Chem **1C**

Laboratory Manual

Spring 2005
Summer 2005
Fall 2005

Kevin M. Simpson, Ph.D.

Department of Chemistry
University of California-Riverside

HAYDEN
HM
McNEIL

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

ISBN 0-7380-1505-9

Hayden-McNeil Publishing
14903 Pilot Drive
Plymouth, Michigan 48170
www.hmpublishing.com

SimpsonK, 1505-9 S05

Chem **1C**

Table of Contents

Safety Precautions in Chemistry 1 Labs

Your laboratory instructor will usually point out the safety-related aspects of each experiment. However, you are responsible for exercising caution in the laboratory, and for being aware of and following safety precautions and procedures (such as those in this section).

A well-run laboratory is generally a safe place, despite the large number of people working with glass, flames, and assorted poisonous chemicals. However, one should always try to minimize the chance of a serious accident occurring, and carrying out laboratory operations in the safest way possible is a part of good lab technique.

There are several types of common laboratory accidents:

1. **Minor explosions.** Any closed container, especially one made of glass, is likely to explode when heated. In addition, an unexpected variety of chemicals reacts violently. Other than cuts, such accidents seldom cause much trouble unless glass gets in the eyes, in which case they can be very serious. There is one absolute rule in the laboratory:

   SAFETY GOGGLES ARE TO BE WORN AT ALL TIMES.

   No one will be admitted to the laboratory or allowed to remain there without goggles. We hope to make wearing goggles be automatic, rather than the subject of a running battle between students and instructors. One can draw a fairly good analogy between safety goggles and safety belts in cars: they're not particularly pleasant to use, one seldom needs them, but anyone who has any sense wears them.

2. **Poisoning.** Dangerous gases can be avoided by the simple precaution of working in the hood any time a noxious gas is involved. It seems that the only other time people are poisoned is when they pipet by mouth (most people apparently know not to eat or drink in the laboratory and to wash their hands before eating afterward). Despite the fact that lots of reputable scientists do it, mouth-pipetting is poor lab technique. Aside from the danger of inhaling a concentrated acid and losing the inside of your mouth, you are likely to contaminate the liquid you are pipetting.

3. **Burns.** Unfortunately, hot glass doesn't look hot. If you hold the back of your hand near an object that may be hot, you can usually gauge from the heat it radiates whether it's too hot to touch. If you burn yourself, immediately run lots of cold water over the burn, and tell your instructor so medical attention can be obtained.

4. **Cuts.** Almost all cuts and lacerations result either from putting glass tubing and thermometers through cork or rubber stoppers or from scrapes against chipped glassware. Using cracked glassware is poor lab technique and is likely to be penalized as such; if you chip something, request a replacement from the stockroom.

5. **Spills.** Concentrated acids and bases are quite soluble in water. If you spill an acid or base on yourself, immediately wash it off and notify your instructor. Also notify your instructor immediately if you spill other solutions on yourself. If any liquid spatters in your eye—this is an EMERGENCY—use the eye wash fountain to wash your eyes; the approved length of time for washing is 15 minutes.

Department Of Chemistry
Laboratory Safety Instructions And Rules

1. **EYE PROTECTION**: One of the most common (and damaging) types of laboratory accidents involves the eyes.

   EYE PROTECTION IS MANDATORY AT ALL TIMES IN ALL TEACHING AND RESEARCH LABORATORIES. NO EXCEPTIONS. PERSONS WITH INADEQUATE EYE PROTECTION WILL BE TOLD TO LEAVE THE LABORATORY.

   a. All persons in a laboratory must wear safety goggles.
   b. Persons who normally wear prescription glasses must wear safety goggles over their glasses. Regular prescription glasses do not provide adequate protection for chemical laboratories.

2. **PROPER ATTIRE:** You will not be allowed in lab unless you are wearing clothing which completely covers the torso and legs (to within one foot of the floor). Shoes must completely enclose the foot. A lab coat or apron is recommended. You may wear shorts only under a full-length lab coat. For your protection, you will not be allowed to attend lab without appropriate attire.

3. **MEDICAL CONDITIONS:** Notify the supervising laboratory instructor immediately if you have any medical conditions (such as pregnancy, allergies, diabetes, etc.) that may require special precautionary measures in the laboratory.

4. **EMERGENCY EQUIPMENT:** Know the locations of the lab fire extinguishers, safety showers, eyewash fountains, hallway emergency telephones, fire alarms, and lab and building exits.

5. **FIRE:** Immediately alert the TA, who will give instructions. A fire confined to a small container or flask can usually be extinguished by covering the container with something nonflammable (e.g. a large beaker). Use a fire extinguisher if necessary, but only if it appears that the fire can be easily contained; if not, pull the fire alarm and exit the building. Go directly to the designated assembly area. Do not use the elevator.

   If a person's clothing is on fire, use the safety shower to put out the flames. If the shower is not readily available, douse the individual with water or wrap the person in a coat or whatever is available to extinguish the fire and roll the person on the floor. Fire blankets must be used with caution because wrapping someone while they are in the vertical position can force flames toward the face and neck.

6. **INJURY:** Immediately report any injury to a Teaching Assistant, no matter how minor. The TA will initiate emergency procedures and arrange for transportation to a medical care facililty. Do not transport a seriously injured person. Call for help. Complete an Incident Report in consultation with your TA as soon as possible, and submit it to the Stockroom staff (see Item 7).

   NOTE: The Student Health Center is open only during the day, from 8:00–4:30. Laboratory injuries after these hours will be treated at the Emergency Room at Riverside Community Hospital or a nearby Urgent Care Center. Students (or their health insurance company) will be assessed Emergency Room charges for off campus treatment. The Chemistry Department (or University) cannot pay. Students under 18 years must submit in advance, a treatment release form signed by parents or guardians to be held on file in the stockroom.

7. **CHEMICAL SPILLS:** Chemical contact with eyes and skin must be *washed* immediately with lots of water for no less than 15 minutes. USE THE EYE WASH AND SAFETY SHOWER. Quickly remove all contaminated clothing. Report chemical spills on persons, tables, or floors to a TA *immediately* regardless of how minor they appear.

8. **EARTHQUAKE:** Exit the laboratory if possible, but *stay in the building* and protect yourself from *breaking windows* or *objects falling* from above. When the quake subsides, quickly check, if possible, that all gas valves are closed and all electrical heating devices are turned off to stop reactions and prevent fires. Exit the building to the designated assembly area (see item 9). Do not use elevators.

9. **BUILDING ALARM:** Leave the building immediately and quietly to the designated assembly area (grassy area between Pierce Hall and the bookstore). Do not return until specifically told to re-enter. Note: Do not leave the building during active shaking from an earthquake.

10. **REPORT OF INCIDENT:** All incidents of fire, explosion, injury, or chemical spills (including mercury from broken thermometers) should be reported immediately to a TA. A written report is required after the incident; the stockroom has forms for filing written reports.

11. **PREPARATION FOR LABORATORY:** All students are expected to have read the experiment thoroughly prior to starting the lab work. Questions about procedures or precautions should be resolved by asking the TA or professor before the experiment.

12. **ADDITIONAL LABORATORY RULES:**
    - **a.** You may not bring nor consume any food or beverage in the laboratories. Smoking and application of cosmetics is not permitted in the labs.
    - **b.** You may not remove chemicals, equipment or supplies from the laboratories or stockrooms without written permission of the instructor, teaching assistant, or Laboratory Coordinator. Removal of any of the mentioned items will be treated as Academic Dishonesty and may result in a grade of F for the course.

c. Do not deliberately smell or taste chemicals.
d. Do not mix reagents unless you are instructed to do so or know the likely results.
e. When diluting concentrated acids or bases, *always add the acid or base to the water* (one way to remember this is that alphabetically acid or base comes before water).
f. Do not use unlabeled chemicals. Report them to the TA.
g. Never adulterate reagents by "pouring back" unused portions into stock bottles or using a contaminated pipet.
h. Do not dump chemicals into trash cans or sinks. Waste chemicals are to be disposed of in specially labeled containers only.
i. Extinguish matches with water and dispose of them in trash cans, *never* in the sinks.
j. Absolutely no horseplay of any kind is permitted in the labs.
k. Do not store chemicals in your lab drawer, unless specifically instructed to do so by your TA (e.g., when an experiment requires more than one lab period). All containers for storing chemicals must be clearly labeled (your name, experiment, and the full chemical name(s) of the contents).
l. No visiting by friends is allowed during lab sessions. Pets or children are not allowed.
m. Do not drink water from lab faucets. This water may not be safe.

Experiment 1

1 Chemical Equilibrium and Le Châtelier's Principle

In Experiment 7 of CHEM 1B we examined a chemical system at equilibrium and measured its *equilibrium constant*. We will now look at how the equilibrium can be shifted by changes in concentration and temperature.

Le Châtelier's Principle

If a chemical equilibrium is perturbed, the effects that will be produced by the perturbation can be readily predicted, based on a kinetic consideration of the way such changes will influence the forward and reverse reaction rates. In the reaction of hydrogen and iodine,

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g) \qquad (1)$$

the rate of formation of hydrogen iodide must be proportional to the number of effective collisions between hydrogen molecules and iodine atoms. If more hydrogen gas is added to the container, the concentration of hydrogen gas will increase and there would be more collisions per second, and therefore an increase in the rate of the forward reaction. Thus the equilibrium is temporarily "shifted to the right."

If, on the other hand, some hydrogen is removed from the container, there will be fewer collisions per second between hydrogen molecules and iodine atoms, resulting in a slower forward reaction. The reverse reaction will predominate until a new equilibrium is established (with more hydrogen molecules). Such changes in concentrations affect the "balance" of the chemical equilibrium in accordance with the principle of Le Châtelier: When some stress is applied to a system originally in

equilibrium, the system (reaction) automatically will shift in such a direction as to relieve the stress and restore the original conditions as much as possible.

In aqueous solution, an important equilibrium is that which involves the dissociation of water into H^+ and OH^- ions:

$$H_2O\ (aq) \rightleftharpoons H^+\ (aq) + OH^-\ (aq)$$
$$K_c = [H^+] \times [OH^-] = 1 \times 10^{-14} \qquad (2)$$

If 0.1 M HCl is dissolved in water, it dissociates to produce a solution 0.1 M in H^+ ions and 0.1M in Cl^- ions. Reaction 2 must occur in such a direction as to maintain the equilibrium. Thus, $[OH^-]$, which in pure water is 1×10^{-7} M is lowered by a shift in reaction to the left. The equilibrium concentration of OH^- becomes 1×10^{-13}. In aqueous solution, Reaction 2 must always be present, along with the equilibria that may exist between the solutes which are also in solution.

Experimental Procedure

(Wear your safety goggles while performing all experiments.)

