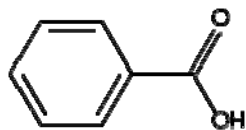
Under the structure cite the reference for your structure.

7. Error Discussion.

Provide an explanation for each of the scenarios that follow. Will your calculated molar mass for the unknown acid be higher or lower if the following were to occur. *The question assumes that you did the experiment without knowing these situations happened. You used the original data   without correcting for these possible errors. Then consider how these possible errors affect the change in the value of the molar mass in its calculation.* You must provide an explanation for how you arrived at your conclusion.

   a) The NaOH is actually 0.150 M, not 0.100 M as labeled.
   b) Your buret has some water in it before adding NaOH solution.
   c) Your pipet has some water in it before you pipet the solution of the acid.
   d) You spilled some solid unknown acid after weighing it and while transferring it to the volumetric flask.

Pre-lab:

1.   Your unknown weak acid will be one of the acids in the following table. **Look up the formula, molar mass, solubility, and pK values in the *Handbook of Chemistry and Physics* for each acid before the first period of the experiment. Copy this table with all data and attach it to a page in your lab notebook or hand write the table with all data into your lab notebook as part of the pre-lab assignment.**

Note: An organic acid, or a carboxylic acid, is characterized by the presence of a carboxyl group. It is represented as -COOH. An acid that has one unit is monoprotic and one that has two carboxyl groups will be a diprotic acid. **If an acid is diprotic it has two pK values**.

Table of Mono and Diprotic Organic Acids

Acid	M.P. (^{o}C)	Formula	Molar Mass	Mono/ Diprotic	pK$_a$	Soluble in water and/or alcohol ?
Adipic or hexanedioic	151-153					
Chloroacetic	63					
t-cinnamic	132-135					
t-crotonic	71.5					
Maleic	134-136					
Malonic	135.5					
D,l mandelic	121					
Oxalic, dihydrate (2H$_2$O)	101.5					
Pimelic	102-104			Diprotic	4.75/ 5.58	
Salicylic or 1-hydroxy benzoic acid	159				2.97	
Suberic	144					
Succinic	187-189					
m-Tartaric	167-170					

2.   It has been determined from a titration curve that an acid is diprotic. 1.2500 g of the acid is dissolved in enough water to make 100.00 mL of solution. 30.00 mL of a 0.1500 M NaOH solution is needed to <u>completely</u> titrate 25.00 mL of the original solution. What is the molar mass of the diprotic acid? Show all steps in the calculation with units.

3.   By the method described in the Chemical Principles section of this experiment, determine if the acid represented in the graph on the next page is a mono or a diprotic acid. Copy this graph and attach in your lab notebook. Identify the 1/4, 1/2, 3/4 and equivalence point on the graph.   What is the estimated $\Delta pH_{3/4-1/4}$? What   is the pK_a if it is monoprotic and pK_{a1} and pK_{a2} if it is a diprotic acid? Show your logic and all steps in your calculation with units.

Titration of an Acid with a Base

pH

mL of Base added

Series1
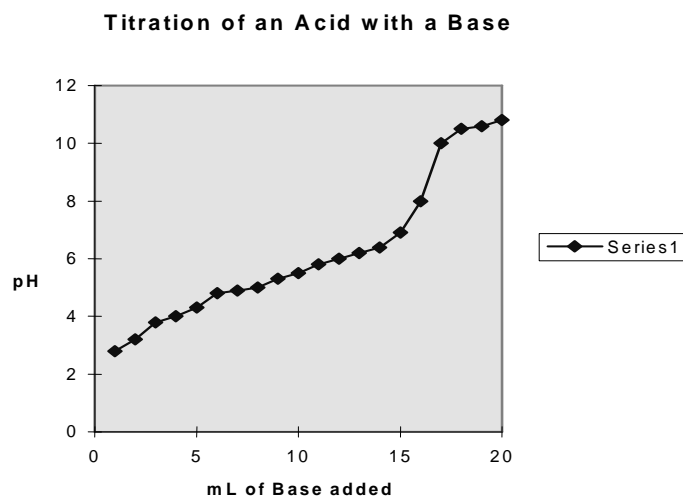
Experiment 5
Acids, Bases, and Buffers

I. Objective: To become familiar with the acid-base properties of salt solutions and acid-base properties of buffer solution and their preparation buffers.

II.   **Chemical Principles:**

  A. What is a buffer?

A buffer is a solution that resists changes in pH upon the addition of acid or base. Buffers typically contain a species in solution that reacts with added acid and another that reacts with added base. Although acids or bases themselves could accomplish this task in theory, in practice if they are in solution together they interact and neutralize each other. Buffers are most often prepared one of two ways from conjugate acid-base pairs: from a weak acid and its conjugate base, or from a weak base and its conjugate acid.

The best buffer is considered one in which the ratio of conjugate acid to its conjugate base is close to one and is concentrated enough to resist pH change.   An effective "buffer region" has the ratio: $10 > \frac{\text{conjugate acid}}{\text{conjugate base}} > 0.1$ and a minimum concentration such that $M_{\text{conjugate acid}} + M_{\text{conjugate base}} \geq 0.1$ M.   Another way to check this is to compare pH with pK: if pH $=$ pK $\pm$ 1 then it is usually within the buffer region.

If 10 mL of 0.10 M HCl is added to a liter of water at pH 7, the pH drops four units to pH 3. If 10 mL of 0.10 M NaOH is added to a liter of water at pH 7, the pH rises about four units to pH 11. But if the 10 mL of 0.10 M strong acid or strong base is added to a liter of blood, the normal pH of the blood (7.4) changes only about 0.1 pH units. Blood and many other bodily fluids are naturally buffered to resist changes in pH.

To explain the properties of a buffer, it is useful to consider a specific example, the acetic acid/acetate buffer system. In one liter of a solution that is 1.0 M in sodium acetate and 1.0 M in acetic acid, the pH drops less than one-tenth of a pH unit when 10 mL of 0.10 M HCl is added. This solution is a buffer; acetate ion from the sodium acetate is the conjugate base of the weak acid acetic acid. Acetic acid by itself in water exists in equilibrium with a small amount of acetate ion, its conjugate base:

$$HC_2H_3O_{2(aq)} + H_2O \rightarrow C_2H_3O_{2(aq)}^{-} + H_3O_{(aq)}^{+}$$
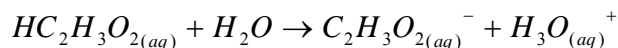
In the buffer solution, a much larger amount of the conjugate base is present than would arise from the dissociation of the weak acid. The relationship among the species present in solution, however, is still governed by the dissociation constant (K_a) for the weak acid, acetic acid.

When acid is added to this buffer, the added **hydronium ion** reacts with the strongest base in the medium, namely the acetate ion, and forms more acetic acid. This reaction consumes added hydronium ion, <u>preventing</u> the pH from rising drastically, and is responsible for the buffering effect. As a result of adding acid to the buffer, the concentration of acetate decreases and the concentration of acetic acid increases. The solution acts as a buffer because nearly all of the added hydronium ion is consumed by reaction with acetate. As the hydrogen ion concentration increases, the acetate concentration and acetic acid concentration must adjust for the value of the equilibrium constant to be maintained. The pH changes slightly to reflect the shift in the equilibrium concentrations, but the change is much smaller than in the absence of the buffer because most of the added acid is consumed by its reaction with the acetate ion. This example of an acetic acid/acetate ion buffer is typical of other buffer systems.

When the concentrations of species involved in equilibria change, the equilibrium constant does not change. The equilibrium is temporarily out of balance, and all concentrations shift to restore the equilibrium. Any change in conditions that disrupts the balance within a system at equilibrium is referred to as a stress on that equilibrium. The system is stressed by being out of balance, and concentrations change to relieve that stress. The general principle that governs such changes is called Le Chatelier's Principle: if a system at equilibrium is subjected to a stress, the system will react in a way that partially relieves that stress. In buffered systems, the addition of an acid or base to a buffer stresses the equilibrium established in that system. By adding acid to the acetic acid-acetate buffer, the concentration of hydronium ion on the right in the equation is increased and the system responds by consuming the hydronium ion, forming more acetic acid. The reaction proceeds to the left until equilibrium is reestablished. When base is added, it reacts with hydronium ion to decrease its concentration, thereby stressing the system. In response, more acetic acid dissociates to partially restore the hydronium ion concentration and balance the equilibrium. The reaction proceeds to the right until equilibrium is reestablished.

Buffers are of great importance in living systems. Both <u>the rates</u> of biochemical reactions and their equilibrium constants are very sensitive to the availability of hydronium ions. Many biochemical reactions involved in vital processes like metabolism, respiration, the transmission of nerve impulses and muscle contraction and relaxation take place within a narrow pH range. Le Chatelier's Principle and the same types of chemical reactions that apply for the acetic acid-acetate buffer system govern the behavior of the physiological buffers.

An important buffer in the blood consists of bicarbonate ion and dissolved carbon dioxide in the form of carbonic acid. These two species constitute the conjugate acid-base pair of the buffering system. The pH of the blood can be altered by the ingestion of acidic or basic substances, and the carbonate/bicarbonate buffer system compensates for such additions and maintains the pH within the required range. This buffering system is

intimately tied to our respiration, and an exceptional feature of pH control by this system is the role of ordinary <u>breathing</u> in maintaining the pH.

B. Acid Buffers: Mixtures of a weak acid and its conjugate base

Chemical reactions can be very sensitive to changes in the pH of a solution. For example, the acid catalyzed oxidation of iodide ion by bromate ion occurs twice as fast if the pH is reduced by only 0.16 units. The effects of high or low pH on biological systems can be lethal; hence, the body has a powerful buffering system in blood to maintain the pH at about 7.4. The components of this buffer system are primarily HCO_3^-, CO_3^{2-}, $H_2PO_4^-$ and HPO_4^{2-} ions.

An acid buffer usually contains a weak acid in equilibrium with its conjugate base so that added protons or hydroxide ions can react with one of the two components. The net ionic equations that describe these reactions are:

(a) The addition of a strong acid to a buffer containing a weak acid, HX, and a salt containing the anion of the weak acid, MX:

$$H_3O^+ + X^- \rightarrow HX + H_2O(l)$$
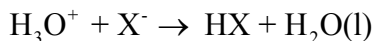
(b) The addition of a strong base to the same buffer:

$$OH^- + HX \rightarrow X^- + H_2O(l)$$
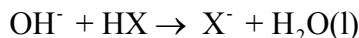
The pH will change, but not nearly as drastically as it would if there were no buffer present. For instance, the equilibrium constant for a weak acid is

$$K_a = \frac{[H_3O^+][X^-]}{[HX]} \quad \text{or rearranging} \quad [H_3O^+] = K_a \frac{[HX]}{[X^-]}$$

Note that $[H_3O^+]$ depends on the ratio of $[HX]/[X^-]$. Thus, if the ratio of the concentration of acid to base changes between 0.1 and 10, the range of pH is:

$$pH = pK_a \pm 1.0$$

where K_a is the equilibrium constant for the weak acid HX.

C. Base Buffers: Mixtures of a weak base and its conjugate acid

Let's look at a mixture of ammonia and ammonium chloride solutions for our base buffer.

Ammonia is a weak base, and the position of this equilibrium will be well to the left:

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

Adding ammonium chloride to this adds lots of extra ammonium ions. According to Le Chatelier's Principle, that will tip the position of the equilibrium even further to the left.
Addition of acid to this buffer:
The most likely basic substance which a hydrogen ion is going to collide with is an ammonia molecule. They will react to form ammonium ions.

$$NH_{3(aq)} + H^+{}_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)}$$

Most, but not all, of the hydrogen ions will be removed. The ammonium ion is weakly acidic, and so some of the hydrogen ions will be released again.

b. Addition of base to this buffer:
The hydroxide ions from the alkali are removed by a simple reaction with ammonium ions.

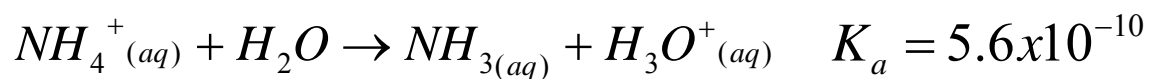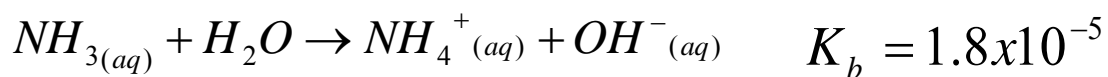$$NH_4^+{}_{(aq)} + OH^-{}_{(aq)} \rightleftharpoons NH_{3(aq)} + H_2O_{(l)}$$

Because the ammonia formed is a weak base, it can react with the water - and so the reaction is slightly reversible. That means that, again, most (but not all) of the hydroxide ions are removed from the solution.

c. Calculations involving buffers:

SSuppose you are asked to make 50.0 mL of an ammonia buffer solution using 30.0 mL of 1M NH₄Cl and 20.0 mL of 1M NH₃.

30.0 mL
of 1M NH₄Cl

50.0 mL of
Buffer

20.0 mL
of 1M NH₃
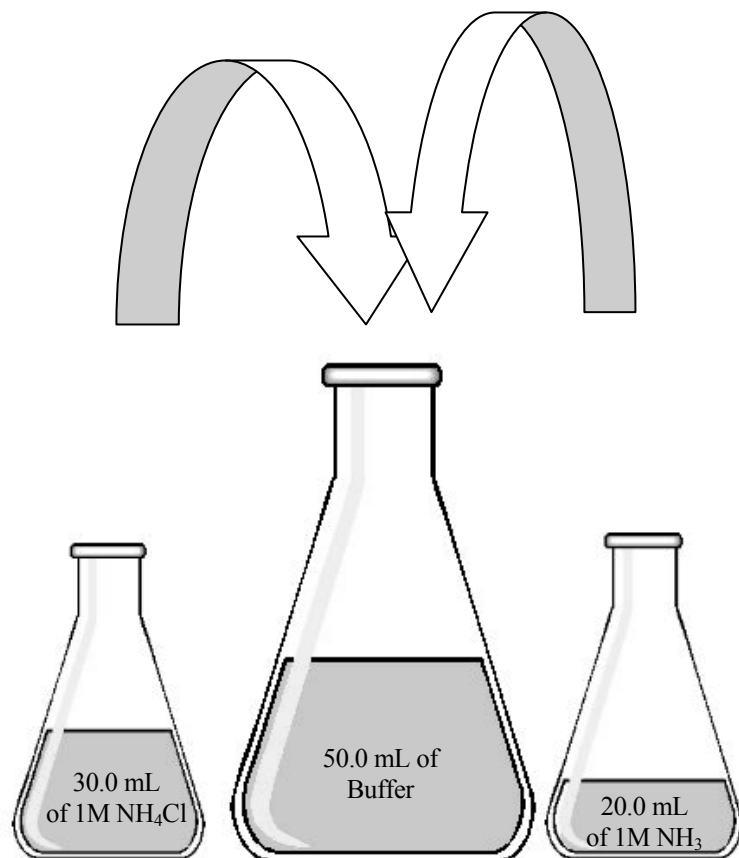
Always write the relationship between the conjugate acid-base pairs:

$$NH_{3(aq)} + H_2O \rightarrow NH_4^+{}_{(aq)} + OH^-{}_{(aq)} \qquad K_b = 1.8x10^{-5}$$

$$NH_4^+{}_{(aq)} + H_2O \rightarrow NH_{3(aq)} + H_3O^+{}_{(aq)} \qquad K_a = 5.6x10^{-10}$$

Calculate the new molarities after making the buffer:

$$0.0200\ L\ NH_3 \times \frac{1\ mol}{L\ NH_3} \times \frac{1}{0.0500\ L} = 0.400\ M\ \ NH_3$$

$$0.0300\ L\ NH_4^+ \times \frac{1\ mol}{L\ NH_4^+} \times \frac{1}{0.0500\ L} = 0.600\ M\ NH_4^+$$

What is the pH of this buffer:

Since you are asked to calculate the pH, use the Ka expression and insert the new molarities.

$$NH_4^+{}_{(aq)} + H_2O \rightarrow NH_{3(aq)} + H_3O^+{}_{(aq)}\ \ \ K_a = 5.6x10^{-10}$$
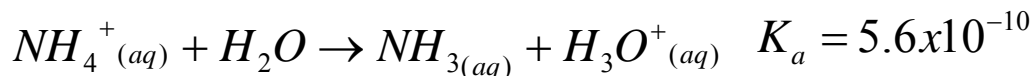
$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{[0.400][H_3O^+]}{[0.600]}$$

$$[H_3O^+] = 8.4 \times 10^{-10}$$

Now plug into your pH equation.

$$pH = -\log[H_3O^+]$$

$$pH = 9.07$$

Calculating the pH of the buffer after adding acid:

Suppose you are told to divide your buffer in half to perform the addition of acid, therefore, you will be adding acid to 25.0 mL of the buffer above. You first must determine what will react with the HCl in your buffer. You have NH_3 and NH_4^+ present. Since acids don't react with other acids, the HCl will react with NH_3 only.
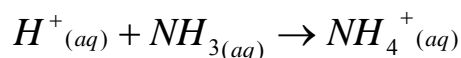
Set up your reaction and calculate the new concentrations.

$$0.001\ L\ HCl \times \frac{0.500\ mol}{L\ HCl} = 5.0 \times 10^{-4}\ moles\ HCl\ or\ H^+\ will\ be\ added$$

$$0.0250 \ L \ buffer \times \frac{0.400 \ mol \ NH_3}{L \ buffer} = 0.01 \ moles \ NH_3 \ present \ in \ buffer$$

$$0.0250 \ L \ buffer \times \frac{0.600 \ mol \ NH_4^+}{L \ buffer} = 0.0150 \ moles \ NH_4^+ \ present \ in \ buffer$$

Show reaction for what actually reacts:

$$H^+_{(aq)} + NH_{3(aq)} \rightarrow NH_4^+_{(aq)}$$

|	H$^+$	+	NH$_3$	→	NH$_4^+$
Initial moles	5.0x10^{-4}		0.01		0.015
Change in moles	-5.0x10^{-4}		-5.0x10^{-4}		+5.0x10^{-4}
After rxn	0		0.00950		0.0155

Remember that addition of an acid to your buffer will *increase* the acidic portion of that buffer.

Now calculate new concentrations for each species:

$$NH_3 : \frac{0.00950 \ mol}{0.026L} = 0.365 \ M \ \ NH_3$$

$$NH_4^+ : \frac{0.0155 \ mol}{0.026L \ NH_4^+} = 0.596 \ M \ NH_4^+$$

Stop and look at your new molarities. Do they make sense? Yes, the base portion of the buffer decreased in molarity after the addition of HCl and the acidic portion (NH$_4^+$) increased in molarity. Now you can calculate the pH of this new solution.

$$NH_4^+_{(aq)} + H_2O \rightarrow NH_{3(aq)} + H_3O^+_{(aq)} \qquad K_a = 5.6x10^{-10}$$
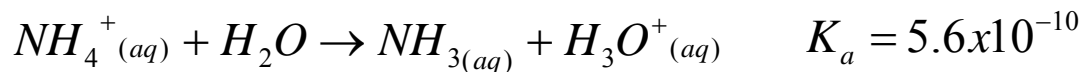
$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{[0.365][H_3O^+]}{[0.596]}$$

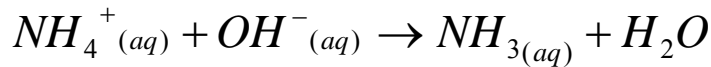$$[H_3O^+] = 9.14 \times 10^{-10}$$

$$pH = -\log[H_3O^+]$$

$$pH = 9.03$$

Since the ΔpH is less than 1, we have not destroyed the buffer capacity with the addition of HCl.

<u>What is the pH of the buffer after adding 1 mL of 0.500 M NaOH to the other half of your original buffer?</u>

Set up the reaction to show what is actually reacting.

$$NH_4^+{}_{(aq)} + OH^-{}_{(aq)} \rightarrow NH_3{}_{(aq)} + H_2O$$

	NH_4^+	+	OH^-	$\rightarrow$	NH_3
Initial moles	0.015		5.0×10^{-4}		0.0100
Change in moles	-5.0×10^{-4}		-5.0×10^{-4}		$+5.0\times10^{-4}$
After rxn	0.0145		0		0.0105

Remember that adding NaOH to your buffer will add to the basic portion of that buffer.
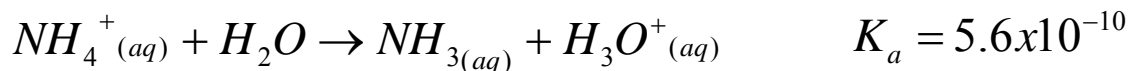
Calculate new molarities.

$$NH_3 : \frac{0.0105\ mol}{0.026L} = 0.404\ M\ \ NH_3$$

$$NH_4^+ : \frac{0.0145\ mol}{0.026L\ NH_4^+} = 0.558\ M\ \ NH_4^+$$

Notice the molarity for the base has increased.

Calculate the new pH for this half of the buffer.

$$NH_4^+{}_{(aq)} + H_2O \rightarrow NH_3{}_{(aq)} + H_3O^+{}_{(aq)} \qquad\qquad K_a = 5.6x10^{-10}$$

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{[0.404][H_3O^+]}{[0.558]}$$

60

$$[H_3O^+] = 7.73 \times 10^{-10}$$

$$pH = -\log[H_3O^+]$$

$$pH = 9.11$$

The pH has increased after adding NaOH, just as you would expect.

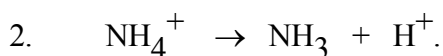**Example problem for preparing an ammonia/ammonium acetate buffer:**

Prepare 50.00 mL of a buffer having pH = 9.50 from 0.100 M NH_4Cl and 0.100 M NH_3.

Given: K_a = 5.6 x 10^{-10}, (then pK_a = 9.25. (How did we find pK_a?))

Solution:

1.   pH = 9.50 = $-\log[H^+]$, so $[H^+]$ = $10^{-9.50}$ = 3.16 x 10^{-10}.

2. $NH_4^+ \rightarrow NH_3 + H^+$.

The equilibrium expression for the acid NH_4^+ is: $K_a = \dfrac{[H^+][NH_3]}{[NH_4^+]}$.

3.   We know from the given data and the problem:

K_a = 5.6 x 10^{-10} and $[H^+]$ = 3.16 x 10^{-10}.

Substitute these into the equilibrium expression.

$$K_a = \frac{[H^+][NH_3]}{[NH_4^+]} = 5.6 \times 10^{-10} = \frac{[3.16 \times 10^{-10}][NH_3]}{[NH_4^+]}.$$

Divide both sides by 3.16 x 10^{-10} to get:

$$1.77 = \frac{[NH_3]}{[NH_4^+]}.$$

4.   "[ ]" means molarity and we know by definition molarity = $\dfrac{\text{moles of solute}}{\text{Liter of solution}}$.

The buffer solution is made by mixing the 0.100 M NH_4Cl and 0.100 M NH_3 in the same container, so there is one final total volume of solution.

Call the final volume V_{Total}.

The number of moles of each starting chemical, and the volume of each starting chemical is different, but we have the above ratio to find them. We can set up a series of equivalents:

$$1.77 = \frac{[NH_3]}{[NH_4^+]} = \frac{\text{moles } NH_3 / V_{Total}}{\text{moles } NH_4^+ / V_{Total}} = \frac{\text{moles } NH_3}{\text{moles } NH_4^+} =$$

$$= \frac{0.100 \frac{\text{moles}}{\text{Liter}} \text{ x volume of } NH_3}{0.100 \frac{\text{moles}}{\text{Liter}} \text{ x volume of } NH_4Cl} = \frac{\text{volume of } NH_3}{\text{volume of } NH_4Cl}$$

5. So we have the ratio: $1.77 = \dfrac{\text{volume of NH}_3}{\text{volume of NH}_4\text{Cl}}$

and from the statement of the question we know that
    volume of NH_3 + volume of NH_4Cl = 50.00 mL.

We can make the substitution: volume of NH_3 = 50.00 mL − volume of NH_4Cl

giving us: $1.77 = \dfrac{50.00 - \text{volume of NH}_4\text{Cl}}{\text{volume of NH}_4\text{Cl}}$

or: 1.77 x volume of NH_4Cl = 50.00 − volume of NH_4Cl.