PART A. Equilibria of Acid-Base Indicators

Chemical substances called acid-base indicators change color in solution in response to a change in $[H^+]$. One such indicator is called methyl violet, which we will denote by the formula HMV. In solution, HMV establishes the following equilibrium:

$$\underset{\text{yellow-green}}{HMV\ (aq)} \rightleftharpoons H^+\ (aq) + \underset{\text{violet}}{MV^-\ (aq)} \qquad (3)$$

The color of the indicator in solution is strongly dependent upon the hydrogen ion concentration. A change to the system which affects the hydrogen ion concentration would therefore be expected to shift the direction of equilibrium in reaction 3, and change the color of the indicator solution.

Step 1. Place three drops of the dilute methyl violet indicator solution into a 100-mL test tube. Do not add any water; the solution has already been diluted. Record the color. Note that methyl violet in its acidic form (HMV) will appear greenish rather than yellow, except in very acidic solutions.

Step 2. Select a reagent that should force the equilibrium to go to the other form (color), and add it drop by drop until the color change is complete. If the reagent you choose works, write its formula on the Report Sheet. If it doesn't, try another until you find one that does. Use 2 M reagents.

Step 3. Systems in equilibrium are reversible. Therefore, the reaction can be driven to the left or right repeatedly by changing the conditions of the system. Select a reagent that should force the system in Step 2 to revert to its original color. Add this reagent drop by drop until the color appears as the original one. If your first choice is incorrect, choose another reagent. Be sure to record the formula of the reagents used.

PART B. Solubility Equilibrium

Lead chloride is an example of an ionic substance that exhibits only a very small solubility in water. It dissolves according to this reaction

$$PbCl_2\ (s) \rightleftharpoons Pb^{2+}\ (aq) + 2\ Cl^- \qquad (4)$$

The equilibrium constant for this reaction is written as

$$K_c = [Pb^{2+}] \times [Cl^-]^2 = K_{sp} \qquad (5)$$

For the equilibrium to exist there must always be *some* $PbCl_2$ present, even though it does not enter into the expression for the equilibrium constant because it is a solid. The equilibrium constant is called the solubility product, given the symbol K_{sp}.

Step 1. Set up a hot-water bath in a 30- or 50-mL beaker on a hot plate.

Step 2. Place 10 drops of 0.25 M lead nitrate into a 100-mm test tube (assume that 10 drops is 0.35 mL). Add 5 drops of 0.25 M HCl to the same test tube, cap tightly and shake. Record your observations.

Step 3. To the same test tube, add 5 more drops of 0.25 M HCl, cap tightly and shake. Record the total volume of HCl added.(At this point in time, you should have added 10 drops of HCl and 10 drops of lead nitrate for a total volume of 0.70 mL.)

Step 4. Place the test tube in the hot water bath for 30 seconds. Cap tightly and shake. Repeat two more times. Record your result.

Step 5. Place the capped test tube under cold tap water. Record your observations.

Step 6. Fill a clean 10 mL graduated cylinder with distilled water.

Step 7. To the test tube, add 10–15 drops of distilled water from the graduated cylinder. Continue adding 10–15 drops until the precipitate just disappears. Be sure to tightly cap and shake the tube after each addition of water.

Step 8. After the precipitate has dissolved, record the volume of distilled water used. The volume used will be the initial volume in the graduated cylinder minus the final volume in the graduated cylinder (approximately 2 mL).

PART C. Equilibria Involving Complex Ions

Many metal ions exist in solution as complex ions, with the central metal ion bonded to other ions or molecules, called ligands. Complex ions may be converted to other complex ions by addition of other ligands. This often is accompanied by a change in color of the complex.

The cobalt (II) ions forms the pink complex ion $Co(H_2O)_6^{2+}$ in aqueous solution. Chloride ligands can replace the water ligands to form the ion $CoCl_4^{2-}$. This ion, which is blue, is stable in solutions with a large concentration of Cl^-, according to the following equilibrium:

$$Co(H_2O)_6^{2+}\,(aq) + 4\ Cl^-\,(aq) \rightleftharpoons CoCl_4^{2-}\,(aq) + 6\ H_2O \qquad (6)$$

Step 1. Place 1 or 2 large crystals of cobalt chloride hexahydrate into a 50 mm test tube. If the crystals are really fine, you will need to use approximately 10–15 crystals.

Step 2. Add 5–7 drops of 12 M HCl, using a micropipet. Place a stopper on the test tube and shake until the cobalt chloride is completely dissolved. Record your observations.

Step 3. Add enough water to the test tube to bring the volume to 3/4 full. Replace the stopper and shake well. Record the new color.

Step 4. Place the test tube into the hot-water bath prepared in part B and note any color change.

Step 5. Cool the stoppered test tube under cold tap water and record your observations.

Waste disposal: All waste should be placed in the designated waste container.

Chemical Equilibrium and Le Châtelier's Principle 1 Report Sheet

Name _____

Time _____

M T W R F

PART A. Acid-Base Equilibria

1. Color of methyl violet in water: _____

2. Reagent causing color change: _____

3. Reagent causing shift back: _____

Explain, by considering how changes in $[H^+]$ will cause Reaction 3 to shift, why the reagents in Steps 2 and 3 caused the solution to change color. (Note that Reactions 2 and 3 must both go to equilibrium after a reagent is added).

PART B. Solubility Equilibrium

1. Volume of 0.25 M $Pb(NO_2)$ added in Step 2: _____ mL

2. Moles of Pb^{2+} added in Step 2: _____ moles

3. Observations:

4. Volume of 0.25 M HCl used: _____ mL

5. Moles of Cl^- used: _____ moles

6. Observations in hot water:

   Observations in cold water:

7. Volume of H_2O added to dissolve $PbCl_2$: _____ mL

8. Total volume of solution: _____ mL

9. Explain why $PbCl_2$ did not precipitate immediately on addition of HCl. (What condition must be met by $[Pb^{2+}]$ and $[Cl^-]$ if $PbCl_2$ is to form?

10. What do your observations in Step 4 and 5 tell you about the sign of ΔH in Reaction 4?

11. Explain why the $PbCl_2$ dissolved when water was added. (What was the effect of added water on $[Pb^{2+}]$ and $[Cl^-]$? In what direction would such a change drive Reaction 4?)

12. Given the number of moles of Pb^{2+} and Cl^- in the final solution in Step 8, calculate the Ksp for $PbCl_2$.

_____

C. Equilibria Involving Complex Ions

1. Color of $CoCl_2 \cdot 6\ H_2O$: _____
2. Color in solution in 12 M HCl: _____
3. Color in diluted solution: _____
4. Color hot solution: _____
5. Color of cooled solution: _____
6. Formula of Co(II) complex in solution in
   a. 12 M HCl _____
   b. diluted solution _____
   c. hot solution _____
   d. cooled solution _____

7. Explain the color change that occurred when

   a. water was added in Step 3.

   b. the diluted solution was heated. (How did the increasing temperature affect the value of K_c? What is the sign of ΔH in Reaction 6?)

1 Chemical Equilibrium and Le Châtelier's Principle

Prelab

Name _____

Time _____

M T W R F

You are given a box in which PCl_5 (g), PCl_3 (g), and Cl_2 (g) are in equilibrium with each other at 546 K. Answer the following questions given that the decomposition of PCl_5 to PCl_3 is endothermic:

1. Give the equilibrium equation for this reaction:

2. Explain what influence the addition of Cl_2 to the box will have on the equilibrium (explain in terms of [PCl_5]):

3. Explain what effect reducing the volume of the box will have on the equilibrium (explain in terms of $[PCl_5]$):

4. Explain what effect raising the temperature of the box will have on the equilibrium (explain in terms of $[PCl_5]$):

Experiment 2

2 pH Measurements

We will be using the equilibrium concepts from the last couple of labs to understand acids and bases. A *strong* acid or base describes a reaction in which the equilibrium favors the products. *Weak* acids and bases describe reactions in which the equilibrium favors the reactants. We will also take a look at buffer systems, which may be viewed as systems where Le Châtelier's principle is exploited. You should review the basic rules of logarithms for this laboraory.

Defining Acids and Bases

Several definitions of acids and bases are used in chemistry. The following table summarizes the three common definitions:

	Definition of Acid	Definition of Base
Arrhenius	produces H^+ ions (protons) in aqueous solution	produces OH^- ions in aqueous solution
Brønsted-Lowry	proton donor	proton acceptor
Lewis	electron pair acceptor	electron pair donor

The Arrhenius model is somewhat limited, since (1) it only applies to aqueous solutions, and (2) it allows for only one type of base. Be careful not to confuse the Brønsted-Lowry model with the Lewis model. Note that in the Brønsted-Lowry definition an acid *donates a proton*, while in the Lewis definition an acid *accepts an electron pair*.

Autoionization of Water and pH

Water is *amphoteric*; it can act as either an acid or a base. In fact, water is so good at acting as either an acid or a base that if nothing else is around for a water molecule to react with, it will react with another water molecule. This type of behavior is called *autoinization*:

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)} \quad (1)$$

Note that rather than a bare hydrogen ion (also referred to as a *proton*), $H^+_{(aq)}$ exists as a hydrated species, $H_3O^+_{(aq)}$, called the *hydronium* ion. For simplicity, chemists often use the notation $H^+_{(aq)}$ for the $H_3O^+_{(aq)}$ ion.

The equilibrium expression for this reaction (1) is:

$$K_w = [OH^-]\,[H_3O^+] = [OH^-]\,[H^+] = 1.0 \times 10^{-14} \text{ (at 25° C)} \quad (2)$$

$[H_2O_{(l)}]$ is not included because it is assumed to be constant. The value of K_w, the *ion-product constant for water*, varies according to the temperature at which it is measured.

A primary concern for this lab is the concentration of the hydronium ion, $[H_3O^+]$. The hydronium ion is important because we will use it to calculate the pH according to:

$$pH = -\log [H_3O^+] \quad (3)$$

Notice that if we take the equilibrium expression for the autoionization of water and solve for the concentrations of ions, we get:

$$[H_3O^+] = [OH^-] = 1.0 \times 10^{-7} \text{ (at 25° C)} \quad (4)$$

Therefore, by combining equations (3) and (4) we obtain:

$$pH = -\log (1.0 \times 10^{-7}) = 7.0 \quad (5)$$

Thus the pH of *pure* water at 25° C is 7.0. In general the lower case "p" prefix means "take the negative log of (the concentration of) whatever follows."

Since the pH of pure water is 7.0, we define 7.0 to be ***neutral*** pH. If the pH is greater than 7.0, then the hydroxide ion concentration, $[OH^-]$, is greater than the hydronium ion concentration, $[H_3O^+]$, and we say that the solution is ***basic*** (or *alkaline*). If the pH is less than 7.0, then the hydronium ion concentration, $[H_3O^+]$, is greater than the hydroxide ion concentration, $[OH^-]$, and we say that the solution is ***acidic***.

A common misconception is that the pH scale runs from 0 to 14. In actuality, pH values can be less than 0 or greater than 14. The following will always be true for an aqueous solution at 25° C:

$$pH + pOH = 14.0 \quad (6)$$

The same rules that we discussed in Experiments 15 and 16 also apply to the equilibrium of water. If the hydronium ion concentration is increased, then the hydroxide ion concentration must decrease, and vice versa. Keep in mind that the expression for the equilibrium constant K_w must be satisfied. If you know the concentration of one of the species, we automatically know the concentration of the other species.

We will measure the pH of solutions by two different methods. In the first method we will use *indicators*, chemicals which change color over a relatively short pH range (approximately 2 pH

units). By matching the color of your unknown solution (with indicator) to several solutions of known pH (with indicator) you will be able to estimate the pH of your unknown solution to within 0.3 pH units. In the second method you will use an instrument called the pH meter (which uses electrodes sensitive to the hydronium ion concentration). Be sure to review the "Calibrating pH meters" section in the *Miscellaneous Procedures and Equipment* portion of this lab manual.

Weak Acids and Bases

Acids and bases which do not undergo substantial ionization in water are said to be weak. A weak acid will ionize according to:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)} \quad (7)$$

The ionization constant for a weak acid, K_a, is:

$$K_a = [H_3O^+]\,[A^-] / [HA] \quad (8)$$

For example, let's look at the dissociation of acetic acid, CH_3COOH, in water:

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)} \quad (9)$$

Acetic acid is a weak acid, therefore not much of it dissociates. But what would happen if we dissolved acetic acid in an aqueous solution of sodium acetate ($NaOOCCH_3$) instead of in pure water? Would the amount of dissociation be greater or smaller? Since you have already mastered Le Châtelier's Principle, you know that by increasing the concentration of one of the products (the acetate ion, CH_3COO^-), the equilibrium will shift to offset this change by forming more reactants. Therefore less of the acetic acid will dissociate.

Indicators

An *indicator* is a weak acid that undergoes a color change when it's converted to its conjugate base. Let HIn be a generic indicator. In its non-ionized form, HIn, it has a certain color, which we will label as color #1. After donating a proton to become its conjugate base, In^-, it will have a different color (color #2):

$$\underset{\textbf{color \#1}}{HIn} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + \underset{\textbf{color \#2}}{In^-} \quad (10)$$

In order to understand indicators a little better, let's re-examine the expression for the indicator's equilibrium constant (from equation 8):

$$K_a = [H_3O^+]\,[In^-] / [HIn] \quad (11a)$$

We can re-arrange this as:

$$\frac{[H_3O^+]}{K_a} = \frac{[HIn]}{[In^-]} \quad (11b)$$

If an indicator's equilibrium is predominantly to the left (i.e., $[HIn] >> [In^-]$), then the indicator will display color #1. On the other hand, if the indicator's equilibrium is predominantly to the right (i.e., $[HIn] << [In^-]$), then the indicator will display color #2. By our re-arranged equation (11b), we can think of the relationship between [HIn] and $[In^-]$ as being determined by the K_a value for the indicator and the pH of the solution. Thus,

if $[H_3O^+] >> K_a$, then $[HIn] >> [In^-]$,
color #1 is observed

if $[H_3O^+] \approx K_a$, then $[HIn] \approx [In^-]$,
mix of color #1 and #2 is observed

if $[H_3O^+] << K_a$, then $[HIn] << [In^-]$,
color #2 is observed

In the above equations we write ">>" or "<<" to indicate that one side is greater than the other by at least a factor of 10. We could re-write the above conditions in terms of pH (rather than $[H^+]$):

if pH < $pK_a - 1$	color #1 is observed
if pH ≈ pK_a	mix of color #1 and #2 is observed
if pH > $pK_a + 1$	color #2 is observed

These distinctions are very important if you want an indicator to be useful. For example, phenolphthalein is an indicator with a pK_a value of approximately 9.0. If phenolphthalein is added to a solution whose pH is less than 8, it remains colorless. However, if the solution's pH is above 10, it will turn red. (From a pH of 8 to 10 the solution will be pink.) Thus phenolphthalein could be useful for differentiating a solution whose pH is 7 from another solution which is 11. The indicator methyl orange (pK_a = 3.8) would not be able to differentiate between these two solutions (it would be yellow at pH 7 and pH 11.)

Note: The $pK_a \pm 1$ range for indicator color changes is useful to remember, but is not always the case. Some indicators, such as methyl orange, have a color-change range of only 1.2 (rather than 2) pH units. Also, some indicators have more than two colors. For example, polyprotic indicators, like thymol blue and bromcresol green, can exhibit more than two distinct colors.

Buffer Solutions

The pH of human blood is approximately 7.4. The enzymes that catalyze the reactions necessary to sustain life are so pH sensitive that if the pH of blood were to change by more than even 0.5 in either direction, you would die. Blood must have some means of resisting changes in pH. This is exactly what *buffer solutions* do—they can resist large changes in pH when small amounts of acid or base are added.

A buffer solution is made up of a *weak acid* and its *conjugate base* (or a *weak base* and its *conjugate acid*). The acid's function is to neutralize any added base, and the base's function is to neutralize any added acid. You will go into buffers in more detail in lecture; for now it is sufficient to know that acids and bases neutralize each other according to:

$$H_3O^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons 2\ H_2O \qquad (12)$$

Let's look at an example of a buffer system to see exactly how it works. Examine the solution we discussed previously; a solution of acetic acid (CH_3COOH) and sodium acetate ($NaOOCCH_3$). Note: this is a solution of a *weak acid* and its *conjugate base*. There are two ways of getting the corresponding conjugate into solution. One way is to simply add a salt containing the conjugate. Another way is to make the conjugate by titrating a weak acid (or base) with a strong base (or acid).

But how exactly does a buffer solution resist a large change in pH? Let HA be a weak acid and consider the following (which is a simplification of Equation (7)):

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)} \qquad (13)$$

If the concentrations of HA and A^- are approximately equal, what will happen if we add hydrogen ion (think of it as a Le Châtelier's Principle problem)?

We are adding a product, so the system will shift toward the reactants to use up some of that product. If we add hydroxide ion, however, it's not quite clear what will happen. Since

hydroxide ion and hydrogen ions neutralize one another, adding hydroxide is the same as removing a product. The system shifts to offset this change by having HA form more hydrogen ions and A^-. This is how buffer systems can absorb hydrogen and hydroxide ions without causing large changes in the pH.

For the reaction in equation (13), the equilibrium constant is:

$$K_a = [H^+]\,[A^-] / [HA] \qquad (14)$$

Rearranging this equation and solving for the hydrogen ion concentration gives:

$$[H^+] = K_a \bullet [HA]/[A^-] \qquad (15)$$

In order to design a successful buffer, both [HA] and $[A^-]$ should be fairly high. Why is this a necessity? Let's see what happens when we add a little acid to the solution. The concentration of the base will decrease slightly (it is used to neutralize the added acid), and the concentration of the weak acid will increase slightly. The main point is that the ratio $[HA]/[A^-]$ will not increase very much. (Notice that if this ratio doesn't change much, then equation (15) tells us that the $[H^+]$ will not change much. It may help to visualize this: consider the ratio 100/90. Increase the top by 2 and decrease the bottom by 2 to get the fraction 102/88. Or we could instead decrease the top by 2 and increase the bottom by 2 to get 98/92. So long as both [HA] and $[A^-]$ are fairly high (and approximately the same), the ratio will not change significantly.

Experimental Procedure

(Wear your safety goggles while performing all experiments.)

Note: You will work with a partner on Parts A, B, and C

PART A. Using Indicators to Determine pH

Obtain a microwell plate and place 4–5 drops of 0.1 M HCl into each of five wells along a row. To each of these five wells add 1 drop of the indicators listed in the table below (one indicator to a well!).

Indicator	Useful pH Range							
	0	1	2	3	4	5	6	7
Methyl violet	Yellow	XXX	Violet					
Thymol blue	Red		XXX	Yellow				
Methyl yellow	Red			XXX	Yellow			
Congo red	Violet				XXX	Orange-red		
Bromcresol green	Yellow				XXX		Blue	

XXX = mix of former and latter colors

Compare the colors you observe with the information in the table above to estimate the pH of the solution (to within one pH unit). For example, say 2 to 3, or 4 to 5.

Repeat the above procedure with the following solutions (in place of HCl), added to a different row of the well plate:

0.1 M NaH_2PO_4
0.1 M $HC_2H_3O_2$
0.1 M $ZnSO_4$

Indicate the colors you observe and the approximate pH.

PART B. Using pH Meters to Determine pH

For the duration of this lab period you will be using pH meters to measure the pH of your solutions. Refer to Appendix I for directions in standardizing and operating the meter and electrodes. The electrodes are extremely fragile; ***be very careful when handling the electrode probe***. Nothing but liquids and soft tissue (Kimwipes) should touch the glass tip of the pH electrode.

Measure out about 5 mL of a 0.1 M solution of each of the following substances into medium (16 × 125 mm) test tubes:

NaCl Na_2CO_3 $NaC_2H_3O_2$ $NaHSO_4$

Be sure to rinse your electrode probe in distilled water and blot dry with a Kimwipe in between measurements (***be very careful!***). After measuring the pH, add a drop of bromcresol green to the solution and record the color observed.

Write a net ionic equation (that explains why the observed pH is reasonable) for each solution that has a pH less than 6 or greater than 8. Next explain whether or not the colors obtained using bromcresol green are reasonable.

PART C. Properties of Buffers

In this portion of the experiment you will prepare one of the following buffer systems:

$HC_2H_3O_2 - C_2H_3O_2^-$
acetic acid-acetate ion

$NH_4^+ - NH_3$
ammonium ion-ammonia

$HCO_3^- - CO_3^{2-}$
hydrogen carbonate-carbonate

The sources of these ions will be ammonium and sodium salts containing these ions. *Select only ONE of these buffer systems for your experiment.* Follow these steps to make your buffer:

1. Use a graduated cylinder to measure out 15 mL of a 0.10 M solution of one of the following: $HC_2H_3O_2$, NH_4Cl, or $NaHCO_3$. Place this into a 100 mL beaker. Rinse out the graduated cylinder with distilled water and use it to add 15 mL of the 0.1 M conjugate base of your buffer system (see conjugate pairs above). Measure and record the pH of your mixture. Calculate K_a for the acid.

2. Add 30 mL of water to your buffer mixture, mix, and pour half of the resulting solution into another 100 mL beaker. Measure the pH of the diluted buffer. Calculate the K_a again. Add five drops of 0.10 M NaOH to the diluted buffer and re-measure the pH. To the other half of the diluted buffer add 5 drops of 0.10 M HCl and again measure and record the pH.

3. Make a buffer mixture containing 2 mL of the acid component and 20 mL of the solution containing the conjugate base. Mix, and measure the pH. Calculate the K_a again.

To that solution add 3 mL of 0.10 M NaOH (this should be more than your buffer can handle). Measure and record the pH.