Collecting terms gives:2.77 x volume of NH_4Cl = 50.00 mL

so: **volume of NH_4Cl = 18.05 mL**

and: **volume of NH_3 = 31.95 mL.**

III.   Experimental Procedures

Acetic acid/sodium acetate buffer:

Note: For each experiment requiring a calculation show the method and logic used in the calculation. Be sure to completely show all steps and units in each step. Use a pH meter to measure pHs. Prepare appropriate tables for each experiment to record your lab data. Remember to carefully record all procedures and observations.

1. Using a graduated cylinder to measure volumes, prepare a buffer solution from 20.0 mL of 0.10 M acetic acid and 30.0 mL of 0.10 sodium acetate.
   a. Calculate the pH of the buffer. ($K_a = 1.8 \times 10^{-5}$)
   b. Measure the actual pH of the solution using your pH meter.
   c. Compare the experimental result in (b) to the calculated value in (a). Determine the % error.

2. Divide your buffer solution in (1) into two equal 25.0 mL volumes. Calculate the expected pH of the following solutions and then measure the pH of each.
   a. To one of the 25.0 ml solutions add 5.0 mL of 0.10 M HCl and measure the pH.
   b. To the second add 5.0 mL of 0.10 M NaOH and record the pH.
   c. Compare the experimental results with the theoretical results. Why are there differences in their pHs?

3. Carry out the following measurements and also calculate the expected pH of the following solutions:
   a. Measure the pH of deionized water.

b. Add 5.0 mL of 0.10 M HCl to 25.0 mL of water and measure pH

c. Add 5.0 mL of 0.10 M NaOH to a new sample of 25.0 mL of water and measure pH.

e. Is water a buffer? Explain.

Waste Disposal:
   All waste can be disposed of down the drain

Ammonia Buffer:

Buffer solutions with a specified pH can be made in a variety of ways. In the pre-lab assignment question 2 you did calculations showing quantities of compounds required to prepare three buffer solutions with a pH of 9.00.

1. Prepare each of the three buffer solutions and measure their pHs. Develop appropriate tables with titles, headers, etc. to record your data and results.

2. It is likely that the experimental pHs for the three solutions are not exactly 9.00. Consider what you could easily do to **adjust the pHs to 9.00 for each** case. Remember, this solution is now a buffer. Develop a proposal in your lab manual and bring it to your instructor for approval. If approved, carry out the proposed procedures and record completely all procedures and data.

3. Divide each of the 3 buffer solutions into two 25 mL samples with some left over unused. You will then have 6 solutions. To one set of those buffer solutions, you will add 1 M (**1 M, not 0.1 M**) HCl drop wise until you reach a pH of 8.00. Keep track of how many drops it takes for each of those solutions to reach a pH of 8.00.

4. To the remaining set of buffer solutions, you will repeat the steps in #3 except this time add 1M NaOH drop wise until you reach a pH of 10.

Waste Disposal:
   All waste can be disposed of down the drain

   IV.   Laboratory Report:

1. Typed Title page.
2. Signed prelab and an addition page showing any corrections that are needed.
3. Copy of all laboratory data.
4. Computer generate tables to clearly display your buffer results. Sample tables are shown below.

Table I: Acetic acid/sodium acetate Buffer

Buffer	pH theoretical Initially	pH observed Initially	% Error	pH theoretical after adding acid	pH observed after adding acid	% Error	pH theoretical after adding base	pH observed after adding base	% Error
$HC_2H_3O_2/$ $C_2H_3O_2^-$									
H_2O									

Hand write your calculations under the table.

Is water a buffer ?   Explain using observations from Table 1 and definitions.

Table II: Ammonia Buffers

Buffer	# Drops of HCl to reach pH = 8.00	# Drops of NaOH to reach pH = 10.00
1) NH_3/NH_4^+ (aq) solutions		
2) NH_3/solid NH_4Cl		
3) NH_3/titrated with HCl		

5. Answer the following questions:

    a. Looking at your data collected from the ammonia buffers you prepared, which one of the three was the better buffer? Which solution preparation was the best buffer against HCl? Which was the best buffer against NaOH?

    b. Looking at the method of preparation and molarities in the prepared solutions;   Explain why you think the particular preparation chosen in answer (a) above buffered better against HCl or NaOH.

    c. Using your text book or internet sources, **summarize the use** of another chemical buffer in our body, environment, or industrial usage. **Include your reference.**   Just saying "so and so is a buffer" does not answer this question.

V.   Pre-Lab

1. a. What is the pH of a solution prepared by adding 20.0 mL of 0.10 M acetic acid and 10.0 mL of 0.10 M sodium acetate?

b. What is the pH after the addition of 1.0 mL of 0.10 M HCl to 15 mL of the solution?

c. What is the pH after the addition of 1.0 mL of 0.10 M NaOH to 15 mL of the original solution?

d. Explain why the solution prepared in part a is a buffer solution. Hint: re–read the first page of this experiment.

2.   Answer the following questions about preparing the same buffer solution using three different methods. All three buffers are to have a pH of 9.00. Be sure to show your logic clearly and with all steps in the calculation.

a. Given two separate solutions, 0.100 M ammonia and 0.100 M ammonium chloride, calculate the volume of each solution required to form 60.0 mL of a mixture that has the desired pH.

b. Calculate the amount of solid NH_4Cl to add to 60.0 mL of 0.100 M ammonia to form a mixture that has the desired pH. Assume no volume change in the solution.

c. Calculate the volume of 0.100 M HCl that is required to react with 50.0 mL of 0.100 M ammonia to form a mixture that has the desired pH.
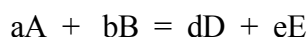
Experiment 6
Solubility Product Constant (K_{sp}) for Calcium Sulfate

I. Objective:

To determine the solubility-product constant for calcium sulfate.

II. Chemical Principles:

The equilibrium constant for a generalized chemical reaction,

$$aA + bB = dD + eE$$

is defined as:

$$K = \frac{(a_D)^d (a_E)^e}{(a_A)^a (a_B)^b}$$

where the a's are the activity of the various species. The activities of pure solids and liquids are unity, while the activities of solute ions depend on their charges and concentrations. Technically, equilibrium constants are defined in terms of activities as written above and not with concentrations expressed in molarity. The relationship between activity, a_A, and the more frequently used molarity, $[A]$, for species A, is

$$a_A = \gamma_a [A]$$

where γ_A (Greek symbol lower case gamma) is the "activity coefficient" of A and is determined by experiment. Therefore, we can also write the equilibrium constant for the reaction above as:

$$K = \frac{[D]^d [E]^e}{[A]^a [B]^b} \times \frac{(\gamma_D)^d (\gamma_E)^e}{(\gamma_A)^a (\gamma_B)^b}$$

$$\text{where} \quad K_c = \frac{[D]^d [E]^e}{[A]^a [B]^b} \quad \text{and} \quad K = K_c \times \frac{(\gamma_D)^d (\gamma_E)^e}{(\gamma_A)^a (\gamma_B)^b}$$

It is useful to classify equilibria into two classes, homogeneous and heterogeneous, The equilibrium for calcium sulfate in water is a heterogeneous system because two phases are present:

$$CaSO_4(s) = Ca^{2+}(aq) + SO_4^{2-}(aq)$$
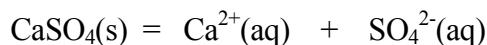
The equilibrium constant expression for calcium sulfate has a typical form for K.

$$K = \frac{(a_{Ca^{2+}})(a_{SO_4^{2-}})}{(a_{CaSO_4})}$$

The activity coefficient for a solid is one; therefore we can rewrite the equation as

$$K = (a_{Ca^{+2}})(a_{SO_4^{-2}})$$

An approximation in dilute solution is that activities equal molarities. When we use this approximation we express K as the solubility product constant, K_{sp}.

$$K_{sp} = [Ca^{2+}][SO_4^{2-}]$$

We will use K_{sp} as our expression for the equilibrium constant of a solid in equilibrium with its ions in water when we do problems in the text. However, in this experiment we first experimentally determine the value of K_{sp}. Then we use an equation for the activity coefficients, called the Debye-Huckel equation, to approximate the activities of Ca^{2+} and SO_4^{2-} and thus calculate an approximate value of K. The percent error in both Ks (or pKs) will be determined.

The equilibrium constant for a slightly soluble salt is determined experimentally by determining the equilibrium concentrations (moles/liter) of its ions. Because the concentrations of the various ions are simply related to each other by the stoichiometry of the equilibrium, it is never necessary to analyze experimentally for the equilibrium concentration of more than one species.

In the case of $CaSO_4$, the stoichiometry of the reaction tells us that when $CaSO_4$(s) dissolves, Ca^{2+} and SO_4^{2-} form in equal amounts. Thus, if we measure the concentration of Ca^{2+} in a saturated solution, we also know the concentration of SO_4^{2-}. After calculating K_{sp} you will use the Deby-Huckel equation to calculate K.

Activity is proportional to molar concentration by the following expression:

$$a = \gamma M$$

You can interpret γ, the activity coefficient, as a factor that "corrects" molarity to represent the true concentration of ions in solution.. In very dilute solutions, the activity coefficient $\gamma \approx 1$, so that $a \approx M$; but at higher concentrations, $\gamma < 1$, i.e., the activity is less than the molar concentration indicates.

Activity coefficients for ions in non-ideal solutions are less than one because electrostatic forces between oppositely charged ions present in solution tend to "tie-up" the ions. That

is the positive and negative ions are attracted to each other, particularly as concentration increase, and ion-pairs are formed. These ion-pairs decrease the number of "free" ions in solution.

Based on an electrostatic model for ions in solution, an equation has been developed to calculate an approximate value of γ, the activity coefficient for an ion. One might guess that it depends on both the charge of an ion and the concentration of all other kinds of ions in solution. Indeed, the Debye-Huckel limiting law gives the following result which is valid for very dilute solutions.

$$\gamma = 10^{-0.510Z^2\sqrt{\mu}}$$

γ = the activity coefficient of an ion

Z = the charge of the ion

μ = the ionic strength, a measure of the concentration of *all* ions in solution.

μ = $1/2\ (M_1Z_1^2 + M_2Z_2^2 + M_3Z_3^2 + ...)$ where M is the molarity of each ion and Z is the charge of the ion.

Sample Problem:

A solution is 0.001 M in MgCl$_2$ and 0.003 M in NaCl.

a. Calculate the molarity of each ion in the solution.

b. Calculate the ionic strength of the solution.

c. Calculate the activity coefficient of the Mg^{2+} ion using the Debye-Huckel equation.

Solution:

a. The 0.001 M MgCl$_2$ solution gives [Mg^{2+}] = 0.001 M and [Cl$^-$] = 0.002 M

The 0.003 M NaCl solution gives [Na$^+$] = 0.003 M and [Cl$^-$] = 0.003 M.

The total [Cl$^-$] in solution from both salts is the sum, 0.005 M.

b. $\mu = \dfrac{1}{2}(M_{Ca^{2+}}Z^2_{Ca^{2+}} + M_{Na^+}Z^2_{Na^+} + M_{Cl^-}Z^2_{Cl^-})$

$\mu = 1/2[0.001(2)^2 + 0.003(1)^2 + 0.005(1)^2] = 0.006.$

c. The activity coefficient for the magnesium ion is:

$$\gamma = 10^{-0.510(2^2)\sqrt{0.006}} = 10^{-0.158}$$

We can solve for gamma by using the 10^x function on a scientific calculator. This gives for magnesium ion: $\gamma = 0.70$

The Mg^{2+} ions in this solution are still primarily in an ion form rather than as ion pairs because the activity coefficient is closer to one than to zero. The activity of the Mg^{2+} ion is:

$$a = \gamma M = 0.70 \, (0.001 \, M) = 0.0007 \, M.$$

III. Experimental Procedures:

1. Upon arriving in the laboratory, you will see a large (2000 mL) beaker on the instructor's desk being vigorously stirred. The milky white suspension is a mixture of $CaSO_4(s)$ and water. After about an hour, it is assumed that the solution is saturated and that equilibrium has been established between the $CaSO_4$ and water.

2. The instructor will filter this solution. The filtrate is a clear liquid, just saturated with Ca^{2+} and SO_4^{2-} ions. Each student should bring a clean, dry 250 mL Erlenmeyer flask to receive about 100 mL of the solution for subsequent analysis. This amount of solution is sufficient for three 25 mL titrations of the saturated solution.

3. Pipet a 25.00 mL aliquot of the calcium sulfate filtrate into a clean (not necessarily dry.....WHY?) 250 mL Erlenmeyer flask. Add 8 drops of Eriochrome black T indicator and about 10 mL of the ammonia buffer to the Erlenmeyer flask. Place the Erlenmeyer flask on a magnetic stirrer and titrate with a standard solution of EDTA. At the end point the purple solution will turn to a sky blue color. Do the titration in triplicate. If you do not have good precision obtain an additional sample of the saturated calcium sulfate solution and do an additional titration.

4. Calculations.

   The stoichiometry of the analysis is simple. The net ionic equation for the titration is:

   $$Ca^{2+}(aq) + H_2Y^{2-}(aq) \rightarrow CaY^{2-}(aq) + 2H^+(aq)$$
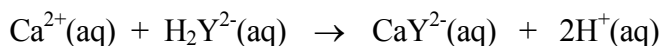
   One mole of calcium ions is stoichiometrically equivalent to one mole of EDTA (H_2Y^{2-}) ions at the equivalence point of the titration:

   moles Ca^{2+} = moles EDTA

   moles $Ca^{2+} = V_{(EDTA)} \, M_{(EDTA)}$

From the number of moles of Ca^{2+}, its molarity can be calculated:

$[Ca^{2+}]$ = moles Ca^{2+}/L Ca^{2+} = moles Ca^{2+}/ 0.02500 L

From the stoichiometry of the solution we know that: $[Ca^{2+}] = [SO_4^{2-}]$. K_{sp} is calculated from:

$$K_{sp} = [Ca^{2+}][SO_4^{2-}]$$

IV. <u>Laboratory Report [Show method and steps for all calculations after tables or data]</u>

1. Title page
2. Pre-lab and corrections to pre-lab
3. Copy of laboratory data from laboratory notebook
4. Prepare a table summarizing all experimental data. Report the precision of your titration data in ppt (parts per thousand - see experiment 2). Use your volumes to determine precision and then **use the average volume for all calculations to follow**.
5. Report your average values in a table format: the number of moles of EDTA used, number of moles of Ca^{2+} that reacted, and the molar concentrations of Ca^{2+} and SO_4^{2-}. Use the proper number of significant figures in all calculations.
6. Prepare a table containing the following information: calculated K_{sp} of calcium sulfate and its pK, and literature values of K_{sp} and pK$_{sp}$, and the percent error between pKs.
7. Prepare a table that contains the following information: Use the Debye-Huckel limiting law to calculate activity coefficients for calcium and sulfate ions, and a K and pK based on the activities. Calculate the percent error between pK based on activities and pK based on literature value.
8. Explain what specific error in calculating your K_{sp} value would occur, compared to the situation in which no errors occur, if
   a. the $CaSO_4$ solution was not saturated?
   b. you measured 25.50 mL instead of 25.00 mL using a pipet.
   c. the end point of the titration that you observed was 2 mL before the true equivalence point.
   d. you spilled some of your solution after you had measured it out.
   e. the EDTA concentration was calculated incorrectly and was actually higher than reported on the reagent bottle.
9. a. Would a particular metallic ion with a charge to ion radius that is large have a higher or lower activity coefficient, γ, than one with a lower charge to ion radius? Explain.
   b. Why does an increasing concentration of ions in a solution decrease the activity coefficient for a metal ion? Explain without using the Debye-Huckel equation.
10. Look up $CaSO_4$ on the Internet. Determine its **common** (not chemical) name and some of the uses that are made of it. Cite your references.

V. Pre-Lab:

1. A solution contains 0.010 M $CaCl_2$. Calculate the molarity of each ion in solution, the ionic strength of the solution, and the activity coefficient for the calcium ion and its activity.

2. Repeat the calculations for the chloride ion in the same solution.

3. The K_{sp} for CaF_2 3.9 x 10^{-11}. Assuming that calcium fluoride dissociates completely upon dissolving and that there are no other important equilibria affecting the solubility, calculate the solubility in pure water, of calcium fluoride in m/L and in g/L.

4. Calculate the solubility of CaF_2 in 0.10 M NaF.

5. Calculate the solubility of CaF_2 in 0.10 M $Ca(NO_3)_2$.

6. Would $CaCO_3$ be more, or less, soluble in an acid solution? Explain.

7. Would CaF_2 be more, or less, soluble in an acid solution? Explain.

8. Draw a diagram of a beaker containing a saturated solution of calcium sulfate with solid present showing what is happening to ions and solid at the microscopic level.

Experiment 7
Qualitative Analysis: Anions

I. Objective:

Determine the identity of anions in a mixture. This is accomplished by: (1) studying the chemical and physical properties of six anions and (2) then developing a chemical method for separating and identifying the six anions in an unknown solution.

II. Chemical Principles:

In this experiment and several future experiments you will be studying the chemical and physical properties of selected ions in order to determine a method for separating and identifying them in an unknown solution. The method is termed qualitative analysis.

Your instructor will review several techniques used in the experimental procedures.

- **Precipitation Techniques**:
  Precipitation of a solid occurs when the ion product for the solid exceeds the solubility product. For this experiment you will follow the directions in your lab book.

- **Heating in a Water Bath**:
  At the beginning of the period, place a beaker of water on the hot plate and bring it to a gentle boil.   If a mixture requires heating, place a test tube containing the solution or heterogeneous mixture into the beaker of hot water.

- **Centrifuging a heterogeneous solution:**
  This is a technique used to separate precipitates from a solution. Ensure the solid in a mixture held in a test tube is thoroughly dispersed and not stuck to the sides of the test tube. You may have to wash down the sides of the test tube with the solvent.

  You must always have a counter test tube on the opposite side of your test tube in the centrifuge before you turn on the centrifuge. The counter test tube is a test tube with an equal volume of another solution or of water. Set the centrifuge setting to about 4 and let it spin for ~ 2 minutes. Turn off the centrifuge and let it come to a stop.
  Take out your test tube and look to see if the solid is at the bottom. If not, centrifuge it again until it does. The liquid above the solid should be clear and is called the **decantate**. It may be colored, but it should be clear.

- **Completeness of Precipitation**:
  After centrifuging a mixture with a solid add a drop or two of the precipitating agent to the liquid above your solid to insure that the solid has completely precipitated. Continue to add the reagent until you no longer observe precipitation. You may have to repeat this procedure several times.

- **Decanting a Liquid from a Solid**.
  If the precipitate is packed in the test tube and does not move you can simply pour the solution off. If the precipitate is light and fluffy and is easily disturbed, then you must decant slowly. To pour the solution from a test tube without the solid, hold a clean, glass stirring rod to the open end of the test tube. The solution will flow down the length of the rod into another test tube and any solid should remain in the test tube or on the stirring rod. In some cases you can use a capillary pipet to remove the excess liquid.

- **Washing Solids**:
  After centrifuging and separating the solid from the supernatant liquid the solid will still be wet from the precipitating reagent. To wash the solid add the indicated amount of wash liquid (quite often water) to the tube and mix well with a glass stirring rod. After mixing thoroughly, centrifuge, and decant off the wash liquid. The wash can be discarded unless otherwise indicated. You should wash precipitates at least twice. If you do not do this step unwanted ions may remain with the precipitate and will interfere with future identification test.

- **Evaporating a Liquid**:
  To reduce the volume of liquid in a test tube you must heat the liquid gently and slowly in either a test tube in a water bath or in an evaporating dish. If you warm it too quickly your compound could decompose. Heat it gently to the desired degree of reduced volume. Do not evaporate to dryness.

- **Transferring a Solid:**
  Transferring a solid from one test tube to another is accomplished by using a liquid that does not dissolve the solid. Once the liquid is added, stir the mixture to cause the solid to be suspended, and then transfer to the second test tube. Then centrifuge the mixture and remove the supernatant liquid. To transfer a solid to another type of vessel a clean, dry "rubber policeman" is used.

- **Adjusting the pH of solutions:**
  Many reactions will only occur if they are done in an acidic or basic environment. If the solution must be acidic, add a drop of acid to the solution. Moisten the end of a glass stirring rod with the solution and then touch it to pH paper. **If blue litmus paper turns red, the solution is acidic. If red litmus paper remains red, the solution is acidic. In some cases a more exact pH is required and you use pH paper. Try to minimize dilution of the unknown solution.**

- **Recording procedures and observations:**
  Anions have specific reactions and you will learn these by doing some chemical reactions with solutions containing known anions. You must **be very observant** and write down your experimental procedures as done and your observations in detail **in your laboratory notebook**. **Examples of details to be recorded are listed on the next page:**

1. Experimental procedures as done. Establish a format in your laboratory notebook that enables you and your instructor to easily review your experimental procedures and observations. An example of a possible format is:
   a. Develop a title or descriptor for each experimental procedure.
   b. Record experimental procedures and observations as you do them.
   c. Summarize key experimental observations
2. Reagents and their concentrations
3. pH of the solutions.
4. Formation of a precipitate, including nature and color of solid.
5. Formation of a gas. (not just the escape of air bubbles)
6. A color change in the solution.
7. A significant heating or cooling of the solution resulting from the reaction.
8. Disappearance of a precipitate.

- **Anion analysis:**
  Anion analysis is usually performed in a series of steps involving chemical reactions. You will study several chemical reactions of a group of anions to assist you in developing a procedure to separate and identify the anions in a mixture. As you carry out the experimental procedures you should note that there are several key steps in the separation and identification process:

1. Addition of $AgNO_3$ under acid conditions to determine which anions form insoluble silver salts.
2. Addition of $Ba(C_2H_3O_2)_2$ under slightly basic conditions to determine which anions form insoluble barium salts.
3. Addition of a strong acid to the anions to determine if a gas forms.
4. Addition of an oxidizing agent such as $KMnO_4$ under acid conditions to determine if an anion is oxidized.
5. Addition of ammonia to an insoluble salt of an anion to determine if a metal complex ion forms.
6. Special tests which are unique for a specific anion.

In this experiment you will develop a qualitative analysis scheme, a diagram that shows how to separate and identify the following anions: **Cl^-, I^-, SO_4^{2-}, CO_3^{2-}, NO_3^-, PO_4^{3-}**

III. Experimental Procedures:

A. General Procedures:

1. All glassware used in this experiment must be free of interfering contaminants. Thus, before you start class each period you must clean your test tubes with soap and deionized water and rinse them thoroughly with deionized water. You do not have to fill the test tube with deionized water; only the water in contact with the surface of the glass rinses the surface. Invert the test tubes in your test tube rack to allow the water to drain and to keep dust out.

2. At the start of each laboratory place a beaker of deionized water bath on a hot plate and heat the water until it gently boils (not vigorously). It will be used daily for heating solutions that are in test tubes.

3. Record all experimental observations as per requirements listed on previous page. At the end of your experimental procedures and observations you are to summarize your observations using the following table in your laboratory notebook. You should construct this table in a landscape mode rather than in a portrait mode.
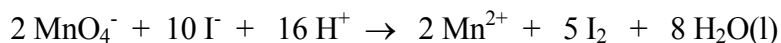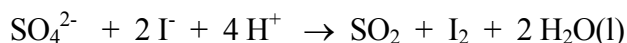
Table I. Description..

|	----AgNO$_3$ tests- Proc 1-- Procedure 1				Ba(C$_2$H$_3$O$_2$)$_2$ tests Procedure 2		Oxidizing Rxns Proc 3			Special 4 & 5
Anion	AgNO$_3$	Add HNO$_3$	Add NH$_3$	Add HNO$_3$	Ba(C$_2$H$_3$O$_2$)$_2$	Add HNO$_3$	H$_2$SO$_4$	KMnO$_4$	(NH$_4$)$_2$MoO$_4$	Nitrate Test
Cl$^-$										
I$^-$										
SO$_4^{2-}$										
NO$_3^-$										
CO$_3^{2-}$										
PO$_4^{3-}$										

B. Specific Procedures:

1. Place 3 drops of one of the anions solutions into two test tubes and repeat for each of the other anion solutions. (making a total of twelve test tubes). Add a few drops of 0.10 M AgNO$_3$ into each of the twelve test tubes and record your observations. If a precipitate forms in any test tube, centrifuge and decant the supernatant liquid. You should have two test tubes for each anion which formed a precipitate with silver (I) nitrate. To one of the test tubes containing a solid add 6 M HNO$_3$ and to the other test tube slowly add about ½ mL of 15 M NH$_3$ (concentrated solution). Mix each mixture thoroughly using a clean, glass stirring rod. [Note: If the solid only disperses in the acid or base, it is not soluble]. If a solid dissolves in ammonia, add 6 M nitric acid until the pH of the solution is acidic. **Check the pH**. Record whether a solid forms or does not.