4. Place 25 mL of distilled water into a 100 mL beaker. Measure the pH. Add five drops 0.10 M HCl and measure the pH again. Add ten drops of 0.10 M NaOH to this solution, mix, measure and record the pH.

Select a pH different from any of those observed in your experiments. Design a buffer system for that pH value by selecting the appropriate volumes of your acidic and basic components (see "buffer solutions" section in discussion above). Make the buffer and measure its pH. Demonstrate your buffer system's ability to your T.A.

Waste disposal: all waste solutions should be placed in the designated waste container.

pH Measurements 2 Report Sheet

Name _____

Time _____

M T W R F

PART A. Using Indicators to Determine pH

	Color of 0.1 M solution:			
Indicator	**HCl**	**NaH_2PO_4**	**$HC_2H_3O_2$**	**$ZnSO_4$**
Methyl violet				
Thymol blue				
Methyl yellow				
Congo red				
Bromcresol green				
pH range				

Circle the observation(s) which were most helpful in estimating the pH range of each solution.

PART B. Using pH Meters to Determine pH

Compete the pH and color (observed with bromcresol green) for each of the 0.1 M solutions tested.

	NaCl	Na_2CO_3	$NaC_2H_3O_2$	$NaHSO_4$
pH				
Color				

Write a net ionic equation (to explain the measured pH) for any two solutions that have a pH less than 6 or greater than 8:

Solution _____ Equation _____

Solution _____ Equation _____

Explain whether or not the color observed with bromcresol green was reasonable for each of the four solutions:

pH Measurements 2 Report Sheet

Name _____

Time _____

M T W R F

PART C. Properties of Buffers

Buffer system selected: _____

Weak acid name: _____

pH of buffer _____ $[H^+]$ = _____ K_a = _____

pH of diluted buffer _____ $[H^+]$ = _____ K_a = _____

pH after addition of five drops of NaOH _____

pH after addition of five drops of HCl _____

pH of buffer in which $[HA]/[A^-] = 0.10$ _____ K_a = _____

pH after addition of excess NaOH _____

pH of distilled water _____

pH after addition of five drops of HCl _____

pH after addition of ten drops of NaOH _____

pH of buffer solution to be prepared _____

Average value of K_a K_a = _____
(average of the three K_a values above)

[HA]/[A^-] in buffer _____
(use [H^+] = K_a • [HA]/[A^-])

<u>Volume 0.10 M HA</u>
Volume 0.10 M NaA needed in buffer _____

Volume 0.10 M HA used: _____ mL Volume 0.10 M NaA used: _____ mL

pH of prepared buffer: _____

2 pH Measurements

Prelab

Name _____

Time _____

M T W R F

Show your calculations for each of the questions below.

1. Find the pH of a solution whose hydrogen ion concentration is:

   a. 1×10^{-6} M _____

   b. 0.01 M _____

   c. 10 M _____

2. A solution of a weak acid was tested with the indicators used in this experiment. The colors observed were:

Methyl violet: violet	Congo red: violet
Thymol blue: yellow	Bromcresol green: yellow
Methyl yellow: orange	

   What is the approximate pH of the solution? _____

3. The pH of a 0.10 M HCN solution is 5.2.

   What is the $[H^+]$? _____

   What is the $[CN^-]$? _____

   What is the K_a? _____

4. Formic acid, HFor, has a K_a value of 1.8×10^{-4}. You need to prepare a buffer having a pH of 3.40 from 0.10 HFor and a 0.10 M NaFor solution. How many mL of the NaFor solution should you add to 20 mL of the 0.10 M HFor to make your buffer?

   _____ mL

5. When five drops of 0.10 M NaOH were added to 20 mL of the buffer in question 4, the pH went from 3.39 to 3.42. Write a net ionic equation to explain why the pH did not go up much higher:

Experiment 3

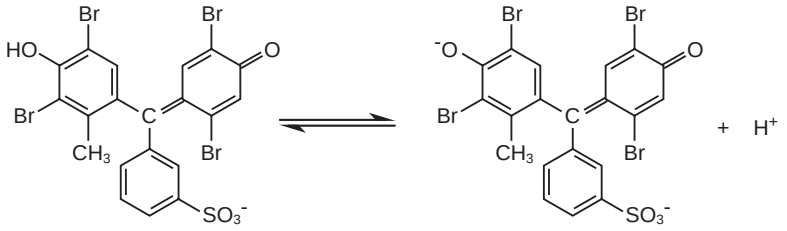
3

K_a of an Indicator

Introduction

In Experiment 2, you determined the acid dissociation constant of acetic acid from the pH of solutions of two different concentrations of acetic acid. In this experiment, you will determine the acid dissociation constant of acetic acid in a different (and usually more accurate) manner from the measured pH of acetic acid-acetate buffer solutions of known concentration.

You will also determine the acid dissociation constant of bromcresol green, a commonly-used indicator for acid-base titrations. Bromcresol green changes from yellow in acidic solutions to blue in basic solutions, and this color change can be used to signal the equivalence point of an acid-base titration. The structures of the acid and base forms of bromcresol green are shown below:



Yellow (acid) form
HIn

Blue (base) form
In^-

Bromcresol green

The following notation will be used throughout this experiment:

Acetic acid = HAc = $HC_2H_3O_2$
Acetate ion = Ac^- = $C_2H_3O_2^-$

Bromcresol green (acid form) = HIn
Bromcresol green (base form) = In^-

You will determine the dissociation constant of bromcresol green by measuring the pH and the Absorbance of solutions containing both bromcresol green and the acetic acid-acetate buffer; as shown in the *Calculations* section, the absorbance can be used to determine the ratio of the concentrations of the acid and base forms of bromcresol green.

Experimental Procedure

(Wear your safety goggles while performing all experiments.)

Note: You will work with a partner on this experiment.

Note: Always measure the pH to ±0.01.

Preparation of solutions

First, obtain 25 mL of bromcresol green solution.

Solution A (bromcresol green indicator in acetic acid): Pipet into a 250-mL volumetric flask the following:

10.0 mL of 3.0×10^{-4} M bromcresol green solution
25.0 mL of 1.60 M acetic acid (HAc)
10.0 mL of 0.200 M KCl solution

Dilute the solution to the mark, mix the solution, and pour it into a 250-mL Erlenmeyer flask.

Note: The KCl serves to maintain a constant ionic strength (essentially, the total concentration of ions in the solution). Equilibrium constants in ionic solutions depend to some extent on the ionic strength of the solution and, for accurate work, it is necessary to maintain constant ionic strength.

Solution B (bromcresol green indicator in sodium acetate solution): Rinse the 250-mL volumetric flask with distilled water, then pipet into it the following:

10.0 mL of 3.0×10^{-4} M bromcresol green solution
10.0 mL of 0.160 M sodium acetate solution

Dilute the solution to the mark, mix the solution, and pour it into a 400-mL beaker.

Standardize the pH meter

Use the instructions in Appendix I. Measure the pH of Solution B, and record the pH.

Absorption spectrum of the base (In^-) form of bromcresol green

Use the Spectronic 20 spectrometer to determine the absorption spectrum of Solution B (the sodium acetate solution of the indicator, a solution in which the indicator will be in its base form). Directions for the use of the Spectronic 20 may be found in Appendix H. Use distilled water as the blank. Read the Absorbance every 20 nm over the range 380–660 nm. The absorbance spectrum can be plotted with the Graphical Analysis computer software (instructions will be provided).

After completing measurement of the spectrum, redo the measurement of the absorbance at the wavelength of maximum *absorption* (λ_{max}). Record the result. (This check is done to make sure

the wavelength has been accurately set before you go on to the next step.)

Pour the solution from the cuvet back into the beaker; do not throw out any of the solutions used for absorbance measurements until the end of the experiment.

Measurement of pH and % Absorbance

Pipet 5.0 mL of Solution A (the acetic acid-indicator mixture) into the beaker containing Solution B. Mix the resulting solution, then measure both the pH and the absorbance of the solution at the wavelength λ_{max}. Record the results.

Use the answer to *Prelab Exercise* question 2c to determine how much solution A must be added to make solution B equimolar in acetate (Ac^-) and acetic acid (HAc). When this amount of solution A has been added to solution B, go on to determine the absorption spectrum for this solution.

Measure pH and absorbance for three additional 5.0 mL additions of Solution A, recording the results. After each measurement of the absorbance, *pour the solution from the cuvet back into the beaker*. Do not dispose of the solution. Before each measurement of the absorbance, rinse the cuvet by pouring the solution from the beaker back and forth several times into the cuvet (this procedure ensures that the solution in the cuvet has the same composition as the solution in the beaker).

Absorption Spectrum of acid (HIn) + base (In^-) forms bromcresol green

Measure the absorbance every 20 nm over the range 380–660 nm of the solution that is equimolar in acetate (Ac^-) and acetic acid (HAc) as in Step 3. Record the data, and graph the absorption spectrum. After measuring this spectrum, check to be sure that the absorbance at the wavelength λ_{max} has not changed significantly; that is, that you have returned the wavelength setting exactly to λ_{max}.

Absorption Spectrum of acid (HIn) form of bromcresol green

After the five additions of Solution A (a total of 25.0 mL), add 1.0 mL of 6 M HCl, record the pH, and measure the absorption spectrum over the range 380–660 nm. This spectrum will be that of the indicator in its yellow—its acid—form. Record the absorbance at λ_{max} and graph the absorption spectrum using the provided software.

Waste Disposal: Dispose of all solutions in the waste container provided in the laboratory.

Calculations

The acid dissociation constants K_{HAc} for acetic acid and K_{HIn} for the indicator bromcresol green are, respectively,

$$K_{HAc} = \frac{[H^+]\,[Ac^-]}{[HAc]} \qquad (1)$$

$$K_{HIn} = \frac{[H^+]\,[Ac^-]}{[HIn]} \qquad (2)$$

Using the Henderson-Hasselbalch equation [see experiment 17], these can be written as (see Prelab Assignment question 2(a)) :

$$pK_{HAc} = pH + \log \frac{[HAc]}{[Ac^-]} \qquad (3)$$

$$pK_{HIn} = pH + \log \frac{[HIn]}{[In^-]} \qquad (4)$$

In order to determine $pK_{HAc} = -\log K_{HAc}$ and $pK_{HIn} = -\log K_{HIn}$ one needs to know that $pH = -\log[H^+]$ and that the ratios of the concentrations of the acid and base forms of each species. In this experiment, the ratio $[HAc]/[Ac^-]$ is determined by calculating the relative concentrations of acetic acid and acetate present

in each solution (that is, after each addition of the acetic acid-indicator solution). The ratio [HIn]/[In^-] will be determined from the spectrophotometric data (that is, the absorbance of the solution after each addition of the acetic acid-indicator solution).

I. K_{HAc} for Acetic Acid.

When Solution A is added to Solution B, the resulting solution is an acetic acid-acetate buffer solution. This can be expressed as:

$$pK_{HAc} = pH + \log \frac{N_{HAc}}{N_{Ac^-}} \qquad (5)$$

where N_{HAc} and N_{Ac-} are the number of moles of HAc and Ac^- present in the solution. By calculating N_{HAc} and N_{Ac-} and measuring the pH, one can determine pK_{HAc}.

Use your pH data and the equation above to calculate five values for K_{HAc}, one for each addition of the acetic acid-indicator solution. Average the results to obtain a best value, and calculate the value of K_{HAc} corresponding to this average value.

Notes:

1. If one of your calculated values differs greatly from the others, exclude that value from the average. See a Teaching Assistant if it is difficult to tell if a value is discordant.

2. The value you calculate will be different from the literature value for K_{HAc} mainly because of the effect of the ionic composition (that is, the ionic strength of the solution).

3. Before any of Solution A has been added it is possible to treat the solution as a solution of the weak base Ac^-. Use the pH of this solution to calculate the base dissociation constant of Ac^- (see your T.A. for help), and from that value calculate the acid dissociation constant K_{HAc}. Note that small amounts of acidic impurities in Solution B make such calculated values less accurate than those determined from the buffer solutions obtained after addition of Solution A.

II. K_{HIn} for Bromcresol Green.

From the equations above you can see that pK_{HIn} can be determined from the pH of the solution and the ratio [HIn]/[In^-]. This ratio is determined using your data and Beer's law:

$$\text{Absorbance} = A = \epsilon\, b\, c$$

The absorbance of a solution containing both HIn and In^- can be expressed as the sum of the absorbances of the two species:

$$A = \epsilon_{HIn}\, b\, [HIn] + \epsilon_{In-}\, b\, [In^-]$$

where ϵ_{HIn} is the absorption coefficient of the acid form HIn, ϵ_{In-} is the absorption coefficient of the base form In^-, and b is the path length.

Also, the total concentration of indicator (C) can be expressed as

$$C = [HIn] + [In^-] \qquad (7)$$

The details of the analysis/derivation

The original solution of indicator in sodium acetate (Solution B) is sufficiently basic that essentially all the indicator is in the In^- form. Thus the Absorbance (A_b) of this solution can be written as

$$A_b = \epsilon_{In-}\, b\, C \qquad (8)$$

The final solution after addition of the HCl is sufficiently acidic that essentially all the indicator is in the HIn form. Thus the Absorbance (A_a) of this solution can be written as

$$A_a = \epsilon_{HIn}\, b\, C \qquad (9)$$

Substituting and rearranging these equations yields [see Prelab Question 2(b)]:

$$A = A_a \frac{[HIn]}{[C]} + A_b \frac{[In^-]}{[C]} \qquad (10)$$

We can also derive an equation to give the ratio

$$\frac{[HIn]}{[In^-]} = \frac{[A_b - A]}{[A - A_a]} \qquad (11)$$

Consequently, from the absorbances of the base form (A_b), the acid form (A_a), and a solution containing both one can calculate the ratio [HIn]/[In^-]. (Note: for this experiment, the absorbances are determined at the wavelength λ_{max} in order to maximize the change in absorbance during the experiment. Other wavelengths could also have been used.)

Use the equations above and the Report Sheet page to calculate five values for pK_{HIn}, one after each addition of the acetic acid-indicator solution. Determine an average value for pK_{HIn} (exclude obviously discordant values), and calculate the value of K_{HIn} corresponding to this average value for pK_{HIn}.

3 K_a of an Indicator

Report Sheet

Name _____

Time _____

M T W R F

Spectra of Bromcresol Green
Attach graph of Absorbance vs. Wavelength

Wavelength* (nm)	Blue (base) Form (Solution B)	Green Form (equimolar acetate-acetic acid)	Yellow (acid) Form (after Solution A and HCl addition)
	Absorbance	Absorbance	Absorbance
380			
400			
420			
440			
460			
480			
500			
520			
540			
560			
580			
600			
620			
640			
660			

Wavelength of maximum Absorbance of base form of bromcresol green λ_{max} = _____ nm

Experiment 3 Report Sheet

N_{Ac} = moles acetate present in solution B _____ mole Ac^- Molarity HAc in Solution A _____ M HAc

mL Soln A added	pH	Absorbance at λ max.	NHAc = moles $HC_2H_3O_2$ present	$\frac{N_{HAc}}{N_{Ac^-}}$	$\log\frac{N_{HAc}}{N_{Ac^-}}$	pK_{HAc}*	$\frac{[HIn]^{**}}{[In^-]}$	$\log\frac{[HIn]}{[In^-]}$	pK_{HIn}***
0.0		A_b =	X	X	X	X	X	X	X
5.0		A =							
10.0		A =							
15.0		A =							
20.0		A =							
25.0		A =							
25.0 + 1 mL HCl		A_a =	X	X	X	X	X	X	X

Average pK_{HAc} _____ Corresponding K_{HAc}

Average pK_{HIn} _____ Corresponding K_{HIn}

*See Equation (5) **See Equation (11) ***See Equation (4)

3 K_a of an Indicator

Report Sheet

Name

Time

M T W R F

Questions

Answer the questions below and turn in this page with your Report for the experiment.

1. The wavelength at which the absorbance of the blue (base) form of bromcresol green is equal to the absorbance of the yellow (acid) form is called an *isosbestic* point.
   a. What was the wavelength of the isosbestic point in your experiment? _____ nm

   b. As the pH changes, how will the absorbance change at the wavelength of the isosbestic point?

2. In the experiment, the solutions contained the acid-base pair HIn and In^- as well as HAc and Ac^-. However, in the calculations it was assumed that HIn and In^- made no contribution to the pH of the solution. Why is this assumption justified?

3. In the calculations it was assumed that:
   a. Before any acetic acid was added, essentially all the indicator was in the In^- form.
   b. After the HCl was added, essentially all the indicator was in the HIn form.

   Justify these assumptions using the measured pH of these solutions and your experimental value for pK_{HIn} to determine:

   a. The fraction of the indicator in the HIn form in Solution B before any of Solution A was added.

      Answer: _____

   b. The fraction of the indicator in the In^- form after the HCl was added.

      Answer: _____

K_a of an Indicator

3

PreLab

Name

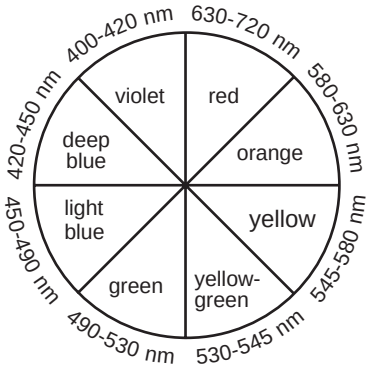
Time

M T W R F

1. Complete the following table to estimate the wavelength of bromcresol green under the following conditions.

   Recall that the color of a solution as perceived by your eyes is the complement of the color of light absorbed by the solution. This means that if an object looks deep blue, it absorbs yellow light preferentially.

	Color observed	Complement color	Wavelength absorbed
Base form (In^-)			nm
Equimolar acid & base			nm
Acid form (HIn)			nm



2. Determine how many mL of solution A (acetic acid-indicator solution) must have been added to solution B (sodium acetate-indicator solution) if the resulting buffer solution is equimolar in acetate and acetic acid? You will need to refer to the Experimental Procedure to answer this question.

   a. Calculate moles Ac^- in solution B.

   _____ mol Ac^-

   b. Calculate the molarity of HAc in solution A.

   _____ M HAc

   c. Calculate volume of Solution A needed when the moles of Ac^- equals moles of HAc.

   _____ mL Soln A

3. K_{HAc} is approximately 2×10^{-5} under your experimental conditions. Use Equation (5) to estimate the pH after the first addition of 5 mL of Solution A.

   a. Calculate pK_a

   _____ pKa

   b. Calculate moles HAc in the 5 mL of solution A added to solution B

   _____ mol HAc

   c. Calculate moles Ac^- in solution B.

   _____ mol Ac^-

   d. Rearrange equation 5 to solve for pH.

   _____ pH

Experiment 4

4

Solubility Product

In this experiment we will be examining the solubilities of salts. We consider a *salt* to be an ionic compound, often comprised of a metal and a non-metal. We will consider a salt to be:

soluble if its solubility (molar concentration) is ≥ 0.1M,
slightly soluble if its solubility is between 0.01M and 0.1M,
insoluble if its solubility is < 0.01M.

We will primarily be concerned with the solubility of lead iodide, PbI_2. Lead iodide has an aqueous solubility of less than 0.002 moles per liter (at 20° C), making it an insoluble salt. The equation for the solution reaction of lead iodide is:

$$PbI_{2\,(s)} \rightleftharpoons Pb^{2+}{}_{(aq)} + 2\ I^{-}{}_{(aq)} \qquad (1)$$

We can write the expression for its equilibrium constant, K, as follows:

$$K = [Pb^{2+}]\ [I^{-}]^2 \qquad (2)$$

There is no denominator, since the only reactant is a pure solid and therefore does not appear in the expression for K. Since the equilibrium constant above corresponds to the dissolution of a slightly soluble or insoluble ionic compound in water, it is known as the ***solubility product,*** K_{sp}. We normally write K_{sp} values without units. In this experiment you will be determining the K_{sp} for lead iodide after spectrophotometrically measuring the molar solubility.

The equilibrium expressed in equation (1) will be established by two different methods. In the first part of the lab we will set up the equilibrium by mixing two solutions, one containing $Pb(NO_3)_2$ and the other containing KI. When these solutions are mixed, the Pb^{2+} and I^- ions in the solutions react to form PbI_2 and precipitation of PbI_2 occur until equation (2) is satisfied. Known volumes of standard solutions of $Pb(NO_3)_2$ and KI will be used. The concentration of I^- ions will be determined experimentally. Once the concentration of I^- ions is known, the concentration of Pb^{2+} can be determined from the stoichiometric relationship shown in equation (1). Finally we can determine the K_{sp} for lead iodide using equation (2).

The method of experimentally determining $[I^-]$ is rather simple. We will separate the solid PbI_2 from the solution. Next we will oxidize the I^- ions to I_2 with potassium nitrite (KNO_2). The concentration of the I_2 will be measured using a spectrophotometer.

In this experiment it is very important to distinguish between potassium nitrite (KNO_2) and potassium nitrate (KNO_3). In this experiment, KNO_3, potassium nitrate, is an "inert electrolyte" that does not participate in any reactions and serves mainly to maintain a constant ionic strength in the various solutions. That is, solubility products depend to some extent on the total concentration of ions in a solution, and maintaining a large and constant concentration of inert electrolytes minimizes such effects. KNO_2—potassium nitrite—acts to oxidize iodide ion (I^-) to molecular iodine (I_2). The oxidation reaction is

$$2\ NO_2^- + 2\ H^+ + 2\ I^- \rightarrow 2\ NO_{(g)} + 2\ H_2O + I_2 \qquad (3)$$

Experimental Procedure

(Wear your safety goggles while performing all experiments.)