2. Place 3 drops of one of the anions solutions into a test tube and repeat for each of the other anion solutions. Add a few drops of 0.2 M Ba(C$_2$H$_3$O$_2$)$_2$ to each. If a precipitate forms, centrifuge, decant, and test the solubility of the solid in 3 M HNO$_3.$

3. (a) Place 3 drops of one of the anions solutions into a test tube and repeat for each of the other anion solutions. To each, add 3 drops of 6 M H$_2$SO$_4$ and mix well. Note any **effervescence** (bubbling) or other changes.

(b) To each of the test tubes from part (a), add 2 drops of 0.02 M $KMnO_4$ and stir. If a reducing anion is present, MnO_4^- will form Mn^{2+}. In the hood, add 20 drops of hexane, a nonpolar organic solvent, to each of the solution and shake vigorously. Observe any color change in the **hexane layer**. Only nonpolar or weakly nonpolar substances will leave the water layer and be extracted into the hexane layer. Why? Molecular iodine is a nonpolar molecule. Why? The net ionic equations showing the reactions of iodide ion and the formation of molecular iodine are shown below:

$$SO_4^{2-} + 2\,I^- + 4\,H^+ \rightarrow SO_2 + I_2 + 2\,H_2O(l)$$

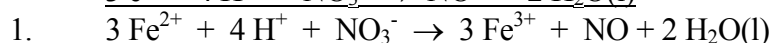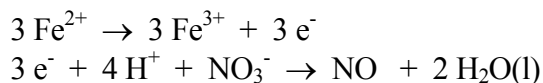$$2\,MnO_4^- + 10\,I^- + 16\,H^+ \rightarrow 2\,Mn^{2+} + 5\,I_2 + 8\,H_2O(l)$$

4. Place 3 drops of one of the anions solutions into a test tube and repeat for each of the other anion solutions.. Check that the solutions are acidic. Adjust the pH of any basic solutions using nitric acid (3 M). Carefully heat the solutions in a water bath for a minute. Do not let the solutions evaporate.

   Add about 3 drops of the ammonium molybdate solution to each of the solutions. If a yellow solid forms it should be $(NH_4)_3PO_4 \cdot 12MoO_3$. If there is no precipitate in the test tube containing PO_4^{3-} ion, warm the solution for a few minutes and see if it appears. The net ionic equation for the formation of the solid is:

   $$3NH_4^+ + PO_4^{3-} + 12MoO_4^{2-} + 24H^+ \rightarrow (NH_4)_3PO_4.12MoO_3(s) + 12H_2O(l)$$
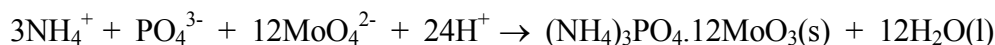
7. Special test for NO_3^-. Your instructor will first demonstrate this test. To a test tube containing 3 drops of a $NaNO_3$ solution and to another test tube containing a solution of NaI, add sufficient solid ferrous ammonium sulfate to saturate the solution (that means, to have a small amount of solid on the bottom of the test tube, but not a large excess). Tilt the test tube 45° and carefully and slowly pour a small amount of fresh, concentrated H_2SO_4 (Do not use 6 M H_2SO_4) down the inside of the test tube. **Do not mix the two layers**. You should see a distinct brown ring form between the two layers. The two net ionic equations for this test are:

   $$3\,Fe^{2+} \rightarrow 3\,Fe^{3+} + 3\,e^-$$
   $$\underline{3\,e^- + 4\,H^+ + NO_3^- \rightarrow NO + 2\,H_2O(l)}$$
   1. $3\,Fe^{2+} + 4\,H^+ + NO_3^- \rightarrow 3\,Fe^{3+} + NO + 2\,H_2O(l)$

   NO which is formed in the previous redox reaction reacts with excess Fe^{2+} to form a metal complex ion. This complex ion is brown in color and forms at the interface between sulfuric acid and the saturated solution of ferrous ion:

   2. $Fe^{2+} + NO \rightarrow [Fe(NO)]^{2+}$

   The complex ion forms a distinctive brown ring. I^- **interferes** with this test; therefore, we do not place NO_3^- and I^- in the same unknown solution.

C. Developing a Qualitative Analysis Scheme

   Before you analyze an unknown solution of anions you must prepare a diagram that
   shows how you plan to **separate and identify** each anion in a mixture that might
   contain all six anions. This diagram is called a qualitative analysis flow scheme.

   Prepare a rough draft of your qualitative analysis scheme for the six anions and have
   your instructor review it. It must be signed by your instructor before you can begin
   your unknown solution.

D. Check your scheme

   Using your qualitative analysis scheme separate and identify the ions in a known
   solution containing the anions except for the nitrate ion. The NO_3^- test is done
   independently on a small aliquot of the known solution. Remember that if iodide ion
   is present in your unknown solution then it will not have nitrate ion, and vice versa.
   Use 5 drops of the known solution and carry out the experimental steps described in
   your scheme. If your results do not match the expected ones in your qualitative
   analysis scheme repeat the experimental procedures to ensure that you did not make a
   mistake in adding chemicals. If it still does not work, see your instructor. In any step
   of your scheme that produces a precipitate you must check for completeness of
   precipitation and also wash precipitates. If you fail to do this it often results in you
   finding false positives in terms of ions in your solution.

E. Unknown

   Obtain an unknown solution from your instructor. This solution contains **one to four
   ions**. Record the unknown number in your laboratory notebook. Using your
   qualitative analysis scheme separate and identify the ions in your unknown solution.
   Reminder: record in detail all experimental procedures and observations.

   The score for the unknown in all experiments involving qualitative analysis is
   determined as follows:

   Score = (maximum points) x Number of ions correctly reported_____
                                  Number of ions in unknown + # incorrectly reported

   Note that in the scoring formula there is a factor for incorrectly reporting ions that are
   not in the unknown.

IV. **Laboratory Report:**

1. Title page with unknown number and anions present in unknown
2. Pre-lab and corrections
3. Copy of all laboratory data in laboratory notebook including Table 1. To earn high marks on qualitative analysis laboratory reports you must record complete and detailed experimental procedures and observation.
4. Rough draft of qualitative analysis scheme signed by instructor.
5. Final copy of qualitative analysis scheme, hand written on white paper, which has no errors or corrections. Each step in the qualitative analysis scheme that has a chemical reaction is sequentially numbered.
6. For each numbered step in the qualitative analysis scheme, type all net ionic equations associated with each step. Show only the final net ionic equation.
7. A typed summary statement providing your logic, with reference to experimental observations, for choosing the ions in your unknown.

V. **Pre-Lab:**

1. (a) Which anions in this experiment are basic anions? Why are they considered basic anions? (b) Write the net ionic equation describing the reaction of each with nitric acid.

2. Which steps in the experimental procedures require you to be careful with strong acids and bases? What do you do if you spill a strong acid or base on your skin?

3. (a) When ammonia is added to solid silver chloride what is the metal complex ion that forms? (b) If the solution containing the metal complex ion is made acidic, why will the silver chloride precipitate? Write net ionic equations describing these two reactions. This series of reactions is used in this experiment to identify and confirm the chloride ion.

4. A mixture of sodium salts may contain one or more of the anions studied in this experiment. All of the salts are readily and completely soluble in cold water. Two samples of this aqueous solution show no precipitate when $AgNO_3$ or $BaCl_2$ is added. What anions are shown to be conclusively present in the unknown solution? Which anions are shown to be definitely absent? For which anions are the tests insufficient to confirm their presence or absence. Explain your logic for each situation.

5. A mixture of sodium salts may contain one or more of the anions studied in this experiment. All of the salts are readily and completely soluble in cold water. When silver nitrate is added to the solution, a precipitate forms. What anions are shown to be conclusively present in the unknown solution? Which anions are shown to be definitely absent? For which anions are the tests insufficient to confirm their presence or absence. Explain your logic for each situation.

Experiment 8
Qualitative Analysis of Silver Group and Barium-Magnesium Group

I. Objective:

To separate the Ag group (Ag^+, Pb^{2+}, Hg_2^{2+}) of ions from the Ba-Mg (Ba^{2+}, Ca^{2+}, Mg^{2+}, NH_4^+, K^+, Na^+) group of ions and identify each in an unknown.

II. Chemical Principles:

Principles of separation and identification of ions are discussed in Experiment 7.

III. Laboratory Procedures:

Silver, Lead, and Mercury are all toxic. Place them in an appropriate waste containers. Mercury is disposed of in its own waste container.

A. 1.   The laboratory procedures are described in section III B. below.   As in Experiment 7, record in your laboratory notebook completely and in detail all experimental procedures and observations.
   2.   After you complete the experimental procedures, complete Table I. You should prepare the table in a landscape mode.

Table I. Summary of Observations

Ions /Procedure=	Flame test 1	HCl 2	Heated test=tube +CrO_4^{2-} 3	CrO_4^2 4	NH_3 5	SO_4^{2-} 6	$C_2O_4^{2-}$ 7	Mg^{2+} test 8	NH_4^+ test 9
Silver									
Lead									
Mercury									
Barium									
Calcium									
Magnesium									
Sodium									
Potassium									
Ammonium									

B. 1.   Your instructor will show you how to do a flame test for ions in a solution. Obtain a sample of each of the nine cation solutions. Prepare a nichrome wire according to your instructor's directions. Clean it with 12 M HCl and then heat it in the blue portion of your gas flame until there is minimal color emitting from the nichrome wire. Dip the clean nichrome wire into a cation solution, place it in the blue portion of the gas flame (near the tip of the blue cone), and observe any emitted color. For
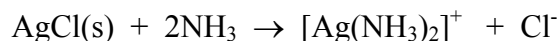
potassium ions, also observe the flame with cobalt glass. You may also want to mix sodium and potassium ions and observe their flames together with cobalt glass and without.

2. Place 3 drops of 0.10 M solution of each of the metal ion solutions into each of nine test tubes. Add 3 drops of 6 M HCl and mix thoroughly. Centrifuge and check for completeness of precipitation by adding an additional drop (or more) of HCl to those solutions that contain a precipitate. Then centrifuge and decant. Throw the decantate away since these are solutions containing known ions. Add 3 or 4 mL of cold deionized water to each solid. Save these for step (3).

3. In a water bath, heat the test tubes that contain precipitates from step (2). Stir during heating. Heat for about 5 minutes. Note if any precipitate dissolves. If a precipitate dissolves, add a drop of K_2CrO_4 to the solution and report the color of any precipitate. Save all test tubes containing precipitates that did not dissolve for step (5)

4. To determine the color of precipitates containing the chromate ion, take 3 drops of $AgNO_3$, $Pb(NO_3)_2$ and $Hg_2(NO_3)_2$ in three separate test tubes. Add a drop of K_2CrO_4 to each solution and report the color of the resulting precipitates.

5. Centrifuge and decant off any solution from precipitates in step (3) that did not dissolve upon heating. To the precipitates, slowly add 15 M NH_3 **(CAUTION)** with stirring until no further changes occurs. You should observe two significant changes:

   Hg_2Cl_2 reacts with ammonia according to an oxidation-
   reduction reaction:

   $Hg_2Cl_2(s) + 2NH_3 \rightarrow Hg(s) + HgNH_2Cl(s) + NH_4^+ + Cl^-$
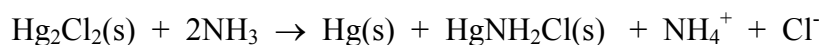
   AgCl reacts with ammonia forming a complex ion:

 $AgCl(s) + 2NH_3 \rightarrow [Ag(NH_3)_2]^+ + Cl^-$

   To the silver solution, add 6 M HNO_3 **(CAUTION)** until a
   precipitate reappears. **Check pH to ensure the solution is acidic.**

6. Place 3 drops of 0.10 M solution of each of the metal ion solutions into `` each of 9 test tubes. Add $(NH_4)_2SO_4$ to each. Report any precipitates.

7. Place 3 drops of 0.10 M solution of each of the metal ion solutions into each of 9 test tubes. Check the pH of each solution. If the solution is acidic, add 0.1M ammonia until pH is 7 to 9. (**If it is quite acidic**, you

may need to use a higher concentration of ammonia)   After the pH is in the 7 to 9 range, then add 3 or 4 drops of $(NH_4)_2C_2O_4$ to each of the samples.

8. Special test for magnesium ion. To 5 drops of the magnesium ion solution, add 1 drop of 5 M aqueous ammonia to make the solution just basic (check the pH) and then add 4 drops of 0.2 M Na_2HPO_4. Mix well and let stand for approximately a min.   What is the precipitate that forms? Centrifuge and decant.   Wash the precipitate twice with hot water. Dissolve the precipitate in 2-3 drops of 2M HCl and add 3-4 drops of magnesium reagent.   Add 8 M NaOH, while stirring, until litmus paper indicates that the solution is alkaline (basic).   Centrifuge the mixture. A lake blue precipitate of magnesium hydroxide proves the presence of the magnesium ion.

9. Special test for ammonium ion: Moisten and attach red litmus paper to the underside of a watch glass. Place 5 drops of 8 M NaOH into a casserole. Add 5 drops of a solution containing ammonium ions. Cover the casserole with the watch glass to which you have attached the red litmus paper.   Warm the casserole gently.   Ammonia gas will evolve and turn the red litmus paper blue indicating the presence of the ammonium ion. The net ionic equation for the reaction is:

$$NH_4^+ + OH^- \xrightarrow{\text{Heat}} NH_3(g) + H_2O(l)$$
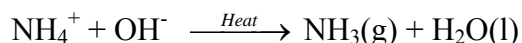
C. Qualitative Analysis Scheme

Before you will be issued an unknown, prepare a rough draft of a qualitative analysis scheme that shows how you plan to separate and identify the nine ions in this experiment. This scheme must be approved by your instructor before you will be issued an unknown. Refer to Experiment 7 for requirements including number of steps in scheme which involve chemical reactions. Prepare for your laboratory report a final, clean qualitative analysis scheme and underneath it write net ionic equations for reactions numbered in the scheme.

D. Unknown.

Obtain an unknown solution from your instructor. **This solution contains one to four ions**. Record the unknown number in your laboratory notebook. Using your qualitative analysis scheme separate and identify the ions in your unknown solution. Reminder: record in detail all experimental procedures and observations.

The score for the unknown in all experiments involving qualitative analysis is determined as follows:

Score = (maximum points) x $\dfrac{\text{Number of ions correctly reported}}{\text{Number of ions in unknown} + \text{\# incorrectly reported}}$

Note that in the scoring formula there is a factor for incorrectly reporting ions that are not in the unknown.

IV. Laboratory Report:

1. Title page with the unknown number and which cations are present in the unknown.
2. Copy of laboratory data pages for this experiment, including Table I. To earn high marks on qualitative analysis laboratory reports you must record complete and detailed experimental procedures and observation.
3. Rough draft of qualitative analysis scheme signed by your instructor
4. Final copy of qualitative analysis scheme, which has no errors or corrections. Each step in the qualitative analysis scheme that has a chemical reaction is sequentially numbered.
5. For each numbered step in the qualitative analysis scheme, type all net ionic equations associated with the step. Write only the final net ionic equations for the qual scheme containing all nine ions.
6. A summary statement providing your logic, with reference to experimental observations, for choosing the ions in your unknown.

V. Pre-Lab:

1. Fill in the following table with the K_{sp} values for any insoluble salt that forms from a metal ion in the left column and the anions in the other columns. If a salt is soluble in water write N/A.

Table II. Selected K_{sp} Values

Metal	Cl^-	OH^-	SO_4^{2-}	CrO_4^{2-}	$C_2O_4^{2-}$
Ag^+	1.8×10^{-10}				
Pb^{2+}					
Hg_2^{2+}					
Ba^{2+}					
Ca^{2+}					
Mg^{2+}					
Na^+					
K^+					
NH_4^+					

2. In a test tube containing a precipitate of $Pb(OH)_2$ in water: What are the concentrations of the lead(II) and hydroxide ions in equilibrium with the solid? Show your calculations.

3. How can $AgCl(s)$ be dissolved completely? Write an equation for the reaction.

4. If HCl is added to a solution containing the following ions; Ag^+, Mg^{2+}, K^+, and Ba^{2+}, which ions should precipitate based on your data in Table II?

5. If sulfuric acid is added to a solution containing the following possible ions: Ag^+, Ca^2 , NH_4^+, and Pb^{2+}, which ions should precipitate ?

6. Of the chloride compounds that precipitate, which is the most soluble? Calculate molar solubilities of each one to prove your answer.

7. If too much HCl is added to the lead solution, a complex ion can form. That ion is $[PbCl_4]^{2-}$. Write a net ionic equation showing how this complex ion forms in solution.

8. Does a chemical reaction occur when a metal ion is placed in a flame and a color occurs?   Explain.   What is the difference between emission and absorption in spectroscopy?

9. Should sodium chromate be added directly to an unknown as a "**special**" test? Explain.

Experiment 9
Determination of Enthalpy and Entropy Change for a Chemical Reaction.

I. **Objective:**

To determine ΔH^o and ΔS^o for dissolving sodium borate in water.

II. **Chemical Principles:**

Most physical and chemical changes are affected by temperature. More than a century ago, observations of temperature effects on everyday phenomena led to a formulation of the laws of thermodynamics, which are mathematical descriptions of the observations. The first law tells us about energy; the second law tells about reversibility and the direction of spontaneous change; and the third law tells us about absolute zero. The laws of classical thermodynamics apply specifically to the equilibrium condition of a system. When these laws are applied to chemical reactions, they relate the equilibrium condition and the temperature of a given reaction to the thermodynamic quantities, ΔH^o, ΔS^o, and ΔG^o. By experimentally studying the effect of temperature on the equilibrium condition for a chemical reaction, we should obtain the fundamental information that we need to calculate these three functions.

There are two commonly used indicators of the expected success of a chemical reaction; K, the equilibrium constant, and ΔG^o, the standard state free energy change. "Successful" reactions, i.e., reactions which "go" over 50% are those with K> > 1, and ΔG^o < 0. As you might expect, there is a relationship between K and ΔG^o. It is:

$$\Delta G^o = -RT \ln K \qquad (1)$$

where **R is the gas constant** and T is temperature in Kelvin. Thus, if we measure K, we can calculate ΔG^o. Further, we know that for changes at constant temperature,

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (2)$$

where ΔH^o and ΔS^o are standard state changes in enthalpy and entropy of reaction.

ΔH^o is simply the heat of reaction (for changes at constant pressure), and ΔS^o is the standard state entropy change. We can see that by determining K at two different temperatures, we can calculate ΔG^o at each temperature, and use these two values of ΔG^o to calculate ΔH^o and ΔS^o. This approach assumes that ΔH^o and ΔS^o are constant over small changes in temperature. In fact, there is no need to calculate ΔG^o at all; we can combine the equations to find

$$-RT \ln K = \Delta H^o - T\Delta S^o \qquad (3)$$

Finally, if we divide equation (3) by -RT, then

$$\ln K = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R} \qquad (4)$$

If there is more than one temperature you can use the Clausius-Clapeyron equation.

$$\ln \frac{K_2}{K_1} = \frac{-\Delta H^o}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] = \frac{-\Delta H^o}{R}\left[\frac{T_1 - T_2}{T_1 T_2}\right] \qquad (5)$$

This equation is derived by using two equations with two unknowns. If more than two temperatures are used, graphing works best and will be described here.

The salt chosen for this experiment is sodium tetraborate decahydrate, better known as borax. Borax is an example of a class of compounds named borates, which contain polyanions composed of trigonal BO_3 and/or BO_4 units linked by bridging oxygen atoms to form chain or ring structures. The reaction that we will study in this experiment is the dissolution of borax in water:

$$Na_2B_4O_7 \bullet 10H_2O(s) \leftrightarrow 2Na^+ + B_4O_7^{2-} + 10H_2O(l) \quad (6)$$
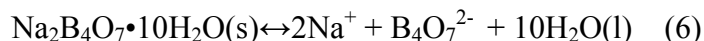
We will calculate the equilibrium constant at four different temperatures, and use these values to determine ΔH^o and ΔS^o for the reaction.

$$K = [Na^+]^2[B_4O_7^{2-}] \qquad (7)$$

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

## III. Experimental Procedures:

A. Titrations

Be sure to record your experimental procedures as you do the experiment. Record the data for each titration in a table format as described on the next page.

Take four test tubes and, with a wax pencil, mark the 5.0 mL level on each by dispensing 5.0 mL of water with a 5.0 mL pipet.. Label them 60°, 50°, 40° and

30°. In a 150-200 mL beaker add about 80 mL of water and approximately 30 g (50 mL) of borax to make a saturated solution. Heat this solution to approximately 65°C. Excess solid must be present to ensure that the system is a saturated solution. However, if there is too much solid, there may not be sufficient liquid for four samples.

Stirring continuously, let the solution cool to 60°C. Allow the excess solid to settle out, and quickly decant a 5.0 mL sample into your test tube. Accurately measure and record the temperature of the saturated solution at the time you pour it. Immediately transfer the sample from the test tube into a clean 125 mL Erlenmeyer flask. Use plenty of deionized water to make certain that no borax remains in the test tube. Resume stirring the saturated solution and allow the beaker to continue cooling to 50°C; decant another sample. Again, transfer the sample to a clean flask. Repeat the procedure for 40°C and 30°C.

Analyze the borax solutions in the four samples obtained at different temperatures by titrating with standardized HCl. The titration reaction is as follows:

$$B_4O_7^{2-} + 2\,H^+ + 5\,H_2O(l) \rightarrow 4\,H_3BO_3 \qquad\qquad (8)$$
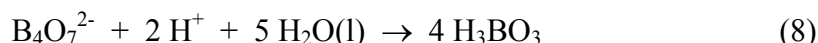
The indicator for this reaction is **methyl orange.** The end point occurs when the color of the indictor just changes from yellow to red.

Record the data for the four titrations using the following table in your laboratory notebook. After the table show a sample calculation for the number of moles of HCl.

Table I. Titration of Borax with HCl _____(concentration)

Sample Temperature (°C)	Initial Volume HCl (mL)	Final Volume HCl (mL)	Total Volume HCl (mL)	Calculated Number of Moles of HCl

B. Waste Disposal

You can dispose of the saturated borax solutions and the solutions titrated with HCl by the following procedures: (1) Check the pH of the four solutions. Adjust the pH of each solution to pH = 6-8 using either HCl or NaOH; and (2) dispose of the solutions in the sink. Remember that borax is used as a type of soap in households.

IV. **Laboratory Report**   (1, 4, 5, 6, 7 are typed.)

1. Title page
2 Pre-lab with corrections to pre-lab.
3. Laboratory notebook pages containing procedures, observations, data and Table 1.
4. A table summarizing the data necessary for you to graph lnK vs 1/T. After the table provide sample calculations for each column requiring a calculated number. Include units with titles of appropriate columns. Remember that temperature, T, is in the unit of Kelvin and an equilibrium constant has no units.

Table II. Summary of Titration Data, K and T

Titration	$[B_4O_7{}^{2-}]$	$[Na^+]$	K	ln K	T	1/T
1						
2						
3						
4						

Information for calculating K:

a). From equation (8): Number of moles of $B_4O_7{}^{2-}$ = 1/2 number of moles of HCl.

We can then calculate $[B_4O_7{}^{2-}]$: $[B_4O_7^{2-}] = \dfrac{\text{moles of } B_4O_7^{2-}}{V_L}$

V_L is the volume of the sample originally collected at each specified temperature.

b). From the stoichiometry of equation (6) we know that
$$[Na^+] = 2[B_4O_7{}^{2-}].$$

c). Finally, K is calculated using equation (7).

5.   A computer generate graph (full page) of ln K versus 1/T. The form of the equation for this graph is y = mx +b, a linear equation. Look at equation (4) and if y is ln K and x is 1/T, it is also a linear equation. Have the computer program generate a best fit linear line and obtain the data necessary to write the linear equation. Determine the slope of the graph and the intercept of the line with the y axis and report these in a table

a. The slope of the line is $\dfrac{-\Delta H^o}{R}$

b. The intercept is $\dfrac{\Delta S^0}{R}$

6. A table summarizing the values, with units, for ΔG^o, ΔH^o and ΔS^o. Underneath this table show details of how these numbers are calculated. Show units with all steps in each calculation.