Note: You will work with a partner on this experiment.

Before starting the experiment, turn on the Spectronic 20 and set the wavelength to 525 nm.

Preparation of Solutions

Tubes 1–4

Measure all volumes of reagents in this lab very carefully. First measure out approximately 35 mL of 0.0120 M $Pb(NO_3)_2$ in 0.20 M KNO_3 into a small beaker. To another small beaker add 30 mL 0.0300 M KI 0.20 M KNO_3 and, in a third beaker add 10 mL of 0.20 M KNO_3. Next label four centrifuge tubes 1 to 4. Pipet 5.00 mL of 0.0120 M $Pb(NO_3)_2$ in KNO_3 into the first four tubes. Add 2.00 mL of 0.0300 M KI in KNO_3 to tube #1. Add 3.00, 4.00, and 5.00 mL of 0.0300 M KI in KNO_3 to tubes #2, #3, and #4, respectively. (If you get confused, analyze the reagent table below.) Add enough 0.20 M KNO_3 to the first three tubes to bring the total volume of each tube to 10.00 mL. The amounts of each reagent in each tube is summarized below:

	Volume of Reagent Required		
Tube #	**0.0120 M $Pb(NO_3)_2$**	**0.0300 M KI**	**0.20 M KNO_3**
1	5.00	2.00	3.00
2	5.00	3.00	2.00
3	5.00	4.00	1.00
4	5.00	5.00	0.00

Cap each centrifuge tube and shake thoroughly. Shaking tubes 1–4 extensively is vital to establish the solid-solution equilibrium. You should shake the centrifuge tubes thoroughly during at least a 15-minute period. That is, shake the tubes for 1–2 minutes, do another part of the experiment for 3–4 minutes, shake the test tubes again, and so on for 15–20 minutes.

Note: Before proceeding, make sure each tube has been shaken for at least 15 minutes. Also, allow at least 4 minutes to let the solid settle.

Reference Solution (Blank)

Before proceeding you must make a reference (blank) solution for this experiment. Mix the following in one of the matched cuvets:

3.0 mL of 0.02 M KNO_2
3.0 mL of 0.20 M KNO_3
2 drops of 6 M HCl

Use this solution to set the 0 Absorbance reading on the spectrometer.

Determining the Absorbance of Solutions 1–4

Prepare a sample cuvet by by filling with 6.0 mL of distilled water, and marking the bottom of the meniscus with a marker provided by your Teaching Assistant. You will use this cuvet for your absorbance measurements so that the volume of liquid in the cuvet is the same for each sample.

Place test tube #1 in the centrifuge for about 2 minutes. If there are any solid particles or yellow color remaining in the liquid repeat the centrifuge step. After centrifugation, you will transfer 3.0 mL of supernatant liquid from the centrifuge tube to the marked cuvet. The precipitate is sticky, floats, and is difficult to transfer. The best way to transfer the liquid is with a Pasteur (disposable) pipet. Fill the marked cuvet with 3.0 mL of 0.02 M KNO_2 (potassium NITRITE!!!), 2 drops of 6 M HCl, and enough of the supernatant solution to reach the mark (very close to 3 mL).

Shake gently (to mix the reagents) and measure the absorbance of the solution as directed by your T.A. Be sure to remove all bubbles from the cuvet before reading the meter. Use the calibration curve (see the next section) to determine the $[I^-]$ that was in equilibrium with PbI_2.

Use this same procedure to analyze the solutions in test tubes #2 through #4. Be sure to use the marked cuvet for all absorbance measurements. Mix and make the measurement for each tube before you proceed to the next!

Preparation of calibration curve

In addition to the four centrifuge tubes listed above, two test tubes are to be prepared with the following mixtures:

Test Tube	0.012 M $Pb(NO_3)_2$ (mL)	0.030 M KI (mL)	0.20 M KNO_3 (mL)
#5	0.0	2.0	8.0
#6	0.0	3.0	7.0

There is no need to centrifuge or shake test tubes #5 and #6, because you are not establishing an equilibrium between solution and solid. Measure the absorbance of the mixtures in test tubes #5 and #6 by the following procedure. To the marked cuvet, add 3.0 mL of 0.02 M KNO_2 (potassium NITRITE!!!), 2 drops of 6 M HCl, and enough of the solution from one of the test tubes to reach the mark (very close to 3 mL). Shake gently (to mix the reagents) and measure the absorbance of the solution as directed by your T.A. Be sure to remove all bubbles from the cuvets before reading the meter.

By determining the absorbance of these two solutions, you will be able to plot your calibration curve (see last data page of this experiment). To construct this calibration curve (concentration vs. absorbance plot) draw a straight line from the origin (0 concentration, 0 Absorbance) through the two points determined by the I^- concentration and Absorbance of test tubes #5 and #6. From this calibration curve, you can determine the I^- concentration in tubes #1–#4. *Plot the calibration curve and show it to your Teaching Assistant before you leave the laboratory.*

Disposal of waste: Lead ion is toxic! When finished, pour all solutions and solids in the centrifuge tubes, test tubes and beakers into the appropriate waste container. Any solid still adhering to the centrifuge tubes, test tubes or beakers can be rinsed with a small amount of 6 M HCl, and the rinse added to the waste container. If the disposable pipets contain any precipitate, cut off the end containing the yellow solid and dispose in the designated container (NOT the waste container for liquids and solids!!!). Dispose of the *uncontaminated* end of the pipets in the regular trash. Anyone caught dumping these solutions down the drain will fail this experiment.

Solubility Product

4 Report Sheet

Name

Time

M T W R F

Tube #:	1	2	3	4	5	6
mL 0.0120M $Pb(NO_3)_2$						
mL 0.0300 M KI						
mL 0.20 M KNO_3						
Total Vol. (mL)						
Absorbance of soln.						
$[I^-]$ at equilibrium (M)						

4 Report Sheet

Solubility Product

Name

Time

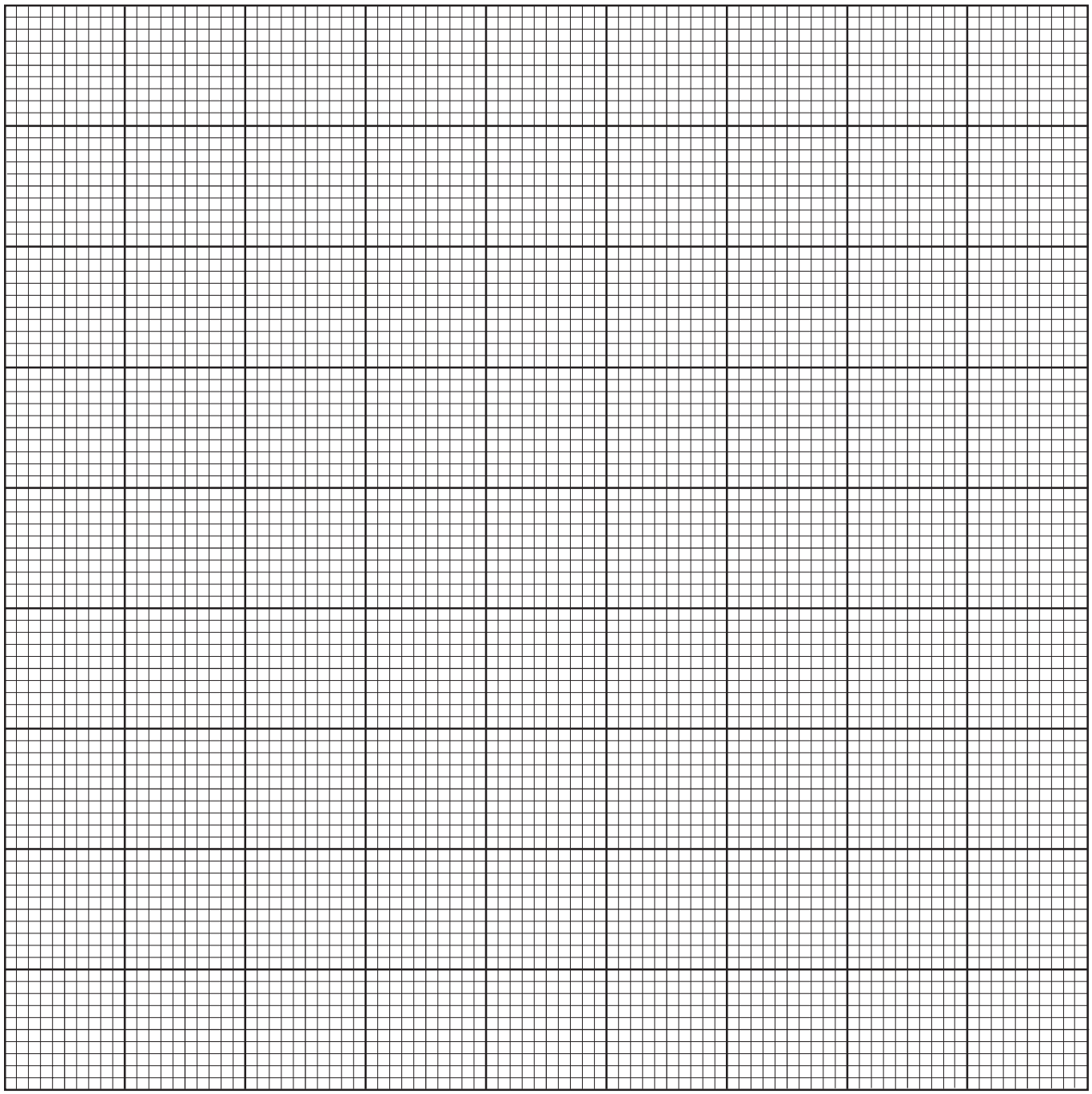
M T W R F

Calculations

	Tube Number					
	1	**2**	**3**	**4**	**5**	**6**
Initial moles of Pb^{2+} ($\times 10^{-5}$)						
Initial moles of I^- ($\times 10^{-5}$)						
Equilibrium moles of I^- ($\times 10^{-5}$)						
Precipitated moles of I^- ($\times 10^{-5}$)						
Precipitated moles of Pb^{2+} ($\times 10^{-5}$)						
Equilibrium moles of Pb^{2+} ($\times 10^{-5}$)						

$[Pb^{2+}]$ at Equilibrium					
K_{sp} PbI_2					
Average K_{sp} PbI_2					

Calibration Curve:



Solubility Product

4

PreLab

Name _____

Time _____

M T W R F

1. Write the equation for the solubility product for lead iodide:

   Explain the meaning of this equation (in words):

2. A student mixed 5.00 mL of 0.0120 M $Pb(NO_3)_2$ with 5.00 mL of 0.0300 M KI and observed a yellow precipitate.

   a. What is the molecular formula of the precipitate? _____

   b. How many moles of Pb^{2+} are present initially? (moles = M · V) _____

   c. How many moles of I^- are present initially? _____

   d. The concentration of I^- at equilibrium is experimentally determined to be 8.0×10^{-3} M.

      How many moles of I^- are present in the solution (10 mL)? _____

e. How many moles of I^- precipitated? (You have already determined how many moles were present initially and how many remained in solution.)

_____

f. How many moles of Pb^{2+} remain in solution? _____

g. What is the concentration of Pb^{2+} in the equilibrium solution? _____ M
(The equilibrium solution is still 10 mL.)

h. Determine K_{sp} of PbI_2 from this data. Show all work. _____

Experiment **5**

5

Determination of Water Hardness

Water that contains magnesium and/or calcium ions in solution is known as *hard water* because these ions react with soap (sodium stearate) to prevent the formation of a lather. Thus these ions interfere with the cleansing action of the soap.

The "softening" of hard water refers to the removal of the magnesium and calcium ions from solution. If the hard water contains enough bicarbonate (HCO_3^-) ion, it may be softened by one of these processes:

Boiling:

$$Ca^{2+} + 2\ HCO_3^- \rightarrow CaCO_3 + H_2O + CO_2$$

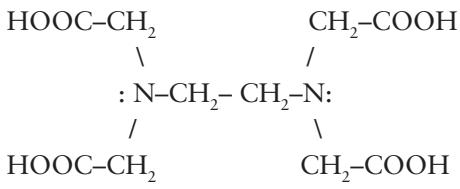
Treatment with slaked lime:

$$Ca^{2+} + 2\ HCO_3^- + Ca(OH)_2 \rightarrow 2\ CaCO_3 + H_2O$$

Water that contains at least two moles of bicarbonate ion for every magnesium or calcium ion to be removed is called *temporary hard water*. If the water contains less HCO_3^-, it is called *permanent hard water*. This type of water may be softened by the addition of soda ash, sodium phosphate, or borax. These agents remove the magnesium and calcium ions by precipitating them as carbonates, phosphates, or borates, respectively.

Hard water cannot be used in boilers—the magnesium and calcium ions precipitate from the boiling water onto the walls of the boiler tubes, forming what is referred to as "boiler scale". The boiler scale reduces the heat transfer properties of the tubes and may even cause them to blow out.

Water hardness is the total concentration of Ca^{2+} and Ca^{2+} ions in water, and is commonly expressed as the number of milligrams of $CaCO_3$ in 1.00 L of water [the same as parts per million (ppm) of $CaCO_3$; 1 milligram (10^{-3} gram) in 1000 g = 1 part in 10^6]. Thus, if $[Ca^{2+}] + [Mg^{2+}] = 1 \times 10^{-3}$ M, we would say that the hardness is 100 mg $CaCO_3$ per liter, or 1 ppm. Water hardness may be determined by titration with a chelating agent (such as EDTA, ethylenediaminetetraacetic acid). EDTA is a chelating agent that can lose four protons:



Conditions can be controlled so that EDTA can complex metal ions in a 1:1 mole ratio. The calcium EDTA complex is shown in Figure 5.1.

In this experiment you will standardize a solution of EDTA by titration against a standard solution of calcium carbonate ($CaCO_3$). Next you will use the standardized EDTA solution to determine the water hardness of an unknown sample. Calmagite can be used as an indicator to detect the end point of the titration. An indicator is necessary because both the EDTA and Ca^{2+} are colorless. Calmagite complexes with magnesium to form $MgIn^-$, which is a wine-red color (In is used to denote indicator). A small amount of the complex will be present in the solution during the titration. As EDTA is added, it will complex with the magnesium and calcium ions and leave the $MgIn^-$ complex alone until essentially all of the magnesium and calcium ions have been converted to chelates. It is at this point that the [EDTA] begins to increase enough to displace Mg^{2+} from the $MgIn^-$ complex. The indicator reverts to its acid form, which is sky blue (and signals the end point of the titration).

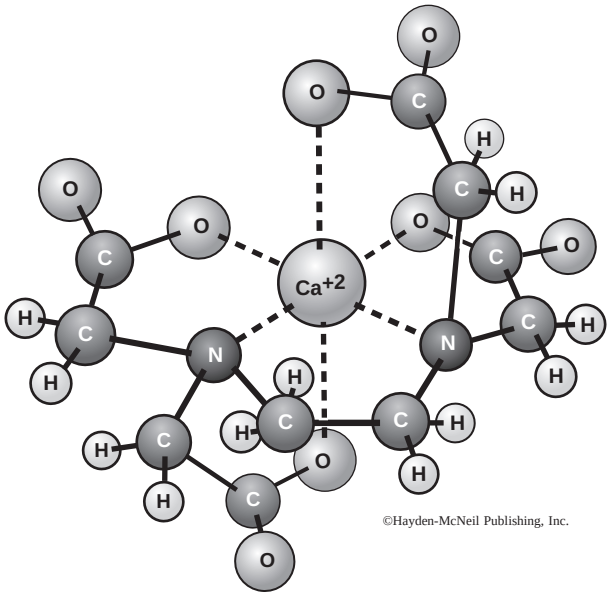


Figure 5.1. Calcium Ethylenediaminetetraacetate Complex

If we designate H_4Y and H_3In as the formulae for EDTA and calmagite, respectively, then the equations for the reactions occuring during the titration are:

main reaction:

$HY^{3-}_{(aq)} + Ca^{2+}_{(aq)} \rightarrow CaY^{2-}_{(aq)} + H^{+}_{(aq)}$
(and same for Mg^{2+})

reaction at end point:

$HY^{3-}_{(aq)} + MgIn^{-}_{(aq)} \rightarrow MgY^{2-}_{(aq)} + HIn^{2-}_{(aq)}$

Note that at the higher pH values under which this reaction will be carried out, the EDTA exists predominately in the partially deprotonated form HY^{3-} rather than as H_4Y.

Experimental Procedure

(Wear your safety goggles while performing all experiments.)

Note: You will work with a partner on this experiment.

Weigh 0.350–0.400 g (+/0.001 g) of calcium carbonate into a clean, dry beaker. Do not use more than 0.400 g calcium carbonate.

Part A: Standardization of Solution

Add 25 mL of distilled water to your large beaker and then, *slowly*, add about 40 drops of 6 M HCl. Cover the beaker with a watch glass and let the reaction continue until all of the carbonate has dissolved. Rinse the walls of the beaker down with distilled water (from wash bottle) and heat the solution until it begins to boil. Add 50 mL of distilled water to the beaker and transfer the solution to the 250-mL volumetric flask (use your stirring rod as a "pathway"). Rinse your beaker and watch glass several times with small portions of distilled water (be sure to transfer these to the flask). Next fill the volumetric flask to the horizontal mark with distilled water (add the last drops slowly using a 1-mL disposable pipet). Stopper the flask and mix the solution thoroughly. Mixing is best achieved by inverting the flask at least 20 times.

Clean your buret thoroughly and dispense about 300 mL of the stock EDTA solution from the carboy into a dry 400-mL beaker. Rinse your buret with a 5–10 mL mL of the EDTA solution at least three times. Drain this solution and then fill the buret with EDTA solution.

You will need to make a blank. Add 25 mL of distilled water and 5 mL of the pH 10 buffer to a 250-mL Erlenmeyer flask. Add 8 drops of calmagite indicator. The solution should now be blue. If the color is faint, add a little more indicator. Next add 15 drops of 0.03 M $MgCl_2$, which should be enough Mg^{2+} to turn the solution wine-red. Read the buret to 0.02 mL (it is not necessary to start at 0.00 mL!!!). Add EDTA solution until the last of the purple color disappears. Titrate slowly near the end point, as the color change is somewhat slow. Only a few mL are necessary to titrate the blank. Read the buret again and determine the volume needed for the blank. Since this is your blank, you must subtract this volume from the total volume used in each titration. Save the solution as a reference for the end point for future titrations.

Pipet three 25-mL aliquots (small test portions) of the Ca^{2+} solution in the volumetric flask into clean 250-mL flasks. Add 5 mL of the pH 10 buffer to each flask, followed by 8 drops of indicator, and 15 drops of 0.03 M $MgCl_2$. Titrate the solution in one of the flasks until its color matches your reference solution. Read the buret. Titrate the other two flasks in the same manner.

Part B: Determination of Water Hardness

Check out a sample of water for hardness analysis. Since the concentration of Ca^{2+} is probably lower than that in the standard calcium solution you prepared, pipet 25 mL aliquots of the water sample for each titration. Be sure to add 8 drops of indicator, 5 mL of pH 10 buffer, and 15 drops of 0.03 M $MgCl_2$ before titrating. Carry out titrations until you obtain three volumes that agree within 2%. If the volume of EDTA required is low (because the water is not very hard) increase the volume of the sample. It should take at least 20 mL of EDTA to reach the end point.

Waste: Pour all waste into the collection container.

Determination of Water Hardness

5 Report Sheet

_____
Name

_____
Time

M T W R F

Mass of $CaCO_3$ sample _____ g

Vol. Ca^{2+} solution prepared _____ mL

Molarity of Ca^{2+} _____ M

Moles of Ca^{2+} in each aliquot titrated _____ mol

Number of moles of $CaCO_3$ in sample (M.W.= 100.1 g/mol) _____ mol

Standardization of EDTA Solution

Determination of blank:

Initial reading: _____ mL Final reading: _____ mL Vol. of blank _____ mL

Titration:	1	2	3
Initial reading (mL)			
Final reading (mL)			
Volume of EDTA (mL)			
Vol. used in blank (mL)			
Vol. used to titrate Ca^{2+}(mL)			
Avg. vol. EDTA (mL)			
Molarity of EDTA (M)			

(Note: Molarity of EDTA = (no. moles Ca^{2+} in aliquot × 1000) / (avg. vol. EDTA in mL)

Determination of Water Hardness

5 Report Sheet

Name _____

Time _____

M T W R F

Determination of Water Hardness (continued)

Titration:	1	2	3
Vol. water used (mL)			
Initial reading (mL)			
Final reading (mL)			
Vol. EDTA (mL)			
Vol. EDTA for blank (mL)			
Vol. EDTA required to titrate water (mL)			
Avg. vol. EDTA *per liter* of water (mL)			

(Note: No. moles $CaCO_3$ per liter of water = No. moles EDTA per liter of water)

No. grams $CaCO_3$ per liter of water _____ g

Water Hardness (1 ppm = 1 mg/L) _____ ppm $CaCO_3$

Unknown # _____

Some helpful notes:

"Avg. vol. EDTA per liter of water" is obtained by dividing the average volume of EDTA by the unknown sample volume (in liters) used in each trial:

$$= \frac{\text{average mL EDTA}}{\text{mL unknown sample}} \times \frac{1000\ \text{mL}}{\text{L}}$$

The "Water hardness" you report is the number of *mg* $CaCO_3$ per liter of water (calculated from the "No. grams $CaCO_3$ per liter water").