7. Answers to questions:
   a. Is this reaction spontaneous at room temperature (25° C)? Explain.
   b. If the reaction is not spontaneous in (a), at what temperature does it become spontaneous? Show all calculations.
   c. Will the calculated value of K be too high or too low if
      1). the original borax solution was supersaturated?
      2). when pouring solution into the test tube you poured out borax crystals with the solution?
      3). the volume of borax solution was less than 4.8 mL but you thought it was 5.0 mL?

      For each situation provide your logic and relate to calculations required.

   d. Is K dependent upon temperature? How does this experiment prove your answer?

V. **Pre-Lab:**

1. The solubility of AgCl in water is 3.97×10^{-6} M at 0 $^\circ$C and 1.91×10^{-4} M at 100 $^\circ$C. Calculate K_{sp} for AgCl at each temperature.

2. Using data from question (1) and the Clausius-Clapeyron equation, calculate ΔH° and ΔS° for the formation of a saturated solution of AgCl.

3. Using data from 1 and 2 above: Calculate the free-energy change at 25 $^\circ$C for the formation of a saturated solution of AgCl in water. What does the sign of the free-energy change tell you about the direction of this reaction? Explain and relate to K_{sp}. At what temperature does AgCl become spontaneously soluble?

4. Calculate the slope of a line for which x1 = 1.00, y1 = 5.00, x2 = 1.50, y2 = 9.00.

Experiment 10
Electrochemistry

I. **Objective:** To measure E_{cell} for several voltaic cells and determine the standard
potential for each half cell. To determine K_{sp} of AgCl and the K_d of
$[Cu(NH_3)_4]^{2+}$.

II. **Chemical Principles:**

We will use a inexpensive voltaic cell (a micro voltaic cell) that mimics a reversible
cell. It has a salt bridge that is different in design from the one shown in your
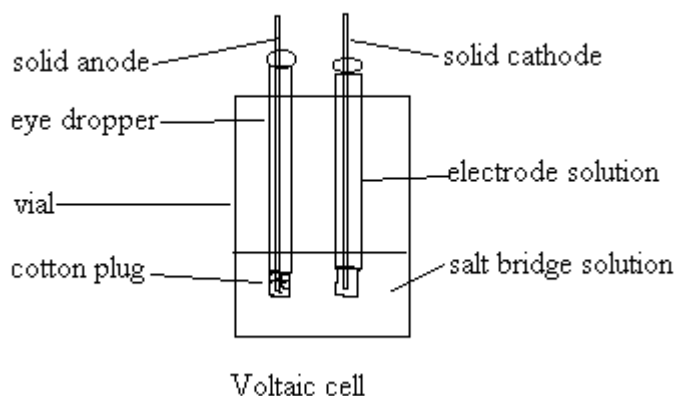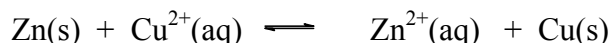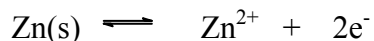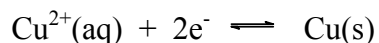textbook.

Voltaic cell

Figure 1

In a micro cell containing a copper wire and copper solution and a zinc rod and a
zinc solution, the cell reaction is:

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

By convention, the cell voltage is positive when the reaction is spontaneous as
written. Oxidation occurs at the anode,

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

and reduction occurs at the cathode,:

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

Electrons flow from anode to cathode in the external part of the cell. In the salt
bridge, negative ions migrate in solution from the cathode to anode, while positive
ions migrate in the opposite direction. The migration of electrons in the outer circuit
and ions in solution maintain charge neutrality in local regions in the system

The cell potential is the difference in the potentials of the cathode and anode; $E_{cell} = E_{cathode} - E_{anode}$. The values of $E_{cathode}$ and E_{anode} refer to potentials for reduction half-reactions. All standard potentials are referenced to reduction half reactions.

The shorthand notation for a voltaic cell is:

$$Zn^0 | Zn^{2+}(1\ M) || Cu^{2+}(1\ M) | Cu^0$$

The relationship between E^o, the standard cell potential, and E, the potential of a cell not at standard state conditions, is given by the Nernst equation:

$$E = E^\circ - \frac{0.0592V}{n} \log Q \quad \text{or} \quad E = E^\circ - \frac{0.0257V}{n} \ell n Q$$

where Q is the reaction quotient and n is the number of electrons transferred.

When all ions are at 1 M, then $Q = 1$ and $E = E^o$. E is related to free energy:

$$\Delta G^o = -nFE^o \quad \text{and} \quad \Delta G = -nFFE.$$

III. Laboratory Procedures:

You will work in pairs but record in your laboratory notebook all experimental procedures and observations while the experiment is done, not after the experiment is completed. Each person turns in an independent laboratory report. Your laboratory instructor will sign your laboratory notebook at the end of each laboratory period.

A. Voltaic Cells   First day

1. Set up the micro cell as shown in Figure 1. In your laboratory notebook draw a diagram of the general voltaic cell and describe the general procedures you will use for the portion of the experiment. Your instructor will demonstrate how to make the cell. The wire that has a black clip is attached to the anode and the one with the red clip to the cathode. When you have hooked the cell up correctly, with zinc as the anode, you should have a voltage of around +1105 mV or 1.105 V. In practice it sometimes is less than this value. *If you observe a negative voltage then switch the connections to the electrodes to show a positive voltage.*

   Prepare Table I in a landscape format in your lab manual. You will need nine horizontal rows to describe the voltaic cells you prepare and a column heading. An example of how you record data is shown for the first

voltaic cell you constructed in procedure (1). The cell potentials shown are *not* the cell potentials that you record; **record what you observe with all digits shown on the voltmeter**.

Table I. (showing all 8 cells) Descriptive Title

Cell Description	Anode	Cathode	E_{cell} (V)	E^o_{cell} (V)
$Zn^o|\ Zn^{2+}(0.1M)|\ |\ Cu^{2+}(0.1M)|\ Cu^o$	Zn	Cu	+0.900	0.900

After you measure the potentials for **all eight** voltaic cells (see procedures (2) and (3)), calculate the standard potential for each voltaic cell using the Nernst equation. **Show sample calculations for a case where Q =1 and Q is not one**.

2. Replace the zinc half cell in procedure (1) with the following half cells and repeat the same observations and measurements as in procedure (1).

$Ag|\ Ag^+ (0.1M)$ $Pb|\ Pb^{2+} (0.1M)$
$Cd|\ Cd^{2+}(0.1M)$ $C|\ Fe^{2+}(0.1M), Fe^{3+}(0.1M)$
$C|\ I^-(0.1M),I_2$
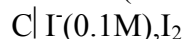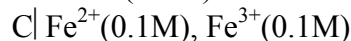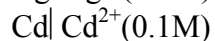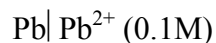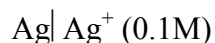
The letter "C" represents a carbon electron electrode, which is an inert electrode. Notice that the concentrations are not one molar; this reduces cost factors. Thus, we are measuring E, not E^o. In the laboratory report you will calculate E^o for all cells.. In a few voltaic cells you will find that $E = E^o$ because in the Nernst equation Q = 1 even if the concentrations are not one molar.

3. Set up two more voltaic cells consisting of two half cells, neither of which uses copper, and record the same data as above. This data will be used in Table V of the laboratory report.

IV.   **Laboratory Report (Part A)** (First day)   **All tables are typed.**

1. Title page
2. Copy of laboratory experimental procedures and data for Part A, including Tables I.
3. Typed Tables I – X with sample calculations (hand write calc is fine).

   Instructions for preparing Tables

1. Prepare Table II summarizing the identified information in the table for all voltaic cells studied using $Cu^{2+}|\ Cu$ as the reference cell. Report all half-cell potentials as standard reduction potentials; the copper-containing cell is the standard reference cell which is assigned a value of exactly 0 V. In some cells it may be the cathode and in others the anode. Be sure to identify whether it is a cathode or anode in a particular voltaic cell before determining the other half-cell standard potential.

Construct this table and all subsequent tables (Parts A, B and C) with short-hand cell notations in a landscape format. Also in this table and subsequent tables show the units for potentials or thermodynamic values with each column heading. They are not shown in most of the sample tables and you will need to show them. Show after each table one sample calculation for each different type of calculation.

Table II. (6 cells using Cu electrode) Descriptive Title

Cell Description	Anode	E^o_{anode} (V)	Cathode	$E^o_{cathode}$ (V)	E^o_{cell} (V)
$Zn \mid Zn^{2+}(0.1M) \parallel Cu^{2+}(0.1M)/Cu$	$Zn(s) \rightleftharpoons Zn^{2+} + 2e-$	−0.900	$Cu^{2+}(aq) + 2e \rightleftharpoons Cu(s)$	0.00	0.900

2. Prepare Table III showing the shorthand notation for all voltaic cells studied. Convert all standard potentials from Table II to standard potentials based on the standard hydrogen electrode with a potential of exactly 0 V and the standard potential for Cu^{2+}/Cu is +0.337 V. Both E^o_{anode} and $E^o_{cathode}$ will be different than in Table II.

Table III (6 cells using Cu electrode) Descriptive Title

Cell Description	E^o_{anode}	$E^o_{cathode}$	E^o_{cell}
$Zn^o \mid Zn^{2+}(0.1M) \parallel Cu^{2+}(0.1M) \mid Cu^o$	− 0.563	0.337	0.900

3. Prepare Table IV using the data from Table III to list the half-cell reactions in order from strongest to weakest oxidizing agent.

Table IV Descriptive Title

Half Reaction	E^o_{exp} from Table III	E^o_{lit} from below	% Error
Reduction equation			

Standard Reduction Potentials in Aqueous Solution at 25^oC

Reduction Equations				E^o
Ag^+	$+$	e^-	$\rightleftharpoons Ag(s)$	+0.799
Fe^{3+}	$+$	e^-	$\rightleftharpoons Fe^{2+}(aq)$	+0.771
I_2	$+$	$2e^-$	$\rightleftharpoons 2I^-(aq)$	+0.536
Cu^{2+}	$+$	$2e^-$	$\rightleftharpoons Cu(s)$	+0.337
$2H^+$	$+$	$2e^-$	$\rightleftharpoons H_2(g)$	0.00
Pb^{2+}	$+$	$2e^-$	$\rightleftharpoons Pb(s)$	-0.126
Cd^{2+}	$+$	$2e^-$	$\rightleftharpoons Cd(s)$	-0.403
Zn^{2+}	$+$	$2e^-$	$\rightleftharpoons Zn(s)$	-0.763

4. Prepare Table V summarizing the data for **the two cells studied that did not contain the copper** half cell in Procedure (3). Compare E^o_{cell} (experimental value)) to E^o_{cell} (calculated) using the data in the table IV to calculate E^o (calculated). Determine the % error.

Table V Descriptive Title

Cell	E^o_{exp} from Table I	E^o_{calc} from Table IV	% Error

5. For the cells $Cu|Cu^{2+}||Fe^{3+}, Fe^{2+}|C$ and $Cu|Cu^{2+}||I_2, I^-|C$, prepare Table VI.

Table VI. Descriptive Title

Cell	$E^o_{experimental}$ Table I	$\Delta G^o_{experimental}$ (a)	$\Delta G^o_{calculated}$ (b)	% Error of ΔG^o
$Cu|Cu^{2+}||I_2,I^-|C$,				
$Cu|Cu^{2+}||Fe^{3+},Fe^{2+}|C$				

(a) ΔG^o (exp.) = $-nFE^o$(exp.) where F is the Faraday constant, 96,485 J/V-mole.
(b) Calculate ΔG^o using $\Delta G^o = \Delta H^o - T\Delta S^o$. Write the balanced equation for each redox reaction. Then use the literature values for ΔH^o and ΔS^o in the following tables to calculate ΔH^o and ΔS^o for each redox reaction.

Thermodynamic Properties of Pure Substances at 25°C and unity activity (1 atm.)

Solid	ΔH^o (kJ/mole)	S^o (J/K mole)
Ag(s)	0.00	42.7
AgCl(s)	-127.0	96.11
Cu(s)	0.0	33.30
Fe(s)	0.0	27.15
I_2(s)	0.0	116.7

Thermodynamic Properties of Aqueous Substances at 25°C and unit activity (1M)

Ion	ΔH^o (kJ/mole)	S^o (J/K mole)
Cl^-(aq)	-167.4	55.2
Cu^{2+}(aq)	64.39	-98.7
Fe^{2+}(aq)	-87.86	-113.49
Fe^{3+}(aq)	-47.70	-293.3
H^+(aq)	0.0	0.0
I^-(aq)	-55.94	109.37

**Instructions for preparing the remainder of the laboratory report the experimental sections in procedures B and C.**

V. Determining the Dissociation Constant of $[Cu(NH_3)_4]^{2+}$--Part B

Principles: *Review the following principles and experimental procedures before starting this section of the experiment. Then develop a format for recording experimental procedures, voltaic cell design and set-up, and data.*

1. Consider the following electrochemical cell:

$$Cu| Cu^{2+} (0.1 \text{ M}) || Ag^+(0.10M)| Ag$$

We prepared this cell in Part A. What happens if we add an excess of ammonia to the copper (II) solution? In the presence of a large ammonia concentration, the copper ion is converted almost entirely to a metal complex ion:

$$Cu^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+}$$
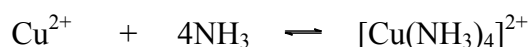
This reaction decreases the amount of copper (II) ion in the cell and alters the cell potential for the redox reaction.

In this part of Experiment 8 you will prepare the previous voltaic cell and measure the cell potential. Then you will add excess ammonia to the copper (II) cell compartment and measure the cell potential. The concentration of the uncomplexed copper (II) ion after addition of ammonia is calculated using the cell potential and the Nernst equation. The value of the dissociation constant for this complex is calculated.

Procedures for Part B:
   (a) Set up the voltaic cell described by the following cell shorthand notation:

$$Cu| Cu^{2+}(0.10M)|| Ag^+(0.10M)| Ag$$
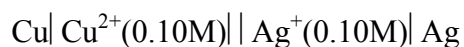
Place a Cu electrode in contact with a Cu^{2+} solution and a silver electrode in contact with a Ag^+ solution. Record the anode and cathode and the cell potential. Calculate and record E^o for the cell as you have done previously.

   (b) Mix 20 drops of 0.10 M copper (II) sulfate with 20 drops of 7 M NH_3 in a small beaker. The drops need to be of equal size. What are the concentrations of copper (II) ions and ammonia in the solution? Record the original and diluted concentrations. Using this new solution set up a voltaic cell similar to the one you prepared in (a) but instead use the mixture you just prepared to replace the 0.1 M copper (II) solution. Record the anode and cathode and the cell potential.

Laboratory Report Part B   (continuing from Part A)

4. Copy of laboratory data for Part B
5. Prepare Tables VII and VIII in a typed format:

Table VII. Descriptive Title

Cell	E_{cell}	E^o_{cell}
Cu$\mid$ Cu^{2+}(0.10M)$\mid\mid$ Ag$^+$(0.10M)$\mid$ Ag		
Cu$\mid$ Cu^{2+} (x M),Cu(NH$_3$)$_4^{2+}$(0.05M)$\mid\mid$ Ag$^+$(0.10M)$\mid$ Ag		//////////

Table VIII. Descriptive Title

	[Cu^{2+}], M	K_d	E_{cell}
Experimental			
Theoretical		1.47 x 10^{-13}	
% Error	//////////////		

sample calculations follow each table.

6.   Error Discussion:
(a) Does an error of one or two hundredths of a volt in your measured cell potential cause a discrepancy between your value for K_d and the value found in literature for K_d? Explain. (b) If you accidentally added 21 drops of 0.10M copper (II) sulfate solution instead of 20 drops and you did not recognize this error, what effect would it have on your voltaic cell potential? Explain.

Instructions for calculating requested data in Tables VII and VIII:

The following redox reaction and the concentrations of the ions determine the cell potential for both voltaic cells:

$$Cu(s) + 2 Ag^+ \rightleftharpoons Cu^{2+} + 2 Ag(s)$$

The effect of adding excess ammonia to copper (II) ion is to change the copper (II) concentration in the second voltaic cell and this changes the cell potential
.

Calculate E^o for the first voltaic cell. Use the Nernst equation to calculate the concentration of uncomplexed copper (II) ion in the second voltaic cell. In the second voltaic cell the concentration of silver (I) ion is essentially its original concentration when the voltaic cell first is set-up and the cell potential is measured. In the Nernst equation the value of "n" is determined from the redox reaction in the voltaic cell, which is the one written above. You also measured E for the cell. One of the forms of the Nernst equation is

$$E = E^\circ - \frac{0.0592V}{n} \log Q$$

We know E, E°, [Ag^+] and n. We can calculate Q. What is the form of Q for the redox reaction? Use the value of Q to calculate the concentration of the uncomplexed copper (II) ion at equilibrium with ammonia and the metal complex ion.

The equation for the dissociation of the metal copper (II) complex ion is:

$$[Cu(NH_3)_4]^{2+} \;\rightleftharpoons\; Cu^{2+} + 4NH_3 \quad \text{and} \quad K_d = \frac{[Cu^{2+}][NH_3]^4}{[Cu(NH_3)_4^{2+}]} \;.$$
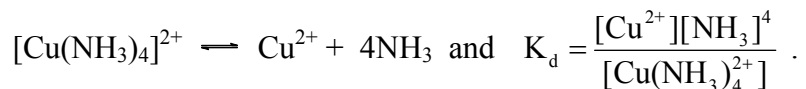
The concentration of uncomplexed [Cu^{2+}] is calculated using the Nernst equation. The copper ion concentration should be quite small, meaning that most of the copper is in the metal complex ion form. Therefore the concentration of the metal complex ion should, to a good approximation, be equal to 0.05M (the same as the initial concentration of the copper (II) ion in the second voltaic cell before it forms a complex with ammonia). The concentration of ammonia at equilibrium is not its initial concentration in the second voltaic cell.

What is the concentration of ammonia in equilibrium with copper (II) ion and the metal complex ion? It is not the original 3.5 M. Consider the reaction for the formation of the copper (II) complex ion:

$$Cu^{2+} + 4NH_3 \;\rightleftharpoons\; [Cu(NH_3)_4]^{2+}$$

We are assuming that most of the copper (II) ion reacts and forms the metal complex ion. This results in the concentration of the metal complex ion as approximately 0.05 M. Using the stoichiometry of this reaction, calculate the approximate concentration of ammonia remaining.

Based on the previous calculations we know the concentrations of ammonia, copper (II) ions and the copper (II) complex ion at equilibrium. Substitute these values into the K_d expression and solve for its value. Compare your calculated value of K_d with the literature value of 1.47×10^{-13}.

VII. Determining the Solubility Product Constant of Silver Chloride—Part C

Principles: *Review the following principles and experimental procedures before starting this section of the experiment. Then develop a format for recording experimental procedures, voltaic cell design and set-up, and data.*

1. A **concentration cell** uses the **same two half-reactions**, but one is an oxidation half-reaction and the other is a reduction half-reaction, and the concentrations of the ions are different in the cathode and anode.
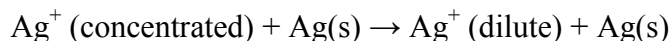
Procedures for Part C:

Set up the following voltaic cell and measure its cell potential:

$$Ag|\ Ag^+\ (0.10\ M)||\ Ag^+(0.10M)|\ Ag$$
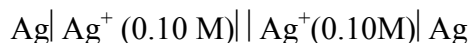
Record the anode and cathode and the cell potential.

The redox reaction that determines the voltaic cell potential is:

$$Ag^+\ (concentrated) + Ag(s) \rightarrow Ag^+\ (dilute) + Ag(s)$$

The direction of the reaction is always from the more concentrated form to the more dilute form.   In this cell the concentrations are the same. What is the value of Q for the redox reaction? What does this mean for E_{cell} and E^o_{cell} ?

2. Prepare a new voltaic cell in which an eye dropper has a 0.10 M KCl   solution (about 2/3 full) and the other is the Ag^+/Ag half-cell. Before using the eye dropper with KCl, add one drop of 0.1 M $AgNO_3$ solution to the KCl   solution and mix thoroughly by inverting the dropper several times.   You   should observe a very faint white color of AgCl(s). Insert a silver electrode into this   mixture and complete the voltaic cell:

$$Ag|\ Ag^+\ (x\ M),\ AgCl(s)||\ Ag^+(0.10M)|\ Ag$$
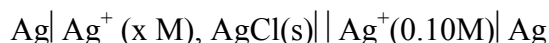
 Measure the voltaic cell potential. Record the anode and cathode and the cell potential.

VIII.   Laboratory Report Part C   continuing from Part B

7. Copy of laboratory data for Part C
8. Prepare Tables IX and X in a typed format.

Table IX   Descriptive Title

Cell	E_{cell}	E^o_{cell}
Ag|Ag$^+$(0.10M)|| Ag$^+$(0.10M)|Ag		
Ag|Ag$^+$(x M),AgCl(s) || Ag$^+$(0.10M)|Ag		///////////////

Table X. Descriptive Title

	[Ag$^+$], M	K_{sp}	E_{cell}
Experimental			
Theoretical		1.8×10^{-10}	
% Error	///////////////		

sample calculations follow each table.

Instructions for calculating requested data in Tables IX and X:

The second voltaic cell prepared in this section is known as a concentration cell. The redox reaction occurs in the direction to make the concentrations of the silver ions in each half-cell the same. E^o for this cell (or any concentration cell) is exactly 0 V. The Nernst equation for this concentration cell takes the form:

$$E = 0 - \frac{0.0592}{n} \log \frac{[Ag^+]_d}{[Ag^+]_c}$$

where c = concentrated solution and d = diluted solution.

Determine the value of Q in the Nernst equation. Use the it to calculate the concentration of silver (I) ion [the more dilute condition] in equilibrium with AgCl. The approximate value of the [Cl⁻] in equilibrium with the solid silver chloride is 0.10 M, assuming that one drop of the silver nitrate solution does not react with an appreciable fraction of Cl⁻. Substitute this value of [Cl⁻] and the calculated value of [Ag⁺] into the solubility product expression for AgCl.
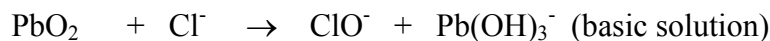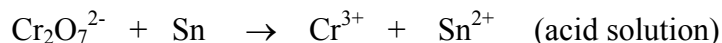
$$K_{sp} = [Ag^+][Cl^-]$$

Compare the calculated value of K_{sp} with the literature value of 1.8×10^{-10}.

Assume in an ideal saturated solution that the silver (I) ion concentration is 1.8×10^{-9} M in the presence of 0.10 M chloride ion and solid AgCl. Calculate the cell potential. Compare this value to the one you measured. Calculate the % error.

IX. Pre-Lab:

1. Balance the following oxidation-reduction reactions by the half cell method:

    $Cr_2O_7^{2-} + Sn \rightarrow Cr^{3+} + Sn^{2+}$ (acid solution)

    $PbO_2 + Cl^- \rightarrow ClO^- + Pb(OH)_3^-$ (basic solution)

2. Write the half-cell reactions associated with the following oxidation-reduction reaction:

    $Ni(s) + Hg_2^{2+}(aq) \rightarrow 2Hg(l) + Ni^{2+}(aq)$
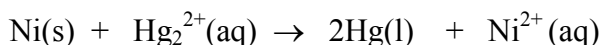
    a) Draw and describe how you would construct a voltaic cell to study this reaction.

b) If the reaction occurs spontaneously in the cell, which electrode is the anode? Explain.

c) Calculate the standard cell potential, E^o.

d) Does the cell potential change if the reaction were written for two moles of Ni(s) reacting? Write the redox reaction using a factor of two moles and answer the question using the Nernst equation. Explain

e) If the cell potential as measured is 1.04 volts, what would be the reduction potential associated with the Ni^{2+}/Ni reaction if the Hg/Hg_2^{2+} half-cell is assigned a potential of 0.00 V? Repeat the question: if the Hg/Hg_2^{2+} half-cell is assigned a reduction potential of -0.80 volts?

Practice with Balancing Redox Reactions
(NOT PART OF PRELAB)

These are not required and are provided for you to practice balancing redox reactions. No answers are provided. However, you can always show the correctness of your balanced redox reaction by checking that (1) the number of atoms of each type are the same on both sides of the equation and (2) the sum of charges are the same on both sides of the equation [Don't forget to include in your calculations the stoichiometric coefficients in front of substances] Both (1) and (2) must be true for the redox reaction to be correctly balanced.

1. HNO_3 + S → NO_2 + H_2SO_4

2. $CrCl_3$ + MnO_2 → $MnCl_2$ + H_2CrO_4

3. $KMnO_4$ + HCl + H_2S → KCl + $MnCl_2$ + S

4. KOH + MnO_2 + $KClO_3$ → K_2MnO_4 + KCl

5. NaCl + H_2SO_4 + MnO_2 → Na_2SO_4 + $MnSO_4$ + Cl_2

6. HNO_3 + I_2 → NO + HIO

7. $FeSO_4$ + H_2SO_4 + HNO_3 → $Fe_2(SO_4)_3$ + NO

8. $Bi(OH)_3$ + K_2SnO_2 → Bi + K_2SnO_3

9. $Mn(NO_3)_2$ + PbO_2 + HNO_3 → $HMnO_4$ + $Pb(NO_3)_2$

10. AsO_3^{3-} + I_2 → AsO_4^{3-} + I^- (basic)

Experiment 11
Sulfide Separations

I.   Objective:

To separate and identify copper, bismuth, cobalt, iron and nickel ions in a solution.

II.   Chemical Principles:

Some metal ions can be separated based on the solubility of their sulfide salts in acid or base conditions. In this experiment we use sulfide ions formed in the equilibrium of H_2S with water to react with metal ions to form metal sulfide precipitates. We continuously generate $H_2S(g)$ by heating thioacetamide in water to create a saturated H_2S solution:

$$CH_3CSNH_2 + 2\ H_2O(l) \xrightarrow{heat} CH_3COOH + NH_3 + H_2S(g) \qquad (1)$$

A saturated solution of H_2S has a H_2S concentration of approximately 0.10 M

The overall equilibrium established in a saturated H_2S solution is pH dependent:

$$H_2S \rightleftharpoons 2H^+ + S^{2-} \qquad K_{overall} = 1.3x10^{-20}$$
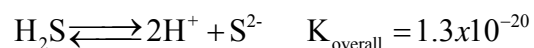
III. Laboratory Procedures:

Thioacetamide is kept in the hood with organic substances. H_2S is toxic. When heating a thioacetamide solution keep it under a hood at all times. Put all waste in the appropriate containers.

You will do all procedures first with a known sample containing all five metal ions and then with an unknown.

Read the instructions for experimental procedures before starting and develop a format in your laboratory notebook for maintaining a complete and detailed record of experimental procedures and observations. There are nine problems associated with different parts of the experiment. You answer these when you do your laboratory report.

1. Place 6 drops of your solution (known or unknown) into a casserole. Add 2 drops of 3% hydrogen peroxide (H_2O_2) and 2 drops of 2M HCl. Heat to reduce the volume to 1-2 drops. Allow the solution to cool. Add 6 drops of 6M HCl and again heat to reduce the volume of the solution. Do not heat to dryness.

2. Add 4 drops of 2M HCl to dissolve all of the residue in procedure (1). Transfer the solution into a test tube. Add 4 drops of 1 M thioacetamide. Mix well and heat in a hot water bath under a hood for about 4 min. Add 8 drops of hot water, 8 drops of 1 M thioacetamide and 1 drop of 1M ammonium acetate ($NH_4C_2H_3O_2$). Adjust the pH to 2-3. Minimize dilution of the solution during adjustment of pH. Heat the mixture for another 4 min. Centrifuge and decant the supernatant liquid into another test tube. Save the decantate for procedure (3) and the solid for procedure (4).

Problem 1: a. What ions are present in the decantate?
  b. What compounds are present in the precipitate?

3. Test the decantate for completeness of precipitation by adding 2 drops of 1M thioacetamide. Mix well and allow it to stand for about 1 min. If more precipitate forms, add 2 drops of water and 2 more drops of 1M thioacetamide. Mix and heat for 2 min. Centrifuge and decant. When the test shows that no more precipitation occurs, transfer the decantate to a casserole. Boil the decantate for ~ 1 min. There should be about 8-10 drops. It contains three ions that will be identified later in the experiment. Save this solution for procedure (9).

4. Use the precipitates that you collected in the previous two procedures. Wash the precipitate three times, once with 10 drops of hot water and twice with 20 drops (made of 10 drops of hot water and 10 drops of ammonium acetate mixed together). Be sure to stir the solid into the liquid each time. Centrifuge and decant after each wash. Do not save the wash solutions.

Problem 2 : One of the solids that you washed is bismuth sulfide. What is the concentration of the bismuth and the sulfide ion in equilibrium with the solid bismuth sulfide in aqueous solution?

Water insoluble salts of a weak acid generally dissolve in a strong acid. However, the solubility of most insoluble metal sulfides is so very small that not even a strong acid causes them to effectively go into solution. Therefore, to dissolve bismuth sulfide and copper sulfide, the oxidizing acid, HNO_3, must be used. CuS(s) will dissolve according to the following unbalanced oxidation-reduction equation:

$$CuS(s) \;+\; HNO_3 \;\rightarrow\; Cu(NO_3)_2 \;+\; S(s) \;+\; NO(g) \;+\; H_2O(l) \qquad (3)$$
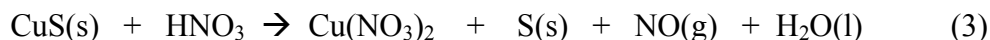
Problem 3: What are the two half reactions?

Oxidation:

Reduction:

Write the overall balanced redox equation.

5. Add 15 drops of 3M HNO$_3$ to the test tube containing the washed precipitate in procedure (4). Mix thoroughly. Transfer the mixture to a casserole and boil gently for ~ 1 min. Keep adding nitric acid and boiling until all the black solid has dissolved. Do not let it go to dryness. This process can take 10 to 20 minutes After the black solid dissolves sometimes there is a solid of a different color remaining. It will not dissolve in the nitric acid. Centrifuge the solution and decant into a test tube. Save the decantate for procedure (6).

Problem 4:
  a. What ions are in the decantate?
  b. What color is the solid that sometimes remains?
  c. What substance makes up the solid? (Look at equation (3) for help!)

6. To the decantate from procedure (5), add 15M NH$_3$, drop wise with constant stirring. Using pH paper to ensure that the solution is distinctly basic.. Stir for ~ 2 min. If a precipitate does not form immediately, wait for at least five more minutes. Centrifuge and decant. Save the decantate for procedure (8).

Problem 5:
  a. What complex ion is in the decantate? What is its color?
  b. Write an equation showing how this complex ion forms.

7. Wash the precipitate remaining in procedure from procedure (6) twice with 15 drops of hot water. Centrifuge and decant.

  To the precipitate, add 3 drops of 8M NaOH and 2 drops of 0.2M SnCl$_2$ and stir. A jet-black precipitate (Bi) proves the presence of bismuth.

  The formation of the black precipitate forms when [Sn(OH)$_4$]$^{2-}$ reacts with the white precipitate, bismuth hydroxide.

  2Bi(OH)$_3$(s) + 3[Sn(OH)$_4$]$^{2-}$ → 2Bi(s) + 3 [Sn(OH)$_6$]$^{2-}$ (4)
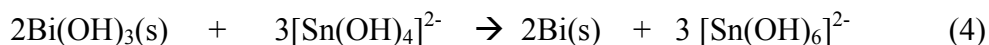
8. The decantate remaining from procedure (6) will be blue in color if [Cu(NH$_3$)$_4$]$^{2+}$ is present. Even if you observe a color, it is wise to verify copper. Place 5 drops of the decantate into a test tube, add 5M acetic acid until the solution is decolorized, and then add 2 drops of 0.2M K$_4$Fe(CN)$_6$. A red precipitate, [Cu$_2$Fe(CN)$_6$], confirms the presence of copper.

Problem 6:
  a. What is the role of the acetic acid? (No, it doesn't just decolorize the solution. It actually enters into a reaction!!) Write this reaction.

9. The decantate that you saved in procedure (3) should be ~ 8-10 drops. Transfer the solution to a test tube, centrifuge to remove any solid particles that may remain and decant. Discard any solid. To identify iron, cobalt, and nickel, separate samples of the same solution will be used. They will not be separated from each other, but will be identified in the presence of each other. That means that some ions will need to be suppressed so that the ion in question can be detected.

10. Separate the solution into three separate test tubes.

   a. *Test for Iron.*
      To one portion, add 1-2 drops of 0.2M KSCN and 1-2 drops of hydrogen peroxide. A blood red solution, $[Fe(SCN)]^{2+}$, proves the presence of iron.

Problem 7:
   a. What is the function of hydrogen peroxide in this reaction? Write an equation to show its function.
   b. Write a reaction showing the formation of the complex ion, $[Fe(SCN)]^{2+}$.

   b. *Test for Cobalt.*
      To a second portion of the solution, add enough solid NaF to form a saturated solution. Mix well by stirring. Then add 10-20 drops of a saturated solution of NH_4SCN in ethanol (excess is needed). A blue solution, $[Co(SCN)_4]^{2-}$, proves the presence of cobalt.

Problem 8:
   a. What is the role of NaF in this reaction? Why do you add it as a solid rather than as a 0.1 M solution? Iron (III) forms a complex ion:

   $$Fe^{3+} + 6F^- \rightarrow [FeF_6]^{3-}$$
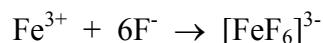
   b. Write an equation showing the formation of the complex ion, $[Co(SCN)_4]^{2-}$.

   c. *Test for Nickel.*
      To a third portion of the solution, add 5M NH_3 to make it basic. If a precipitate of $Fe(OH)_3$ forms, centrifuge and decant. To the clear decantate, add 2-3 drops of dimethylglyoxime and mix thoroughly. Allow the solution to stand ~ 1 min. A strawberry red precipitate, $[Ni(C_8H_{14}N_4O_4)]$, proves the presence of nickel.

      Iron (II) also reacts with the dimethylglyoxime, but the red compound is soluble in water, rather than a precipitate.

Problem 9:

> What is the **formula and structure of the nickel complex** of dimethylglyoxime? You may find this in your textbook. If not, look for it on the internet. It is an example of a coordination compound.

Pre-Lab:

1. All five metal ions are present in a solution and each is at a concentration of 0.10 M. Calculate the pH required to cause the two least soluble metal sulfides to precipitate completely without precipitating any of the remaining three ions. Strategy: To begin this problem, determine for each metal ion the concentration of sulfide ions required to precipitate it. Then, determine which two of the metal sulfides will precipitate first upon addition of sulfide ion. Determine the maximum amount of sulfide that can be added to precipitate these two ions without precipitating the other three ions. Use that amount of sulfide in Equation (2) to determine the pH.

2. (a) If $[H^+]$ of a saturated H_2S solution is increased by adding HCl, in what direction does equation (2) proceed and why? (b) How does this affect the sulfide concentration? (b) Develop a general statement that summarizes how a change in pH of a saturated H_2S solution affects the concentration of sulfide ions. (c) Ammonium acetate is be used in washing precipitates because it decreases pH of a solution. Explain how this occurs.

IV. **Laboratory Report:**

Your laboratory report must be submitted on the day the unknown is completed. It does not need to be typewritten, except for the title page.

1. The title page should include your name, the unknown number, and what ions are in the unknown.
2. Pre-lab and all corrections to pre-lab
3. Submit all pages from your laboratory notebook. On one of the laboratory pages state the logic you used to determine the ions in your unknown.
4. Answer the nine problems on separate, lined paper. Write the question first and then your answer.

Experiment 12
Separation and Identification of Some Cations Using Paper Chromatography

I. Objective: To learn the principles of paper chromatography and apply them to the separation and identification of four transition metal ions, iron (III), nickel (II), cobalt (II), and copper (II). A known solution of the cations will be studied and then the cations in three unknowns will be identified.

II. Chemical Principles:

In prior experiments you have learned how to separate and identify ions by using selective precipitation techniques, observing colors of ions, and using flame tests. You have probably observed that there are variabilities in chemical reactions depending on the conditions and generally there is no unique qualitative test for each cation or anion. Often the separation techniques are not as effective as desired; for example, using small volumes can lead to precipitates that are hard to characterize.

There is another experimental technique available to separate ions called chromatography. The principles are fairly simple and involve selective adsorption of solute species on a solid phase. Let's explore this in more detail. Consider a solution made up of a solvent and two solutes, which will be given the symbols "x" and "o". The two solutes will have differing physical properties, including the tendency to adsorb (attach to the surface) of another substance. The solvent will also have a tendency to adsorb and this must be considered when choosing the adsorbing substance, the stationary phase.

If the mixture is permitted to slowly move over the surface of the stationary phase, a separation will begin to occur because the solutes will have different affinities for the chemical substances making up the stationary phase. Thus as the mixture moves over the surface of the stationary phase one of the solutes, say x, will be more strongly adsorbed than the other solute, o. We can also say that o has a greater affinity for the moving phase than x.

What happens with increasing distance along the stationary phase as the mobile phase moves? The solute x will tend to become bonded to the surface of the stationary phase since it has a higher affinity for it. As x becomes removed from the solution the solute o no longer has to compete with x for the surface of the stationary phase and it will more effectively bond to the surface. Solutes that more strongly bind to the stationary phase are removed more quickly from the solution. This leads to separation of the two solutes and results from a differential rate of migration. A picture of how the two solutes separating might look like the following diagram:

Direction of solution flow across surface of stationary phase $\rightarrow$

---

xxxxxx	*ooooooo*	
xxxxxxx	*o ooo ooooo*	*Paper is wet. Solution is*
xxxxx xx x	*o ooooooooo*	*moving along the paper.*

Distance along surface of stationary phase $\rightarrow$

Notice that the solute species do not all adsorb at the same location; there is a distribution in a localized region.

If the solvent is removed from that stationary phase then the *x*'s and *o*'s will remain in their positions. They are separated and, with the right indicator, they can be identified.

For this chromatography experiment we will use a stationary phase that is based on using cellulose, an organic compound that contains a large number of hydroxyl (-OH) groups. Water is strongly attracted to hydroxyl groups and forms the stationary phase, which is a highly polar surface. Paper is made from cellulose; thus, this stationary phase technique is referred to as paper chromatography.

The experiment is designed so that the mobile phase (solvent and solutes) moves through the paper by capillary action. This is achieved by having the chromatography paper stand in a solution of the mobile phase. The mobile phase will rise in the chromatography paper; capillary attractive forces cause this effect. As the solution rises, the solutes will continually move between the mobile phase and stationary phase, with the more strongly adsorbing solutes not rising as far as the more weakly adsorbing solutes. If a solute spends most of its time in the mobile phase it will be adsorbed far from the starting point. *Water molecules form the stationary phase and thus polar solutes will be more strongly attracted to this surface than non polar ones*.

When the mobile phase reaches a predetermined height, the chromatography paper is carefully removed from the mobile phase and the solvent is removed, usually by evaporation. After the chromatography paper is dry it is sprayed with an indicator to determine the location of the solutes. The solutes react with the indicator to form colored spots. Each solute will have a different retention factor, R_f, which is determined by measuring the distance the solute travels and the distance the mobile phase travels:

$$R_f = \frac{\text{distance traveled by solute}}{\text{distance traveled by mobile phase (solvent)}}$$

The experiment is designed so that a known solution and the unknown solutions are run using the same chromatography paper and under the same conditions. Spots having the same retention factors in the known and unknown solution are probably identical species; thus, the identity of the unknown can be determined.

The separation of Fe(III), Cu(II), Co(II), and Ni(II) or, $[Fe(H_2O)_6]^{3+}$ (yellow), $[Cu(H_2O)_4]^{2+}$ (blue), $[Co(H_2O)_6]^{2+}$ (pink), and $[Ni(H_2O)_6]^{2+}$(green), requires a solvent that causes the four metal ions to have differing physical properties and thus differing adsorbing characteristics on wet cellulose. For this experiment a mixed solvent of water, acetone and HCl is used to create different metal complexes which have differing affinities for the stationary phase of water.

HCl is added to the solution to produce metal chloro complexes such as MCl_3^- and MCl_4^- or metal chloride compounds such as MCl_2 or MCl_3 These metal-chloro species are more strongly attracted to the acetone molecules in the mobile phase than are the other solvated ions. Thus the metal-chloro complexes move more readily in the mobile phase with increasing acetone concentration compared to $[M(H_2O)_x]^{n+}$ complexes. By varying the ratio of HCl to acetone it is possible to change retention values and thus allow optimization of conditions for separation.

III. **Experimental Procedures;**

Two people will work together on this experiment. Two chromatography papers are prepared and each is developed in a different solvent system.

A. Preparation of the Chromatography Paper.
   Note: To carry the paper, use the corners only. The oil on your hands or tongs will make large marks that will disturb your chromatogram. Use gloves in preparing the chromatography paper and when spotting.
   A cellulose based paper designed for chromatography separations is used. Take a sample of the paper that is approximately 11 x 24 cm and draw, with a pencil, a line parallel to the long edge about 2 cm from the edge. Next, place 8/9 small x's about 2.5 cm apart along the pencil line, leaving about 3 cm of space at each end.

B. Spotting the Chromatography Paper.
   Place the paper on another piece of clean paper such as a paper towel. Next, starting in the left corner of the chromatography paper at the first "x", place a tiny spot of each of the four metal ion solutions using a small glass capillary. You do not want the spots large than about 3-4 mm. Continue and spot the fifth "x" with the solution containing all four metal ions, and then the last three "x" 's are spotted with your three unknown solutions. Be sure to record the order of the metal ions and unknowns. Let the paper dry and then repeat this process. Depending on the concentration of the known ions, the numbers of drops necessary will vary.

   The chromatography paper and spots of solutions must be dry before you proceed to the next step.

C. Developing the Chromatography Paper.
Carefully form the paper into a cylinder by stapling the edges and leaving a gap of approximately 0.5 cm between the edges. Fresh solvent is very important in this experiment. Student 1 will mix 10.0 mL of 6M HCl and 35 mL of acetone while student 2 will mix 20 mL of 6M HCl and 25 mL of acetone. Place the solvent in a clean, dry 1000 mL beaker. Cover the beaker with plastic wrap and put in place with a rubber band. Next, place the cylinder in the chromatography chamber.

The paper must not touch the walls of the beaker. Also, the level of the solvent mixture must be below the level of the spots. Quickly seal the chromatography chamber with the plastic wrap and use a rubber band to tightly keep the plastic wrap in place. The solvent will slowly rise in the chromatography paper. Let it rise until it is about 1 cm from the top. This will take 15-35 min. Do not let the solvent rise completely to the top. If this happens, you must repeat the preparation of the chromatography paper and spotting it.

When the solvent has risen to within 1 cm of the top, quickly remove the paper and draw a pencil mark along the solvent front. This must be done immediately before the solvent evaporates. The paper must be dry before spraying with the indicator or determining retention values. Two hoods have been prepared for drying the chromatography paper using a heat gun. Attach the chromatography to the appropriate support and carefully dry it with the heat gun. Do not bring the heat gun too close to the paper or it will char the paper and ruin your experiment. This should take only a few minutes.

D. Indicators.
Before applying an indicator, record the locations and colors of any visible spots. Then, carefully in a hood, spray the chromatography paper with 6 M NH_3. You should thoroughly moisten the paper but do not cause it to be dripping wet. Do not turn your paper to the side. The spots will run.

Note the location and color of any spots while the paper is still wet. Be careful when handling the paper because it has been sprayed with a base. Use tongs to carry the paper. If a white substance forms on the paper, it is ammonium chloride and indicates that the paper was not sufficiently dry.

After the paper is completely dry, spray the paper with a Na_2S solution and record the color of each spot. Because nickel does not show up very well, you will need to spray the paper more than one time particularly where you suspect nickel should appear.

E. <u>Determine Retention Values.</u>

It is likely that each spot on a paper chromatogram is not uniform in size or small; thus it is necessary to estimate the central location. Try to find the darkest area that is central to the spot and draw a pencil line through it. Measure the distance from the initial spot to this line. Repeat this measurement for the mobile phase front. Calculate the retention value for each spot.

F. <u>Identify Cations in Unknowns.</u>

Use the calculated retention values both for the standard solutions and the unknowns, and the color of spots and their intensities, to determine which cations are in each unknown.

Safety: The organic solvent, acetone, is flammable and no open flames are permitted in the laboratory.
Ammonia gas is irritating to your lungs and skin and should be used in the hood.
Sodium Sulfide is corrosive to skin and can affect mucous membranes.
Dispose of all solutions in the appropriate waste containers.

IV. **Laboratory Report (4-7 are to be typed):**

1. Title page with letters for the three unknowns and ions found for each.
2. Data sheets from your laboratory notebook. You should have recorded all procedures in detail, as done, observations during each phase of the preparation of the chromatography paper and results after each spraying. Be sure to label and identify all spots, and the colors and characteristics of the ions on the chromatogram; record in your lab notebook. You should record the positions of each spot and the distance moved from the reference line for all solutes and solvent. Be sure to label steps within procedures, tables and pictures.
3. Attach paper chromatograms sealed in saran wrap.
4. Prepare two tables, one for each solvent system, which summarizes the following data;

Metal Ion/Unknown	R_f Value	Metal Ion(s) Present
Co(II)		--------------------
Cu(II)		--------------------
Fe(III)		--------------------
Ni(II)		--------------------
Unknown #____		
Unknown #____		
Unknown #____		

Show a sample calculation for an R_f value.

5. Compare the R_f values using the two different solvent systems.

Metal Ion	R_f Value (C-1)	R_f Value (C-2)
Co(II)		
Cu(II)		
Fe(III)		
Ni(II)		

Summarize your findings. For example, which indicator helped you the most in identifying the unknown ions and why? In which solvent did the solutes move faster? In which solvent are the ions further apart? If you had to choose only one solvent system for separating and identifying the metal ions, which one and why?

Note: Always give identifying titles to all tables.

6. Questions:
   a. You used a pencil to mark the chromatography paper since the carbon in the "lead" pencil does not dissolve in the solute. Why does carbon not dissolve? What type of pen (ink) will also not produce a chromatogram when water is used as the solvent? Explain using principles based of the polarity of particles.
   b. You are to minimize hand contact with the paper since amino acids, oils, etc. on your skin will form a smudge on the cellulose paper. Why will using a corroded tweezers also cause a smudge when sodium sulfide is sprayed on the paper?
   c. What type of complexes appears when the spots are sprayed with ammonia and why do new colors appear?
   d. What type of substances appear when the spots are sprayed with sodium sulfide and why do new colors appear?
   e. Which ion is the most mobile in the two solvent systems and explain why based on the information in the introduction.

7. Look up chromatography in an organic chemistry book, on the Internet, or use another source. What are some of the things that are separated regularly by different methods of chromatography? Give specific references, one of which is not an internet resource.

V. Pre-Lab:

Read through the entire experiment and be prepared to do the experiment. Bring a ruler to class to prepare tables.

Experiment 13
Synthesis and Characterization of Cis- and Trans- $K[Cr(H_2O)_2(C_2O_4)_2]$

I. **Objective:**

To prepare the cis- and trans- isomers of $K[Cr(H_2O)_2(C_2O_4)_2]$ and study some of their properties.

II. **Chemical Principles:**

A. Isomerism

Many coordination complexes exhibit isomerism. When two or more structures have the same number of atoms and the same molecular formula but different physical and chemical properties, the structures are said to be isomers. There are two principal types of coordination isomerism: structural (also known as constitutional) isomerism and stereoisomerism. Stereoisomers differ only in the spatial arrangement of the ligands around the central atom, whereas structural isomers can differ from each other in various ways.

Structural isomerism includes the following example: a complex cation and anion may have a reversal of the metal sites; $[Co(NH_3)_6][Cr(CN)_6]$ and its isomer $[Cr(NH_3)_6][Co(CN)_6]$. Ionization isomerism results when an ion in a coordination site is switched with an anion not in a coordination site, e.g., the coordinated Br^- is switched with the uncoordinated SO_4^{2-} in $[Co(NH_3)_5Br]SO_4$ to form the isomer $[Co(NH_3)_5SO_4]Br$. Linkage isomerism occurs when a ligand can coordinate to the central atom in more than one way. NO_2^- can coordinate either through an oxygen atom (M-ONO) or the nitrogen atom (M-NO$_2$); $[(NH_3)_5Co(-NO_2)]Cl_2$ and $(NH_3)_5Co(-ONO)]Cl_2$. Therefore, structural isomers are all isomeric forms other than stereoisomers. In this experiment we will study geometric isomers; cis and trans.

Alfred Werner postulated in his coordination theory that the ligands surrounding a central atom would be oriented in different ways to lead to regular geometric patterns. For example, a complex with six ligands would have the ligands oriented about the central atom to produce an octahedral environment. If the octahedral complex is of the MA_4B_2 type, where A and B are both monodentate ligands, then two stereoisomers (geometric) can exist; cis and trans forms. An example is $[Cr(NH_3)_4Cl_2]^+$. The cis isomer has the two chlorides adjacent to each other, while in the trans isomer, the two chlorides are opposite to one another. In this experiment, you will synthesize and study the properties of cis and trans $K[Cr(H_2O)_2(C_2O_4)_2]$. In this compound, one ligand is monodentate (H_2O) while the other ligand, $C_2O_4^{2-}$, the oxalate ion, is a bidentate ligand coordinating to the chromium through two oxygen atoms (those two oxygen atoms which carry a charge).
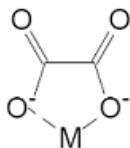
Oxalate ion acting as a bidendate ligand.

B. Spectroscopy

In this experiment you will use the Bausch and Lomb Spectronic 20.

Practically all of us at one time or another have looked at a cup of coffee or tea and noted that it is "strong" or "weak." We judge the strength of the brew by the intensity of the color and so it isn't surprising that scientists have learned how to connect, in a quantitative way, the concentration of a solution and its color. If you think carefully about your experience in correlating the strength of a beverage with the intensity of its color, you may also have noticed that the color appears darker when viewed down through a tall glass than when viewed directly through the narrow part of the glass. Thus, since prehistoric times, it has been well known that " the taller the glass or the stronger the brew, the less the amount of light that can get through."

Actually, there is a quite simple mathematical relationship for this observation called Beer's Law. It is.

$$A = \varepsilon l c$$

where **A** is the absorbance of the solution (a measure of the intensity of color), ε is a proportionality constant, **l** is the path length of light through the cell holding the solution, and **c** is the concentration. While **A** is dimensionless, usually **l** and **c** have dimension of cm and moles/liter, respectively. Beer's Law is named after the scientist A. Beer and has nothing to do with the well-known beverage of the same name.

A spectrophotometer is an instrument for conveniently measuring the absorbance of light of a definite color (wavelength) by a solution of some concentration c held in a cell of a convenient size...often a path length of 1.00 cm. Such a cell is called a cuvette. The essential parts of a spectrophotometer are shown here:
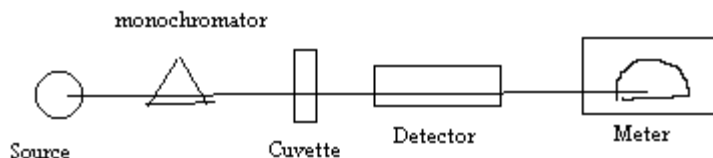
The instrument has five parts:
  1. A light source which produces light ranging in wavelength from about 375 - 650 nm.

2. A <u>monochromator</u> which functions to select light of a single wavelength monochromatic light) and send it to the cuvette with an intensity of I_o.
3. The <u>cuvette</u> or sample holder. After passing through the cell, the intensity of the light is reduced from I_o to I.
4. A <u>detector</u> measures the intensity of light falling upon it.
5. A <u>meter</u> calibrated in both absorbance A and percent transmission T

Percent transmission is defined as: $T = \dfrac{I}{I_o} \text{ x } 100$

while absorbance is defined as: $A = -\log_{10} \dfrac{I}{I_o}$.

Absorbance is more useful to us because it is a simple linear function of path length l and concentration c. That linear dependence is what we have already introduced as Beer's Law: $A = \varepsilon lc$.

III. <u>Experimental Procedures:</u>

Synthesis of cis and trans $K[Cr(H_2O)_2(C_2O_4)_2]$. Work in pairs. Use the hoods.

<u>Trans - $K[Cr(H_2O)_2(C_2O_4)_2].3H_2O$</u> MW = _____
Weight out 6 g of oxalic acid dihydrate and, separately, 3 g of $K_2Cr_2O_7$.
Dissolve 6 g of oxalic acid dihydrate in a minimum amount (5-10 mL) of boiling water in a 250-300 mL beaker. Dissolve 3 g of $K_2Cr_2O_7$ in 5 mL of boiling water in a 50 mL beaker. Slowly add the hot $K_2Cr_2O_7$ solution (Be Careful) to the oxalic acid, covering the beaker with a watch glass while the violent reaction proceeds. Evaporate the solution to near dryness (crust starts to form). Micro crystals should form; however, a thick brown syrup usually results, so add 20 mL of ethanol to the syrup. Transfer the mass, included the ethanol, to a mortar and grind until a slurry results. You should feel and see powdery grit in the slurry. Using a suction filter, filter off the solid and wash with a small amount of acetone.
<u>Both ethanol and acetone are flammable. Do not use if burners are in the room</u>.

<u>Cis- $K[Cr(H_2O)_2(C_2O_4)_2].2H_2O$</u> MW = _____
Do all grinding in the hood. Grind in a mortar 6 g of oxalic acid to a fine powder, set aside and clean the mortar by wiping with a Kimwipe. Grind in a mortar 2 g $K_2Cr_2O_7$ to a fine powder. Add the 6 g of ground oxalic acid dihydrate to the $K_2Cr_2O_7$ in the mortar and intimately mix. Place the mixture into a 6 in. diameter evaporating dish, place **two drops** of very hot water in a small depression in the mixture and cover the evaporating dish with a watch glass. After a few min., a vigorous reaction should occur with evolution of steam and CO_2. If a reaction does not begin, hold the evaporating dish and watch glass with tongs, and heat very gently on a hot plate until the reaction begins.

The product of the reaction is purple viscous liquid. To this purple liquid (syrup or bubble gum) add 20 mL of ethanol and stir the mixture until the product is crystalline. May do this with a mortar and pestle. If the crystalline product does not form, decant off the liquid, and repeat the process with a second portion of ethanol

until the product does crystallize. Filter off the crystalline product, wash with a small amount of acetone, and dry.

Experiments
a. Weigh the products and determine % yield. (Not done if you are given compound from previous semester)
b. Compare the solubility of the cis and trans isomers in water. Since these are very soluble complexes, use an equal amount of water in two different test tubes and add a small amount of the isomers to the two test tubes individually.
c. Test for the purity of the isomers. Place a few crystals of each isomer on their own filter paper. Add a few drops of 1M NH_3 to each crystal on the filter paper. The cis isomer will form a deep green solution, with no precipitate. The trans isomer will form a light brown solid. Attach filter papers inside your report.

Chromium Analysis
In order to analyze for Cr(III) using its absorption spectrum, it is first necessary to construct a calibration curve, using solutions containing known concentrations of Cr(III). For this purpose, the following standard solutions will be provided; 0.010, 0.020, 0.030, 0.040, and 0.050 M $Cr(NO_3)_3$. These give us the Cr in the form of $[Cr(H_2O)_6]^{3+}$.

Using a fixed wavelength of 575 nm, determine the absorbance of each of the five standard solutions. Plot a calibration curve of absorption versus concentration of Cr(III) on the computer. This will be a Beer's Law plot. The best fit line, by linear regression, should go through "0" since A = 0 when c = 0.
Make sure you put the equation for the line on the graph.

Sample Preparation
In order to use the spectrophotometric method of analysis of the synthesized chromium complexes, we need to obtain the chromium in aqueous solution as $[Cr(H_2O)_6]^{3+}$ as in the chromium (III) nitrate solutions.
This is done as follows:

Weigh out and record accurately, by difference, a sample of about 0.25 g of each of the Cr isomers synthesized. Transfer each sample completely to a 50 mL centrifuge tube. Add 4 mL of deionized water and 4 mL of a 10% KOH solution. Place the tube in a boiling water bath for 15 min. A green precipitate will form. What is that precipitate? At the end of the heating period, add an additional 10 mL of water to the tube, mix well with a stirring rod, and then centrifuge the hot mixture at least 2 minutes. Discard the clear supernatant liquid. Then wash the precipitate in the centrifuge tube by adding a 10 mL portion of hot water, mixing and dispersing the precipitate in the water with a stirring rod; then centrifuge again. Discard the clear supernatant wash water. Repeat the washing procedure once again. When the washing is complete, add 2.5 mL of concentrated HNO_3 to the precipitate in the centrifuge tube. Heat on a water bath until all of the green precipitate has dissolved. Allow the solution to cool. Dilute to 10 mL with distilled water and filter, catching the filtrate in a small beaker. (If you do not know how to use a filter funnel, please

consult your instructor.) Transfer the solution, completely, to a 25 mL volumetric flask. Make sure that all of the purple solution is completely transferred to the flask by rinsing the centrifuge tube and filter funnel with small portions of distilled water. Finally, make the solution up to volume in the 25 mL volumetric flask, and mix well. Measure the absorbance of the solution using a cuvette. Use the same wavelength used in preparing the calibration curve. From the straight line equation of the calibration curve, determine the concentration of Cr(III) in the solutions.

IV. <u>Laboratory Report:</u>
1. Title page.
2. Pre-lab with corrections to pre-lab.
3. Attach all laboratory notebook pages.
   This experiment has to be typed except for drawings and calculations, which are done by hand. Include all data, and data tables. Show all calculations clearly.
4. Questions:
   a. Draw the geometric structures for *cis* and *trans* $K[Cr(H_2O)_2(C_2O_4)_2]$ and name each isomer using the IUPAC nomenclature system.
   b. Is the *cis* or *trans* isomer more soluble in water? Do your results agree with the expected dipole moments of the complexes? Explain.
   c. When you tested the purity of the isomers, the products formed were isomers of $K_2[Cr(H_2O)(OH)(C_2O_4)_2]$. Draw the isomers and name them.

   d. Balance the following **redox** equation for the overall reaction which took place for the synthesis of these isomers. Show half reactions.

   $K_2Cr_2O_7 + H_2C_2O_4.2H_2O \rightarrow K[Cr(H_2O)_2(C_2O_4)_2] \bullet xH_2O + CO_2$

   where x = $2H_2O$ for cis and $3H_2O$ for trans.
   e. Calculate % yield. (Not done if your class did not synthesize the compounds.)

5. Chromium Analysis (show calculations with units included in each step):
   a. Comment on the plot of Absorbance versus wavelength (λ). For example, at what wavelength were the peaks observed? Which one are you using for your Beer's law plot and why?
   b. Use a computer graphing program to plot A vs. concentration to form a Beer's law plot. Provide title, and label all axes. Make sure you include regression equation on the graph.
   c. Determine absorptivity, ε, for $Cr(NO_3)_3$. Units for epsilon are $cm^{-1}M^{-1}$.
   d. Determine the concentration of Cr in each isomer using your experimental data. Use the information you developed in your Beer's law plot to make this determination. Show all calculations with units.
   f. Calculate the theoretical %Cr in each isomer. From corrected PreLab.
   g. Compare the theoretical and experimental values for **% Cr**. You calculated the theoretical values in the pre-lab section. Determine the

percent error for each isomer.　Comment on possible cause of errors. Notice this is **% Cr** in the sample, NOT % yield;　do not tell us you couldn't scrape off all the goo during synthesis.

h.　Summarize the above data in the following table:

Table: Title

	Absorbance	Cr　Concentration (Molarity)	%Cr (theor)	%Cr (expt)	% error
Cis					
Trans					

V. **Pre-Lab:**

1. Predict the number of isomers of $[Cr(en)_2Cl_2]^+$. Draw and name them. Remember "en" is a bidentate ligand, ethylenediamine, just as the oxalate ion is bidentate.
2. Square planar complexes, as well as octahedral complexes, can have isomers. Draw the possible isomers of the square planar complex, $[Cu(H_2O)_2(OH)_2]$. Name them.
3. Calculate the molar masses of the *cis* and *trans* isomers prepared in this experiment and the % Cr in each compound.

Experiment 14
Coordination Complexes of Co (III)

I. Objective:

To prepare a series of $[Co(NH_3)_5L]^{(3+n)+}$ complexes where $L = NH_3$, Cl^-, H_2O, NO_2^- and ONO^-. To conduct a systematic study on the effect of different ligands on the optical absorption spectra of $[Co(NH_3)_5L]^{(3+n)+}$.

II. Chemical Principles:

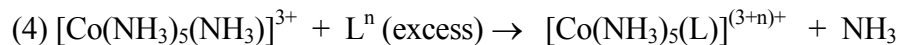### A. Cobalt (III) Complexes.

The cobalt (III) complexes in this experiment are initially prepared from $[Co(NH_3)_6]^{3+}$ which is formed in the presence cobalt (II) chloride with ammonia and hydrogen peroxide. The following standard electrode potentials indicate the favorability of the process:

Reduction Reaction	$E^o(V)$
(1) $H_2O_2 + 2e^- \rightarrow 2OH^-$	1.77
(2) $[Co(H_2O)_6]^{3+} + e^- \rightarrow [Co(H_2O)_6]^{2+}$	1.84
(3) $[Co(NH_3)_6]^{3+} + e^- \rightarrow [Co(NH_3)_6]^{2+}$	0.10

In the reaction hydrogen peroxide acts as an oxidizing agent, converting cobalt(II) to cobalt(III). The presence of ammonia ensures that $[Co(H_2O)_6]^{2+}$ is converted to $[Co(NH_3)_6]^{2+}$. Note that once the $[Co(NH_3)_6]^{2+}$ complex is formed in the presence of excess ammonia, the oxidation of Co(II) to Co(III) can occur easily, whereas if ammonia is not present, the oxidation is not favored. The presence of ammonia stabilized the formation of Co(III). $[Co(H_2O)_6]^{3+}$ is a strongly oxidizing complex and thus is not stable.

One of the ammines in the octahedral complex $[Co(NH_3)_6]^{3+}$ is more labile (easily

displaced) than the other five. This permits the synthesis of various pentaammine complexes by displacement reactions:

(4) $[Co(NH_3)_5(NH_3)]^{3+} + L^n$ (excess) $\rightarrow$ $[Co(NH_3)_5(L)]^{(3+n)+} + NH_3$

In the above reaction, L represents an incoming ligand and n the charge of the ligand.

Cobalt (III) pentaammine complexes are generally rather soluble in water; however, if an excess of HCl is present the chloride salts become insoluble. If only the counter ions H^+ and OH^- are present and the other starting materials are relatively pure, the resulting solid chloride salts are reasonably pure and further purification steps are not necessary.
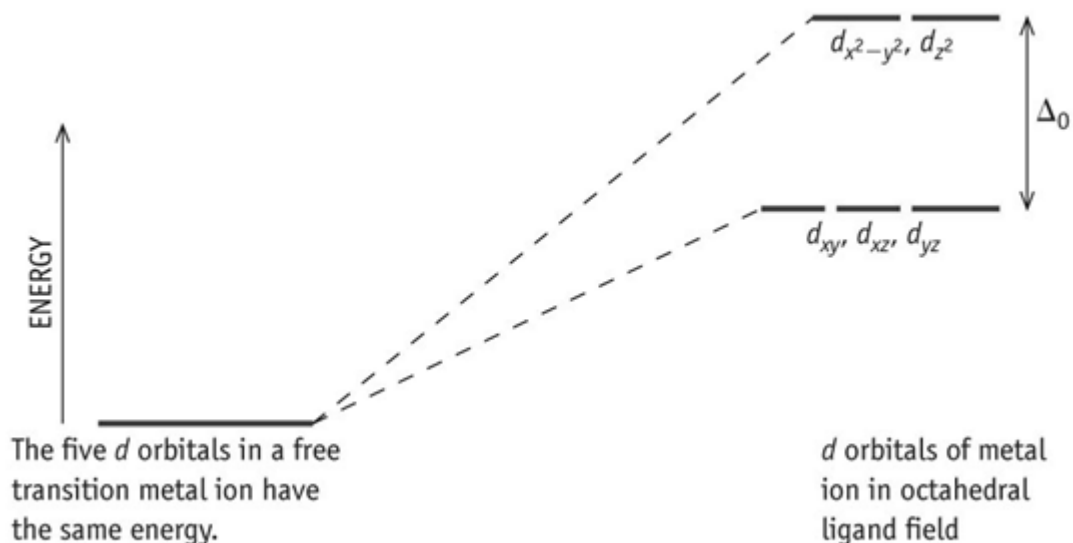
B. Optical Spectroscopy
   Origin of Spectra
   One of the goals of this experiment is to determine the effect of different ligands on the optical absorption spectra of $[Co(NH_3)_5(L)]^{n+}$

To understand why an effect exists, you need to understand the origin of electronic transitions involving d electrons in octahedral metal complexes. Transition elements are defined as those elements which have partly filled d orbitals in any of their common oxidation states. The d orbitals in an isolated transition element atom or ion are degenerate; i.e., have the same energy. However, in solution or in crystals, the metal ion is often surrounded symmetrically by six ligands and the d orbital energy is split by the electrostatic field of the ligands. The difference in energy is called Δ_o. According to the Crystal Field Theory, the five d orbitals are split into two energy levels :

Figure 1. Splitting of the d orbitals in an octahedral field.

$$d_{x^2-y^2}, d_{z^2}$$

$$\Delta_0$$

$$d_{xy}, d_{xz}, d_{yz}$$

ENERGY

The five *d* orbitals in a free
transition metal ion have
the same energy.

d orbitals of metal
ion in octahedral
ligand field

The upper set of two orbitals is designated as the e_g set of orbitals and the lower three orbitals are designated as the t_{2g} set of orbitals. Δ_o represents the energy difference between the higher energy e_g set of orbitals and the lower set of t_{2g} set of orbitals and is referred to as the crystal field splitting energy. The magnitude of Δ_o depends on the electrostatic interactions between the ligands and the d orbitals. If the value of Δ_o is relatively small compared to the energy required to pair electrons in the d orbitals, then electrons will fill both the t_{2g} and the e_g energy levels before pairing. This is said to be a <u>weak field</u>. If the energy required to pair electrons is less than Δ_o, then the d electrons will completely occupy the lower t_{2g} level (maximum of six) first before occupying the higher e_g set of orbitals. This is referred to as a <u>strong field</u>.

For example, there are two possibilities for a d^6 ion such as Co(III).

energy

e_g ↑   ↑
$d(x^2\text{-}y^2)$ dz^2 $\Big\}$ Δ_0 **small**

t_{2g} ↑↓   ↑$_{\Delta_o}$ ↑
d_{xy} d_{xz} d_{yz}

Paramagnetic

energy

e_g ___   ___
$d(x^2\text{-}y^2)$ $_{\Delta_o}$ dz^2 $\Big\}$ Δ_0 **large**

t_{2g} ↑↓   ↑↓   ↑↓
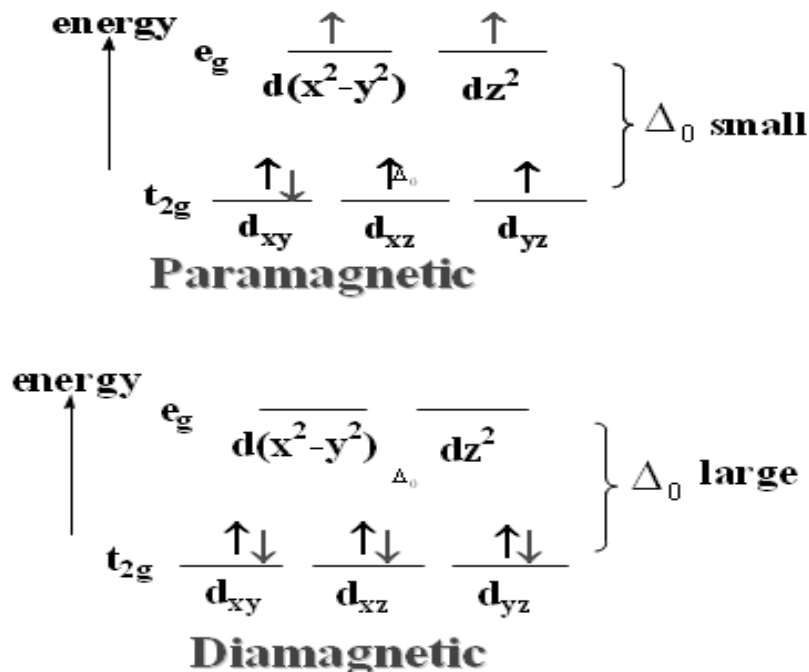d_{xy} d_{xz} d_{yz}

Diamagnetic

Figure 2

The paramagnetic case is an example of a weak field complex and the diamagnetic case is an example of a strong field complex.

One of the simplest transition element ions is Ti^{3+} which exists in aqueous solution as $[Ti(H_2O)_6]^{3+}$. It has only a single d electron and its ground state may conveniently be described as shown in Figure 3.

Figure 3. Aqueous Ti (III) ion in an Octahedral Field (Ground State)

___ ___ e_g

↑ ___ ___ t_{2g}
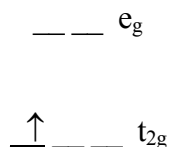
When light is directed at the ions in solution, some light is absorbed, and if the energy absorbed is equal to Δ_o, the single electron is excited from the t_{2g} to the e_g state as shown in Figure 4.

Figure 4. Aqueous Ti (III) ion in an Octahedral Field (excited state)

↑ ___ e_g

___ ___ ___ t_{2g}
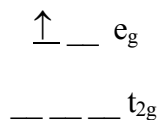
The energy of a photon of electromagnetic radiation is given by

$$\Delta_0 \; = \; E \; = \; h\nu \; = \; \frac{hc}{\lambda}$$

where:

      h = Planck's constant = 6.626×10^{-34} Jsec,
      c = the speed of light = 2.997×10^8 m/s,
      λ is wavelength in meters, and
      ν is frequency (s^{-1}).

Note the energy calculated using this equation is the energy associated with a single photon. **If you are interested in the energy/mole, then you must convert using Avogadro's number (6.02×10^{23} photons/mole) as a conversion factor.**

If $E = \Delta_o$, the light is absorbed at the corresponding wavelength, λ. The light absorbed by transition elements often lies in the visible region of the spectrum, which is consistent with our observation that transition metal compounds are often colored. Copper compounds may be blue, nickel compounds are frequently green, and iron compounds tend to be yellow, for example.

The spectrum of $[Ti(H_2O)_6]^{3+}$ is quite simple consisting of a single broad peak in the visible region of the spectrum. One would expect that other d^1 systems such as V^{4+} or Cr^{5+} would also exhibit similarly simple spectra.

The spectra of Co(III) complexes are more complicated. They possess a d^6 electron configuration and the repulsion energies between the d electrons influence the energies of the d orbitals. The overall result is that several different d-d electron transitions are possible, not just one. You will be measuring the visible spectra of $[Co(NH_3)_5(L)]^{(3+n)+}$ complexes in the 350-650 nm wavelength region. In the 400-650 nm wavelength region only one absorption peak with a measurable λ_{max} occurs, thereby simplifying the measurements and conclusions.

λ_{max} in the 400-650 nm wavelength range for a series of $[Co(NH_3)_5(L)]^{(3+n)+}$ complexes depends on the ligand L. Since $E \propto 1/\lambda$, we see that the shorter the wavelength the greater the energy separation between the d orbitals involved in the electronic transition (i.e., the greater the "crystal field" or ligand-metal electron repulsions.) By measuring λ_{max} for the series of Co(III) complexes you prepared, you can determine the relative impact of the ligands, L, on the crystal field. The ligand, then, can be placed into a series based on their strength of splitting and this is referred to as a spectrochemical series of ligands.

III. Experimental Procedures:

A. Synthesis.   You will prepare only one sample as needed.

1. **[Co(NH₃)₅Cl]Cl₂**   M.W. = _____

In a fume hood, add 5 g of ammonium chloride to 30 mL concentrated aqueous ammonia is a 125 mL Erlenmeyer flask. The combination of NH_4Cl and NH_3(aq) guarantees a large excess of the NH_3 ligand. Stir the ammonium chloride solution vigorously using a magnetic stirring plate while adding 10 g of finely divided $CoCl_2.6H_2O$ in small portions. Next, add 8 mL of 30% H_2O_2 to the brown cobalt slurry, using a buret that has been set up in the hood and filled by the laboratory instructor. An addition rate of about 2 drops per second is usually sufficient, but care should be taken to avoid excessive effervescence in this exothermic reaction. If the reaction shows signs of excess effervescence, turning off the magnetic stirrer momentarily will usually prevent overflow of the solution. When the effervescence has ceased, add 30 mL conc. HCl with continuous stirring, pouring about 1-2 mL at a time. At this point, the reaction may be removed from the hood. Use a Bunsen burner or hot plate to heat the solution to 60°C with occasional stirring. Hold the temperature between 55 - 65°C for 15 min.; this incubation period is necessary to allow complete displacement of all aqua ligands. Add 25 mL deionized water and allow the solution to cool to R.T. Collect the purple product by filtration through a Buchner funnel. Wash it with 10 mL cold deionized water and with 10 mL ice-cold 95% ethanol. (The solutions must be cold to prevent undue loss of product by redissolving). Transfer the product to a watch glass and allow it to dry until the next laboratory period.

Caution: 30% H_2O_2 is a strong oxidizing agent that will cause sever burns and bleaching of skin and clothing. Burets should only be filled by the lab instructor.

2. **[Co(NH₃)₅(H₂O)]Cl₃**. M.W. = _____

Place 2.5 g of compound #1, $[Co(NH_3)_5Cl]Cl_2$, in a 125 mL Erlenmeyer flask, and add 38 mL of 5% aqueous ammonia. Using aqueous ammonia as the solvent prevents displacement of the ammonia ligands. heat on a hot plate in the hood until the compound dissolves. Cool the solution to 10°C in an ice bath, then add a stirring bar, and place the flask on a magnetic stirring plate. Add conc. HCl drop wise with stirring until a reddish precipitate appears and a fog (ammonium chloride vapor) no longer forms above the solution. Under these conditions ligand exchange between $[Co(NH_3)_5Cl]^{2+}$ and $[Co(NH_3)_5(H_2O)]^{3+}$ is very rapid. The aquo complex is isolated by this procedure because it is much less soluble than is the chloro complex. Cool the reaction mixture to below 10°C and collect the product by filtration. Wash the reddish solid with 13 mL of 95% ethanol and allow it to air dry until the next lab period.

3. **[Co(NH₃)₅(ONO)]Cl₂** M.W. = _____

Dissolve 2.5 g of compound #1 in 38 mL of 10% aqueous ammonia in a 125 mL Erlenmeyer flask on a hot plate in the hood. Stir with a metal spatula. Cool the solution to about 10°C in an ice bath, then add 2.0 M HCl until the solution is neutral to litmus paper. The use of 2M HCl rather than conc. HCl dilutes the solution sufficiently that the aquo salt will not precipitate. Add 2.5 g sodium nitrite, followed by 2.5 mL of 6M HCl. Allow the reaction mixture to stand in an ice bath for at least an hour. Filter through a Buchner funnel, then wash the yellow-orange solid with 12.5 mL of ice cold water and 12.5 mL of cold 95% ethanol. Transfer the solid to a piece of filter paper and allow to air dry.

Note: This complex is not stable so will be refrigerated for later use.

4. **[Co(NH₃)₅(NO₂)]Cl₂** M.W. = _____

Dissolve 1.5 g of the nitrito complex, #3, in 15 mL of hot water containing 3.0 mL of concentrated aqueous ammonia. Cool the solution in an ice bath and add 15 mL of conc. HCl. Allow the mixture to stand in the ice bath until precipitation is complete. Collect the product by filtration through a Buchner funnel and wash the pale solid with 12.5 mL of cold 95% ethanol. Allow the product to air dry.

5. **[Co(NH₃)₆]Cl₃** M.W. = _____

Add 2.5 g of CoCl₂.6H₂O and 1.7 g of NH₄Cl to 15 mL water in a 125 mL Erlenmeyer flask. In the hood add 0.5 g activated charcoal and 23 mL concentrated aqueous ammonia. Cool the brown slurry in an ice bath to 0°C, then add 2.0 mL 30% H₂O₂ from a buret as described in the first synthesis. Do not allow the temperature to rise above 10°C. Heat the resulting red-brown solution to 60°C and maintain this temperature for about 30 min. The incubation is needed to ensure complete displacement of all aquo ligands. Cool the mixture to 0°C. The product will precipitate from the solution. Collect the product and the charcoal by filtration. Recrystallization is necessary to separate the product from the activated charcoal. Place the solid in a 125 mL Erlenmeyer flask and add 20 mL hot water and 0.5 mL concentrated HCl. Heat the mixture to 70°C and filter while still hot. Be careful! Place the filtrate in an ice bath and add 0.5 mL cold concentrated HCl. Collect the orange solid by filtration, wash with 12.5 mL ice cold 95% ethanol and allow to air dry.

B. Optical Measurements

1. Prepare approximately 1.00×10^{-2} M solutions of the cobalt complexes using 25.00 mL volumetric flasks. Record the actual mass and volume used. Calculate the experimental molarities.

2. Measure the absorbance (not % transmission) and wavelength of the Co (III) complexes from 350 to 625 nm. Do the ONO⁻ complex first since it is unstable in aqueous solution. Then, using five cuvettes (one for reference), four measurements can be made at each wavelength. The wavelength is then changed, the instrument re-zeroed,

and the four absorbances measured. This procedure is repeated until sufficient data is collected to plot smooth curves of absorbance, A, versus wavelength, λ. Measurements at 5 - 10 nm increments should give a smooth curve.

IV. <u>Laboratory Report (Items 4-7 are to be typed)</u> :

1. Title page.
2. Pre-lab questions with corrections.
3. Laboratory notebook data pages. For this experiment you must record all procedures and observations at each step in a synthesis in detail. Observations include all procedural steps as done, quantities and concentrations of chemicals used, characteristics of each solution, changes in characteristics of solution during synthesis and characteristics of final products.
4. A computer generated plot of A vs. λ for the five Co(III) complexes on the same graph. Use a different symbol for each complex when graphing the data. Include a Legend to identify each symbol on the graph. See Appendix 3.
5. Select the wavelength which has the highest absorbance (A) to use in the table. Calculate Energy, Δ_0, and the absorptivity (ε) at this wavelength. Prepare a table in the following format, listing the compounds **in decreasing order of Δ_o.**

Physical Properties of the Co (III) Complexes

Complex Formula	Color	λ_{max} (nm)	Δ_o (kJ/mol)	ε

6. Prepare two lists: (1) A list of the **ligands** in order of increasing crystal field strength, based on your experimental data and (2) a list of the same ligands based on a spectrochemical series you found in the literature that includes all of them, including ONO^-. Provide the reference for this list. Compare your list to the theoretical list. Are there any variations?

7. $[Co(NH_3)_5(ONO)]Cl_2$ and $[Co(NH_3)_5(NO_2)]Cl_2$ form a pair of constitutional isomers. What is the name of the type of isomerism exhibited by this pair? Explain why you see a different λ_{max} for ONO^- and NO_2^-. Consider the types of metal-ligand bonds and the nature of the interaction between the ligand and metal atom that gives rise to Δ_o. Given your values of Δ_o what conclusion might you make concerning the relative lengths of the metal-ligand bond for these two complexes? Explain.

VI. Pre-Lab:

1. (a)   Using standard reduction potentials explain why $[Co(H_2O)_6]^{2+}$ is not easily oxidized but $[Co(NH_3)_6]^{2+}$ is.   **(b)**   Using the standard reduction potentials, show that one can prepare an ammine complex from $CoCl_2$ and hydrogen peroxide in the presence of ammonia but not in its absence. You will need to write two redox reactions, calculate standard potentials for the reactions, and make conclusions.

2. Complete and balance the following equation:
    $CoCl_2.6H_2O + NH_4Cl + NH_3 + H_2O_2 \rightarrow [Co(NH_3)_5Cl]Cl_2 + H_2O$

3. Write the ground state electron configuration of the following:
    Co Co^{2+} Co^{3+} Ti Ti^{3+}

4. In this experiment you will be preparing 1.00×10^{-2} M solutions of each of the five cobalt(III) complexes. Calculate the mass required to prepare 25.00 mL of each solution.

5. Draw using a three-dimensional perspective each of the five complexes to be synthesized and give for each its name.

Experiment 15
## Preparation of Organic Compounds: Aspirin and Other Esters

I.   Objective:
To prepare simple organic compounds: aspirin and other esters.

II.   Chemical Principles:

Esters are common organic compounds.   They are flavoring agents and give many fruits their "fruity" smell, and are sometimes added to food to add flavor.   Aspirin is used as an analgesic (pain reliever) and as an antipyretic (fever reducer).

Esters contain the functional group represented by $R—\overset{\displaystyle O}{\overset{\|}{C}}—O—R'$.
They can be made by combining a carboxylic acid with an alcohol as in the equation:
(Sulfuric acid is added as a dehydrating agent and catalyst.)

$$R—\overset{\displaystyle O}{\overset{\|}{C}}—OH \ + \ R'—OH \quad \boxed{} \quad R—\overset{\displaystyle O}{\overset{\|}{C}}—O—R' \ + \ H_2O.$$
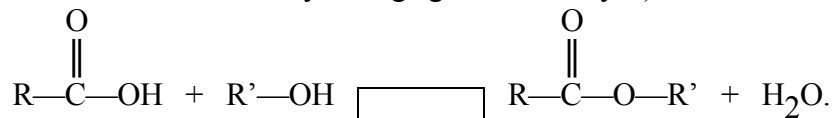
In this experiment we will make several esters in this way.   The reaction is reversible.   In the presence of sulfuric acid the equilibrium favors the products by about 2 to 1 in a process is called esterification.   In the presence of a strong base the equilibrium favors the reactants.   This process is called hydrolysis.

Aspirin will be made by an alternative route.   Salicylic acid is both a carboxylic acid and an alcohol.   It will be reacted with acetic anhydride as shown in an example in Chapter 10 (pg 472-475) of your textbook.

III.   Experimental Procedures:

This experiment will be performed in pairs.   One student will prepare the aspirin while the other prepares the other esters.   Even though the procedures are simple, partners will need to assist each other as certain steps may require more than one pair of hands.
You will need to share data with your partner and each will turn in his/her own individual report.

Safety Precautions:
Acetic anhydride and carboxylic acids are irritating to the skin and eyes.   Use under the hood.
Concentrated sulfuric acid is extremely harmful to the skin, eyes, and clothing and reacts violently with water.
Alcohols are flammable liquids.   Breathing the vapor is dangerous and swallowing small quantities of some alcohols can cause blindness or death.   Use under the hood.

Synthesis of Aspirin: Student 1

Set a large beaker about 1/3 full of water on a hot plate to use as a boiling water bath. Place about 6.0 grams (weigh accurately) of salicylic acid into a 125 mL erlenmeyer flask. Using caution, add 8.0 mL of acetic anhydride to the salicylic acid in the flask.   Carefully add 10 drops of concentrated sulfuric acid to the mixture and swirl the flask to mix the reagents.   While mixing, heat the flask in a beaker of boiling water for about 15 or 20 minutes to dissolve all the solid and allow the reaction to occur.

After the solid has dissolved and reacted, remove the flask from the boiling water bath and cool the mixture in an ice water bath.   To hasten the cooling and crystallization add about 25 mL of water with a small amount of ice.   Continue to stir gently until it appears that no new crystals are forming.

Filter the crystals using a suction filtration system.   Wash the crystals with two 20 mL portions of ice-cold water.   After using the suction filter to dry the crystals as much as possible, set the filter paper with crystals on a paper towel and gently press them with another filter paper to get out as much moisture as possible.   Use a spatula to stir and chop the product to assist with drying.

Weigh the product so that later you can calculate a percent yield.

Synthesis of other esters: (Student 2)

Into five clean, dry, labeled test tubes add 10 drops of liquid carboxylic acid or 0.1 g of solid carboxylic acid and 10 drops of alcohol according the scheme shown in the table below.   Write down the odor of each reactant.

Test Tube Number	Carboxylic Acid	Alcohol
1	Formic	Ethyl
2	Formic	Isobutyl
3	Acetic	Isopentyl
4	Acetic	Ethyl
5	Salicylic	Methyl

Cautiously add 5 drops of concentrated sulfuric acid to each test tube and mix the contents thoroughly.   Put the test tubes into a hot water bath at between 60°C and 70°C for 15 minutes.

Remove the test tubes from the warm water bath, cool in an ice bath, and add 2 mL of cold water to each while gently stirring.   Each should have a thin oily layer on top of the water solution.

Using a clean Pasteur pipet, take a few drops from this top layer and place on a clean watch glass.   With your partner observe the odor of each.   Match the ester from each test tube with one of the following odors: banana oil, rum, raspberry, nail polish remover, oil of wintergreen.

IV. **Laboratory Report:**
   Even though you worked with a partner, each person turns in
   his/her own separate report.
1. Title page.
2. Pre-lab with corrections to the pre-lab.
3. Attach all laboratory notebook pages of procedures and observations including copies
of your partner's data.
4. The report should be typed.
5. Word process a table showing the following:

Test Tube Number	Carboxylic Acid	Alcohol	Name of Ester	Odor
1	Formic	Ethyl		
2	Formic	Isobutyl		
3	Acetic	Isopentyl		
4	Acetic	Ethyl		
5	Salicylic	Methyl		

6. Looking at your corrected values from your prelab as a starting point, use your
experimental data to calculate the % yield of aspirin you and your partner got.
7. If your aspirin was wet when you weighed it (which it probably was) would you have
calculated a % yield that was higher or lower than it should have been ?   Explain why.

V. **Pre-Lab**

1. Draw out the molecules, both products and reactants, for the reaction making aspirin
as described in this experiment.

2. Assuming the specific gravity of acetic anhydride is 1.08, calculate the expected yield
of aspirin in grams if we get 100% conversion of starting materials in this experiment.

3. If the pKa for aspirin is 3.49, calculate the pH of a 0.0100 M solution of aspirin in
water.

4. Give the chemical name of each of the five products that will be made by student 2.

5. Methyl butyrate has the flavor of apples.   What alcohol and carboxylic acid would
you use to synthesize this ester?

Appendix 1
Nomenclature Review Problems

Exercises.

1. Complete the following table:

Binary Compound	Name of Gas	Acid in solution
HF		
HCN		
H_2S		
H_2Se		
HI		

2. Name the following compounds:

Compound	Name
$Co(OH)_3$	
MnO	
Fe_2S_3	
Hg_2Cl_2	
NO	
N_2O_3	
CO	
CO_2	
CS_2	
Cl_2O_5	

3. Complete the table by filling in the missing spaces for each row. The first one is shown as an example.

	Acid Formula	Acid Name	Salt Formula	Salt Name
1	H_2CO_3	carbonic acid	$BaCO_3$	barium carbonate
2		phosphoric	Na_3PO_4	
3	H_2SO_3			cesium sulfite
4			K_2HPO_4	
5			$MgSO_4$	
6	HNO_3			aluminum nitrate
7		permanganic	$KMnO_4$	
8				sodium iodate
9			$CaSeO_4$	
10				calcium perchlorate
11	H_3AsO_4			magnesium arsenate
12		hypobromous	$Ba(BrO)_2$	
13			NaHS	
14				copper (II) nitrite

4. List **six strong acids** that you are to memorize.

5. List at least five salts that form from strong acids. Give formula and name.

6. List at least five salts that form from weak acids. Give formula and name.

Names and Valence of Several Ions

+1		-1			
Hydrogen	H^+	Bromide	Br^{-1}	Chlorite	ClO_2^-
Lithium	Li^+	Chloride	Cl^{-1}	Chlorate	ClO_3^-
Sodium	Na^+	Fluoride	F^{-1}	Perchlorate	ClO_4^-
Potassium	K^+	Iodide	I^{-1}	Acetate	$C_2H_3O_2^-$
Ammonium	NH_4^+	Hydroxide	OH^-	Metaborate	BO_2^-
Copper (I)	Cu^+	Cyanide	CN^-	Bromate	BrO_3^-
Silver (I)	Ag^+	Thiocyanide	SCN^-	Iodate	IO_3^-
Mercury (I)	Hg_2^{2+}	Nitrate	NO_3^-	Permanganate	MnO_4^-
Gold (I)	Au^+	Nitrite	NO_2^-	Hypochlorite	ClO^-

Names and Valence of Several Ions Continued:

+2		-2	
Barium	Ba^{2+}	Carbonate	CO_3^{2-}
Cadmium	Cd^{2+}	Chromate	CrO_4^{2-}
Calcium	Ca^{2+}	Dichromate	$Cr_2O_7^{2-}$
Cobalt (II)	Co^{2+}	Molybdate	MoO_4^{2-}
Copper (II)	Cu^{2+}	Oxalate	$C_2O_4^{2-}$
Iron (II)	Fe^{2+}	Oxide	O^{2-}
Lead (II)	Pb^{2+}	Selenate	SeO_4^{2-}
Magnesium	Mg^{2+}	Silicate (meta)	SiO_3^{2-}
Manganese (II)	Mn^{2+}	Sulfate	SO_4^{2-}
Mercury (II)	Hg^{2+}	Sulfite	SO_3^{2-}
Nickel (II)	Ni^{2+}	Sulfide	S^{2-}
Strontium	Sr^{2+}	Thiosulfate	$S_2O_3^{2-}$
Tin (II)	Sn^{2+}		
Zinc	Zn^{2+}		

+3		-3	
Aluminum	Al^{3+}	Arsenate	AsO_4^{3-}
Antimony (III)	Sb^{3+}	Arsenite	AsO_3^{3-}
Arsenic (III)	As^{3+}	Nitride	N^{3-}
Bismuth	Bi^{3+}	Phosphide	P^{3-}
Cobalt (III)	Co^{3+}	Phosphate	PO_4^{3-}
Gold (III)	Au^{3+}	Phosphite	PO_3^{3-}
Iron (III)	Fe^{3+}		
Nickel (III)	Ni^{3+}		

+4		-4	
Tin (IV)	Sn^{4+}	Carbide	C^{4-}
Lead (IV)	Pb^{4+}	Silicide	Si^{4-}
		Silicate	SiO_4^{4-}

Appendix 2

## Typing Special Characters and Equations with MS Office Word

You will be required for several experiments to prepare sections of the laboratory report in a typed format. This may include typing special characters such as Greek letters or mathematical symbols. Or it may require typing mathematical equations. If you have MS Office Word you can do these tasks somewhat easily.

1. **Special characters:** You can insert many special characters by first clicking on INSERT in MS Office Word and then clicking on SYMBOL. You will see on your computer screen a table of symbols. It may look like:
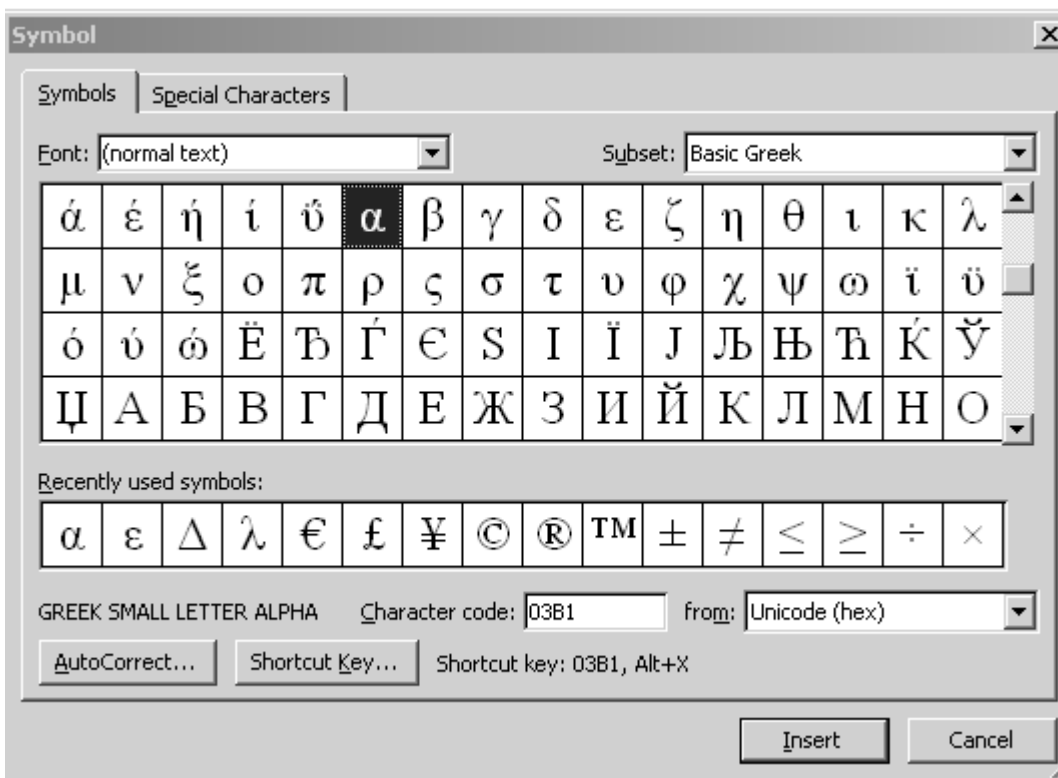

Find the appropriate subset of symbols that you need. In this example you are provided basic Greek symbols. Click on the symbol you need and then click on Insert. It will then appear in your document. Look at all the subsets so you will know if a needed special character is available.

2. **Inserting mathematical equations or special chemical symbols:** Most MS Office Word programs have a special Object called Microsoft Equation Version X.X. (X.X depends on which version you have.). On the INSERT menu find and click on OBJECT. You will see a menu box that is shown on the next page:
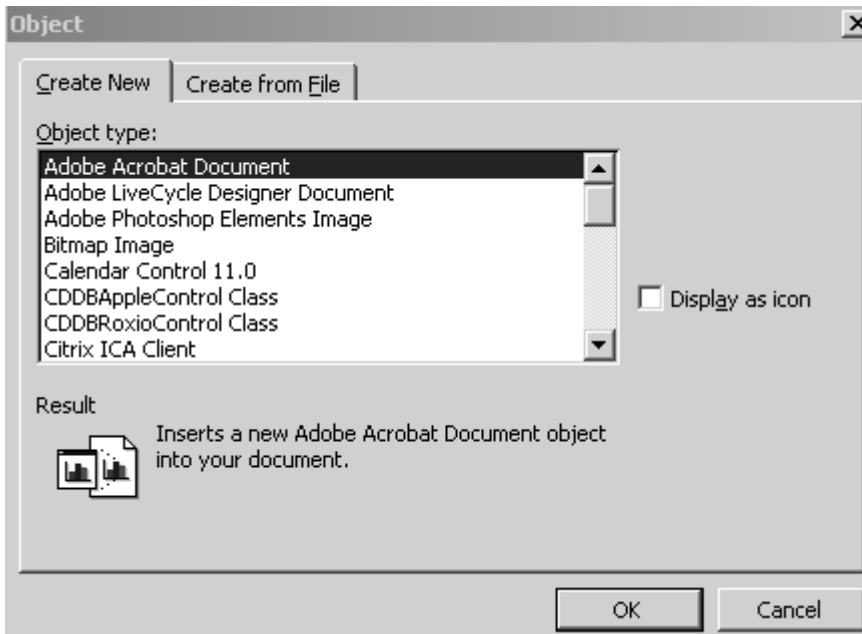
Scroll down the menu and fine Microsoft Equation X.X. Click on it and a new box will appear that looks like the following (this one is a modified version but the basic one is very similar):
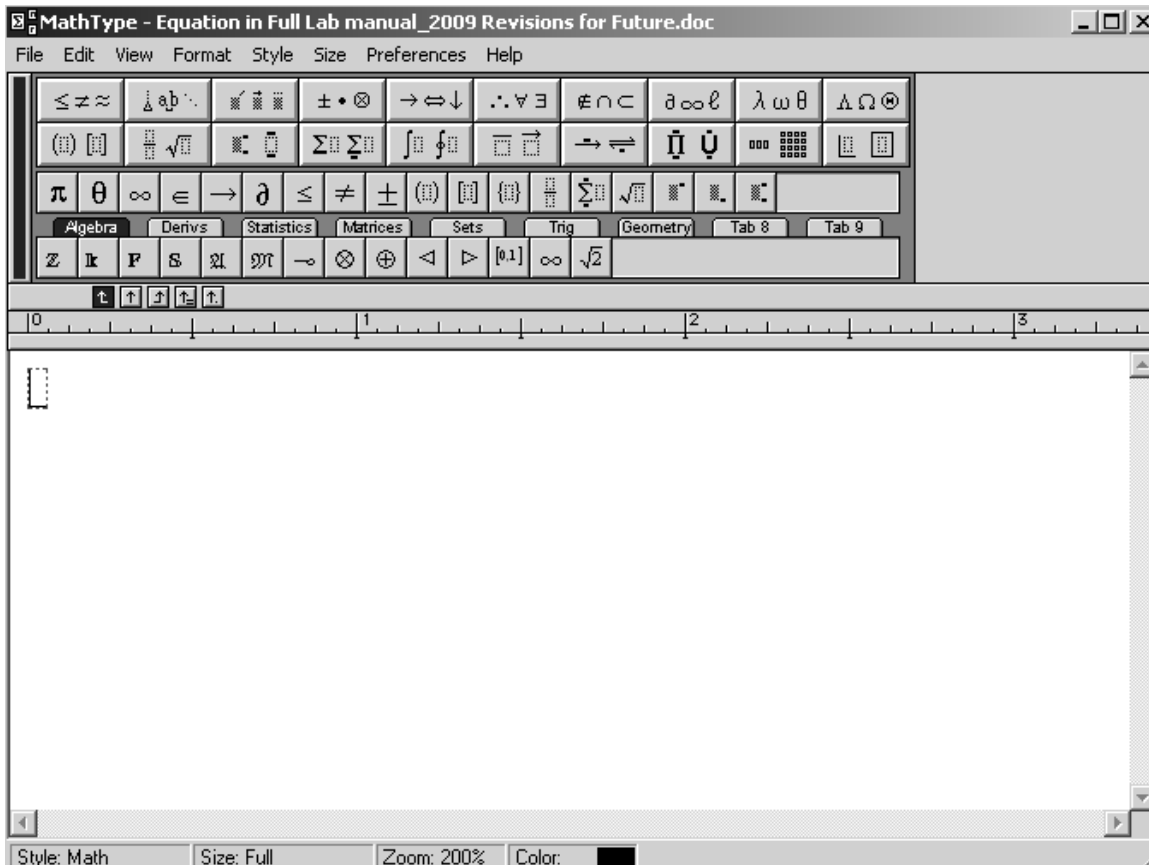
You will see several rectangular boxes with various symbols and mathematical expression. Click on these and explore the possibilities. Here is a simple example of what you can do.
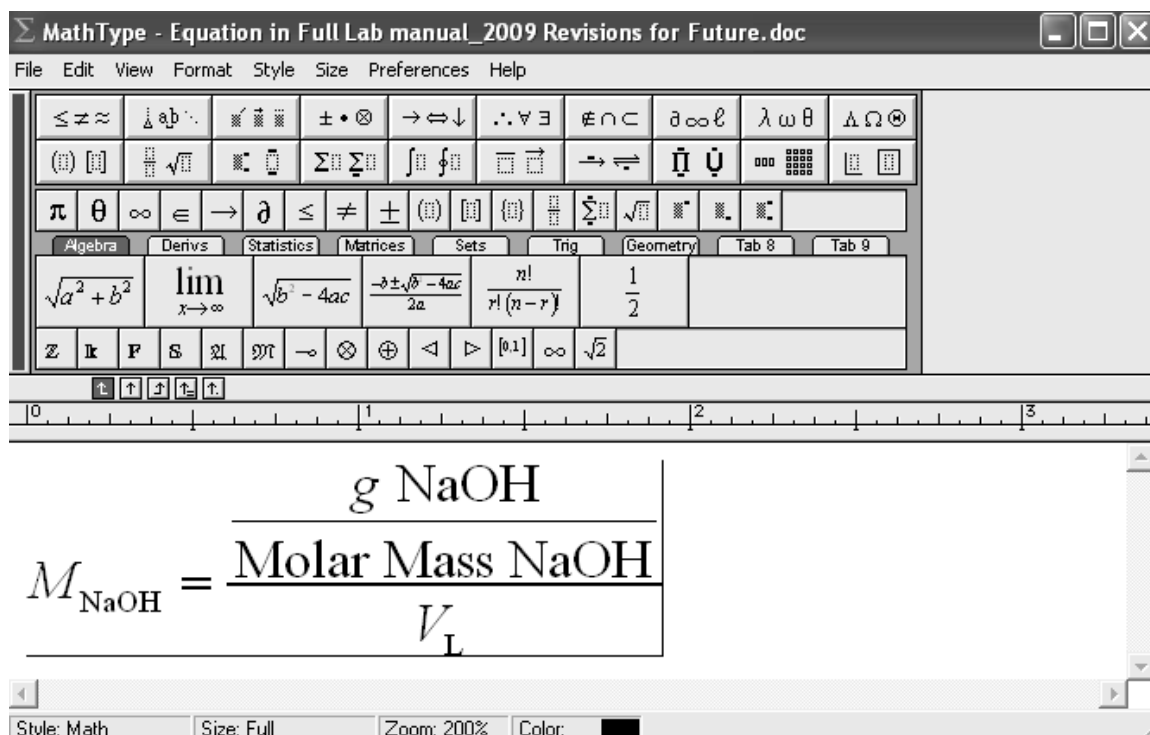
It has math and text styles, subscripts and fractions that are used to create the example. You can use your arrow keys to move through the expression. With practice you can create complex mathematical expressions and write chemical reactions.

3. **Subscripts and superscripts:** You will be using subscripts and superscripts throughout the laboratory course. For example the ion $SO_4{}^{2-}$.

You can use **short cut keys** to do this.   First highlight the part to be made into a subscript or superscript.

      To make the characters into subscripts hold the control button while typing =
      To make the characters into superscripts hold control and shift while typing =
      (which is like typing control +)

Another way is to put them **on your toolbar**. The icons make it easy to do these two tasks. To place them on a toolbar in MS Office word do the following:
    1. Click on a blank area of the tool bar with the right button of your mouse.
    2. Click on "Customize"
   3. You will see the following (next page):
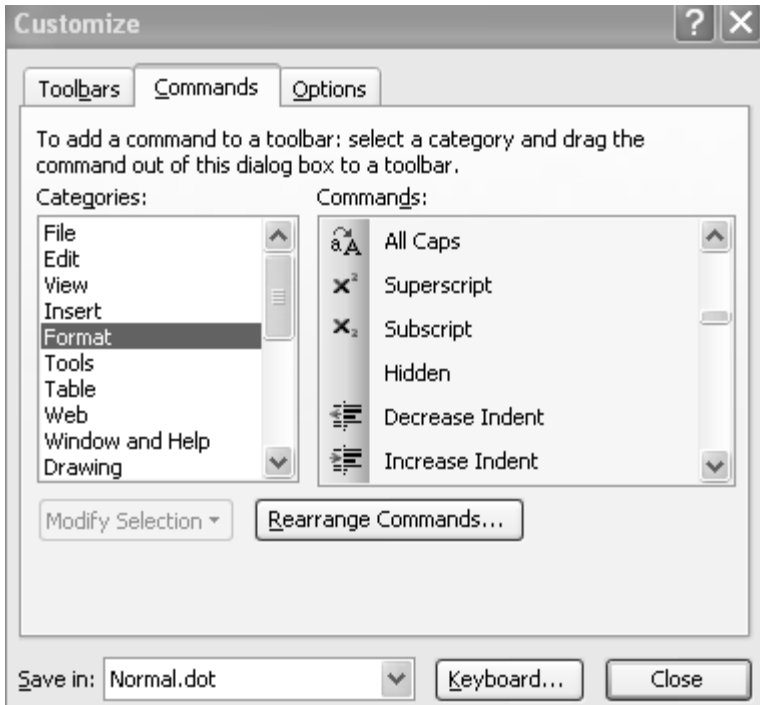
Choose Commands and then find the Format Category. Then look under Commands on the right hand side for superscript and subscript. Select one of the two and drag the icon to the toolbar. Repeat for the other icon. Then close and the task is complete.

Appendix 3

Simple plots on EXCEL

1)   Call up EXCEL

2)   Enter data:
> x data in first column
> y data in second column

if more than one set of data, as in Experiment 13, then
> 3rd set of data in third column
> 4th set of data in fourth column
> Etcetera.

3)   Using mouse select (highlight) all data to be graphed.

4)   Click on Insert Chart.
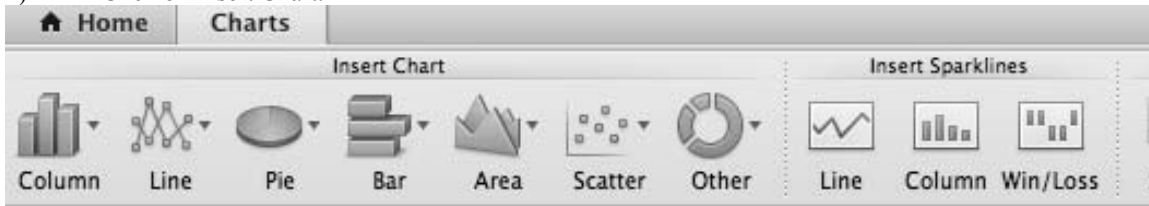
5)   The "Ribbon" shows a variety of charts and graphs.   Choose Scatter Graph, and under Scatter Graph choose "Smooth Marked Scatter".   This shows all data points and connects the data points with a smooth, curved line.
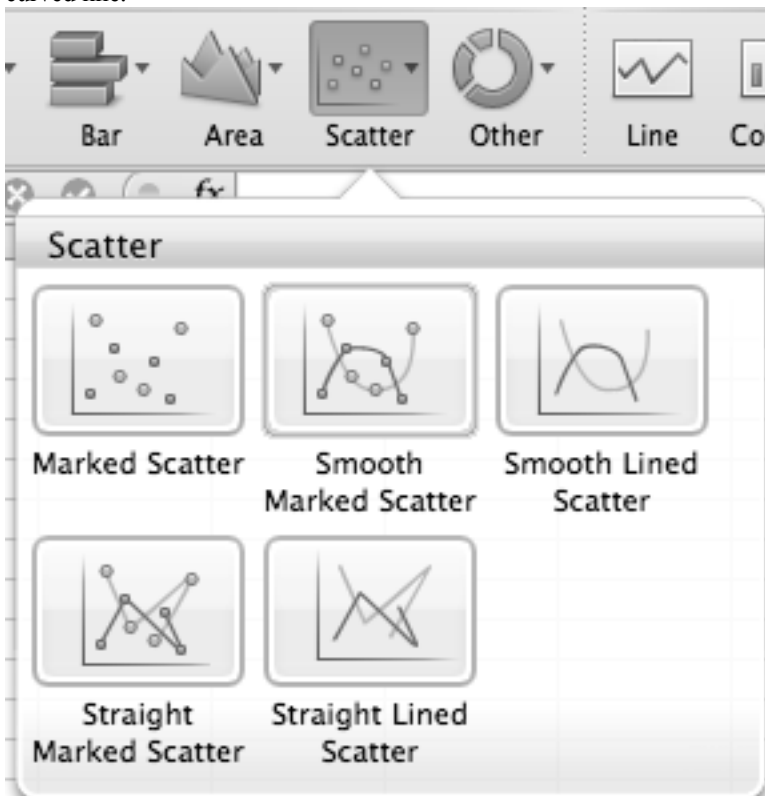
6)   It displays a small copy of the graph.   Either Right click on the graph or from the top menu bar click on Chart.   Choose Move Chart.   Click on "New Sheet" and if you want, you can name the tab that will appear at the bottom of the excel page.   Your data has a tab called "Sheet 1" and your graph defaults to "Chart 1" unless you choose a different name for it.
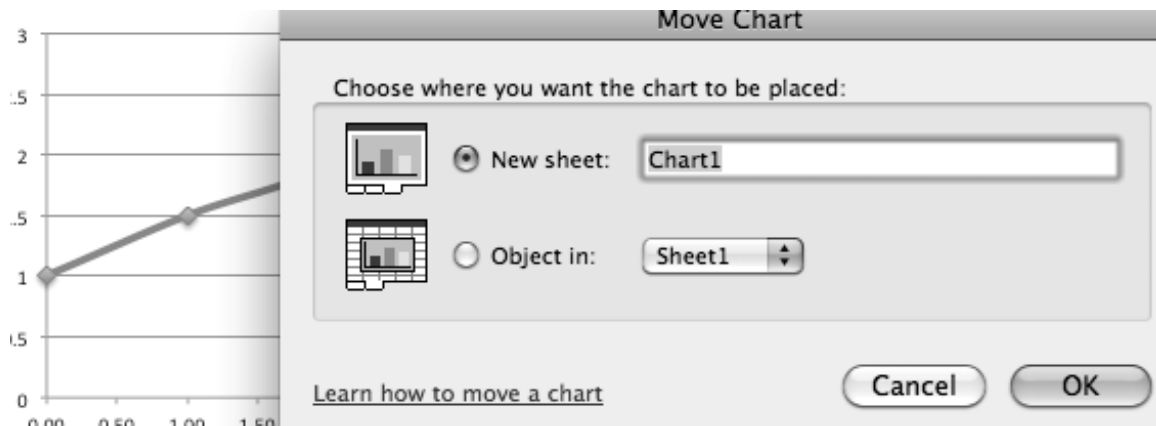
7)   To add features to your graph you can usually double click or right click on an axis or whatever you want to change, or from the top menu bar find what you want in the Chart menu. **In the newer versions of Excel** the "ribbon" has a nice "Layout" of choices.
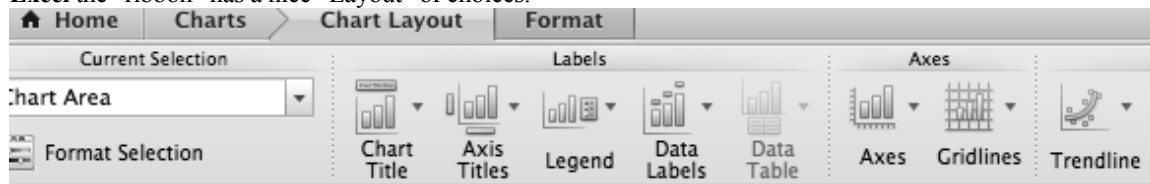
Features you should include are:

    A **Title** for your graph,
    Labels on both x and y axes,
    Do **NOT** put labels on data points.
    Both horizontal and vertical **gridlines**,
    A blank, or clean, not distracting, background,
    Include a Legend **Only IF** you have more than one data series
    as in experiment 13,
    Include a Trendline **Only IF** the experiment asks for it,
    If the computer's automatic settings do not make best use of the graph,
    adjust the axes so the data take up almost the full graph, which may
    mean that the (0,0) point might not be on the graph.
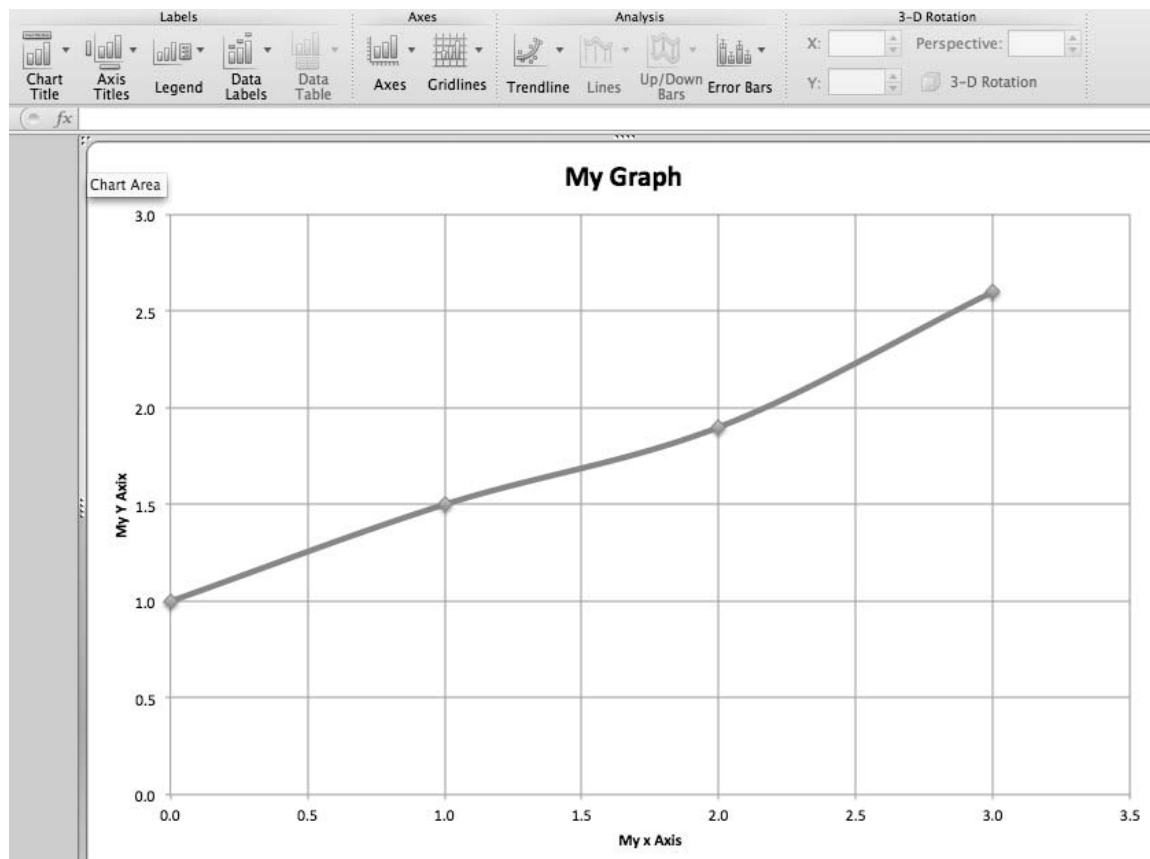
8)　　　In File menu click on page setup and ask for horizontal or "Landscape"
print to make your graph look best.   It should take up the full page so data are easier to read.
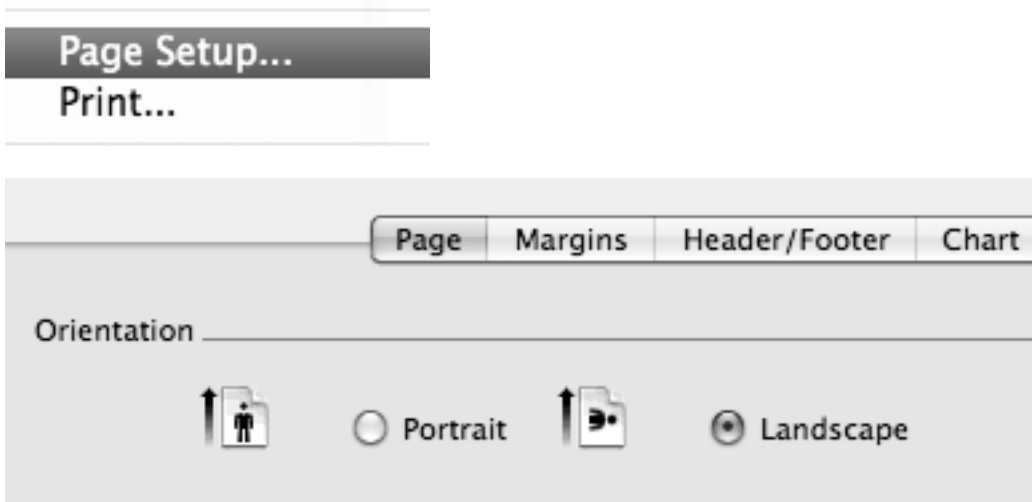
9)　　　In file menu click on Print.

10)　　　Save data and graph, print data if desired (not required unless handwritten data are not available), and quit.

Appendix 4
Monoprotic Acid Determination from Titration Curve

The following is the derivation for the mathematical equation used to determine whether an acid is monoprotic or diprotic using its titration curve.

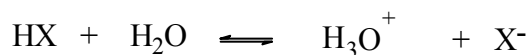The following shows how a monoprotic acid can be distinguished from a diprotic acid. For a monoprotic acid, before the end point, the equilibrium that occurs is:

$$HX \ + \ H_2O \ \rightleftharpoons \ H_3O^+ \ + \ X^-$$

$$Ka = ([H_3O^+][X^-])/[HX]$$

At 1/4 of the way to the equivalence point the concentration of hydrogen ion is 1/4 $[HX]_0$, which is also the concentration of X^- , and the remaining concentration of HX is 3/4 $[HX]_0$.

$$[X^-]/[HX] = (1/4[HX]_o)/(3/4[HX]_o) = {}^1/_3$$

If this ratio (1/3) is substituted into the equilibrium constant expression, and the negative log of both sides is taken we find that the pK_a at the ¼ point of the titration is:

$$-\log K_a = -\log[H_3O^+]_{1/4} - \log(1/3)$$

$$pK_a \ = \ pH_{1/4} \ + \ \log 3$$

By the same reasoning, at 3/4 equivalence point in the titration pK_a is shown to be;
$$pK_a = \ pH_{3/4} \ - \ \log 3$$
The change in pH between the 1/4 point and the 3/4 point then is:

$$\Delta pH = pH_{3/4} - pH_{1/4} \ = \ 2 \log 3 \ = \ 0.954$$

Appendix 5

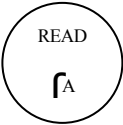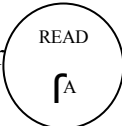## Metler Toledo pH Meter

When you turn on the meter it should read pH. If it reads mV push pH/mV to get pH.

On the left side of display you should see $\underline{\int}^A$, if not hold the "Read" button until $\underline{\int}^A$ appears.

Near the bottom left of display it should show: Bl 7.00 4.00 10.00 1.68 if not repeatedly push the button with 3 bottles until Bl is flashing. Push "Read" again to get back to pH measurement. Calibrate using 3-point calibration.

3-Point Calibration

1. Place the electrode in the calibration (pH 7.0) buffer and press

2. Rinse electrode with distilled water.

3. Place the electrode in the next calibration buffer (pH 4.0 or 10.0) and Press

4. Rinse electrode with distilled water.

5. Place the electrode in the next calibration buffer (pH 4.0 or 10.0) and Press

6. Press the   READ   button to return to sample measurement.

7. Place the electrode in the sample and press   to star   ment: the

decimal point flashes. The display shows the pH of the sample. When the sensor output has stabilized, the display freezes automatically and ∫A appears.

Manual Calibration

If automatic calibration does not work: hold the "Read" button until ∫A becomes ∫.

1. Rinse electrode with DI water.

2. Place electrode in pH 7.00 buffer and press " Read". Repeat for 4.00 and 10.00.

mV Measurement

1. Attach the black clip of the mV lead to the anode.

2. Attach the red clip to the cathode.

3. Press the (READ ∫A) button to start measurement. The display shows the voltage of the

sample.

General Trends in Solubility:
- All ammonium salts and compounds of sodium and potassium are soluble.
- All nitrate, acetate, chlorate and perchlorate compounds are soluble.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.00794																	2 He 4.002602
3 Li 6.941	4 Be 9.012182											5 B 10.811	6 C 12.0107	7 N 14.00674	8 O 15.9994	9 F 18.9984032	10 Ne 20.1797
11 Na 22.989770	12 Mg 24.3050											13 Al 26.981538	14 Si 28.0855	15 P 30.973761	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.955910	22 Ti 47.867	23 V 50.9415	24 Cr 51.9961	25 Mn 54.938049	26 Fe 55.845	27 Co 58.933200	28 Ni 58.6934	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.92160	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.90585	40 Zr 91.224	41 Nb 92.90638	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.90550	46 Pd 106.42	47 Ag 107.8682	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 I 126.90447	54 Xe 131.29
55 Cs 132.90545	56 Ba 137.327	57 La 138.9055	72 Hf 178.49	73 Ta 180.9479	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.217	78 Pt 195.078	79 Au 196.96655	80 Hg 200.59	81 Tl 204.3833	82 Pb 207.2	83 Bi 208.98038	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 (269)	111 (272)	112 (277)	114 (289) (287)		116 (289)			118 (293)

58 Ce 140.116	59 Pr 140.90765	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.92534	66 Dy 162.50	67 Ho 164.93032	68 Er 167.26	69 Tm 168.93421	70 Yb 173.04	71 Lu 174.967
90 Th 232.0381	91 Pa 231.03588	92 U 238.0289	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)