Determination of Water Hardness

5

Prelab

Name _____

Time _____

M T W R F

1. A 0.5100 g sample of $CaCO_3$ is dissolved in 12 M HCl and the resulting solution is diluted to 250.0 mL in a volumetric flask.
   a. How many moles of $CaCO_3$ are used (M.W.= 100.1 g/mol) _____ mol

   b. What is the molarity of the Ca^{2+} in the 250 mL of solution? _____ M

   c. How many moles of Ca^{2+} are in a 25.0 mL aliquot of the soln in b.? _____ mol

2. 25.00 mL aliquots of the solution in problem 1 are titrated with EDTA to the calmagite end point. A blank containing a small measured amount of Mg^{2+} requires 2.50 mL of the EDTA to reach the end point. An aliquot to which the same amount of Mg^{2+} is added requires 28.55 mL of the EDTA to reach the end point.
   a. How many mL of EDTA are needed to titrate the Ca^{2+} ion in the aliquot? _____ mL

   b. How many moles of EDTA are there in the volume obtained in a.? _____ mol

   c. What is the Molarity of the EDTA solution? _____ M

3. A 100 mL sample of hard water is titrated with the EDTA solution in problem 2. The same amount of Mg^{2+} is added, and the volume of EDTA required is 22.51 mL.
   a. What is the volume of EDTA used in titrating the Ca^{2+}? _____ mL

   b. How many moles of EDTA are there in that volume? _____ mol

   c. How many moles of Ca^{2+} are there in 100 mL of water? _____ mol

Experiment **6**

6

Voltaic Cells

Oxidation-reduction reactions are characterized by electron transfer: the species that is oxidized loses electrons, and the species that is reduced gains them. If the electrons that are lost during the oxidation are allowed to flow through a wire and reduce another species, then the redox reaction has produced an electric current that can do useful work. Electrochemical cells can either produce electricity (voltaic cells) or use electricity to make non-spontaneous reactions go (electrolytic cells).

In this experiment we will be working with voltaic cells, also referred to as galvanic cells. Part of the cell must contain the oxidation half-reaction, and another part must contain the reduction half-reaction.

As an example, imagine two beakers, one containing a $FeSO_4$ solution and a piece of Fe metal, and the other containing a $CuSO_4$ solution and a piece of Cu metal. The solution in the beakers contain *electrolytes,* thus electric current will be able to flow through them by the migration of ions (in this case Fe^{2+} and Cu^{2+} cations and SO_4^{2-} anions). The pieces of metal immersed in these solutions are called *electrodes*. An electrode and its electrolytic solution constitute a *half-cell*. One half of the cell will be the oxidation half of the reaction, and the other half will be the reduction half. A metal wire is connected to the two electrodes to connect the two half-cells. This wire will conduct the electrons flowing from the electrode at which oxidation occurs (the *anode*) to the electrode where the reduction occurs (the *cathode*). For all types of electrochemical cells, *the electrode at which oxidation occurs is called the anode, and the electrode at which reduction occurs is called the cathode*. A good way to remember this is to realize that oxidation and anode both begin with vowels, while reduction and cathode both begin with consonants.

In order to keep the current flowing, we need to complete the circuit. This can be accomplished by connecting the two solutions with a *salt bridge*. (A salt bridge is usually a U shaped tube containing an aqueous solution of electrolyte, with porous plugs at the end.) For this experiment, our salt bridge will simply be a semi-permeable paper strip between the two half-cells which provides a way for ions to migrate through the solution and thus forms a complete circuit (the main function of a salt bridge).

How does our voltaic cell work? We observe that the Fe electrode begins to dissolve: it is serving as the anode. The Fe metal is being oxidized to Fe^{2+} ions which go into solution:

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2\ e^- \qquad (1)$$

The electrons lost by this oxidation leave the anode and travel through the conducting wire to the cathode. When Cu^{2+} ions in solution strike the Cu electrode, they are reduced to Cu metal by the electrons flowing into that electrode:

$$Cu^{2+}_{(aq)} + 2\ e^- \rightarrow Cu_{(s)} \qquad (2)$$

As more and more Fe^{2+} ions go into solution in the anodic half-cell, anions from the salt bridge are attracted to that cell, neutralizing the positive charge there. At the same time Cu^{2+} ions are reduced in the cathodic half-cell, and that solution is left with a negative charge (due to the overabundance of SO_4^{2-} ions). Consequently, cations from the salt bridge are attracted into the copper half-cell in order to maintain electrical neutrality. If it weren't for the ions in the salt bridge moving into their respective solutions, the electrical current would quickly die out. Note that in the solutions and salt bridge, anions are attracted to the anode, and cations are attracted to the cathode.

Thus a voltaic cell is composed of the following components: the anode and its electrolyte, the cathode and its electrolyte, and the salt bridge (or membrane for the migration of ions). The following notation (called a *cell diagram*) is used to quickly describe a cell:

anode | ionic species in solution in anodic half-cell ‖ ionic species in solution in cathodic half-cell | cathode

The single vertical lines separate the electrodes from the ions in solution, and the double vertical lines represent the salt bridge (normally a series of vertical dots is used if a membrane or a porous plug is used in place of a U tube). The cell diagram for our cell would look like this:

$$Fe \mid Fe^{2+} \parallel Cu^{2+} \mid Cu$$

The cell shown above may also be written as $Fe,Fe^{2+} \parallel Cu^{2+},Cu$.

Electrochemical Potentials

Let's examine another oxidation-reduction reaction:

$$Zn_{(s)} + Pb^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Pb_{(s)}$$

The half reactions are shown below:

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2\ e^- \quad \text{oxidation}$$

$$Pb^{2+}_{(aq)} + 2\ e^- \rightarrow Pb_{(s)} \quad \text{reduction}$$

The voltage of this cell can be considered to be the sum of the potential of the oxidation half cell and the reduction half cell:

$$E_{cell} = E_{Zn,\,Zn^{2+}} + E_{Pb^{2+},Pb} \qquad (1)$$

oxid. rxn. red . rxn.

The negative electrode in a voltaic cell is (by convention) taken to be the one at which oxidation occurs. The reduction reaction of $H^+_{(aq)}$ was arbitrarily assigned a potential of 0.0000 V, so that other electrode potentials can be determined.

$$H^+_{(aq)} + 2\ e^- \rightarrow H_{2\,(g)}$$
$$E°_{H^+,\,H_2} = 0.0000\ V \text{ (assigned value)}$$

The measured potential for the $Zn,Zn^{2+} \parallel H^+,H_2$ cell is 0.76 V:

$$Zn_{(s)} + 2\ H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2\,(g)}$$
$$E^\circ_{cell} = 0.76\ V$$

Because the reduction of $H^+_{(aq)}$ is 0.0000 V (and the E_{cell} is the sum the oxidation and reduction half-reactions), the potential for the oxidation reaction, $E°_{Zn,\ Zn^{2+}}$, must be 0.76 V. If the potential for a half-reaction is known, the potential for the reverse reaction can be obtained by simply changing the sign:

$$\textit{if } E°_{Zn,\ Zn^{2+}} = +\ 0.76\ V \ldots$$
$$\textit{then } E°_{Zn^{2+},\ Zn} = -\ 0.76\ V$$

Effects of Concentrations of Solute Species

The effect of solute ion concentrations can also be investigated. For a cell (at 25°):

$$aA_{(s)} + bB^+_{(aq)} \rightarrow cC_{(s)} + dD^{2+}_{(aq)}$$

the cell potential, E_{cell}, can be calculated according to:

$$E_{cell} = E^\circ_{cell} - 0.0592/n \cdot \log\left([D^{2+}]^d / [B^+]^b \right) \qquad (2)$$

where E°_{cell} is a constant associated with each particular reaction (called the standard cell potential), and n is the number of electrons involved in either half-reaction. From this equation it is apparent that if the molarities of D^{2+} and B^+ are equivalent or both are unity, then the measured cell potential, E_{cell}, will equal the standard cell potential, E°_{cell}. In fact, we can carry out experiments under these conditions so that the cell potentials we observe are very close to the standard potentials in the tables in your chemistry text.

Addition of Complexing and Precipitating Species

Consider the $Cu,Cu^{2+} \parallel Ag^+,Ag$ cell. This can be written out as:

$$Cu_{(s)} + 2\ Ag^+_{(aq)} \rightarrow 2\ Ag_{(s)} + Cu^{2+}_{(aq)} \qquad (3)$$

Equation (2) can now be applied to get the following:

$$E_{cell} = E^\circ_{cell} - 0.0592 / 2 \cdot \log\left([Cu^{2+}] / [Ag^+]^2 \right) \qquad (4)$$

If we were to decrease the $[Cu^{2+}]$, while keeping $[Ag^+] = 1$ M, the potential of the cell would go up by about 0.03 volts (0.0592/2) for every factor of ten by which we decrease $[Cu^{2+}]$. It is not convenient to change concentrations of ions by several orders of magnitude, so concentration effects in cells are negligible.

In the first part of this experiment you will measure the voltages for several cells. You will then calculate the potentials for many half reactions (by arbitrarily assigning a value of 0.0000 V to a particular half-reaction). You will add a complexing agent (NH_3) to decrease the $[Cu^{2+}]$ shown in reaction (3). Equation (4) will then be used to calculate the $[Cu^{2+}]$, which should be very low.

In a similar experiment you will be determining the solubility product of AgCl. Here you will be surrounding the Ag electrode in a $Cu,Cu^{2+} \parallel Ag^{+},Ag$ cell with a solution of known $[Cl^{-}]$ (saturated with AgCl). The value of $[Ag^{+}]$ will be determined using equation (4).

In two experiments you will be changing the concentration of cations (Cu^{2+} and Ag^{+}). In the first case, Cu^{2+} is in equilibrium with $Cu(NH_3)_4^{2+}$ and NH_3. Using the measured cell potential, we can calculate $[Cu(NH_3)_4^{2+}]$ and $[NH_3]$.

In the last experiment you will have an equilibrium system containing Ag^{+}, Cl^{-}, and $AgCl_{(s)}$. You will use the cell potential to find $[Ag^{+}]$. You know the $[Cl^{-}]$, so you can very easily calculate K_{sp} for AgCl:

$$AgCl_{(s)} \rightleftharpoons 2Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$$
$$K_{sp} = [Ag^{+}]\,[Cl^{-}] \qquad (5)$$

Experimental Procedure

(Wear your safety goggles while performing all experiments.)

Note: You will work with a partner for this experiment.

Voltage Measurements

Check out a pH/millivolt meter and a set of electrodes.

Voltage measurements will be made using solutions in a "Carrou-Cell" and the pH/millivolt meter set to read the cell potential in millivolt (mV; 1000 mV = 1 V). Directions for use of the pH meter for millivolt measurements are in Appendix I.

The procedure using the Carrou-Cell is as follows (refer to Figure 6.1 below):

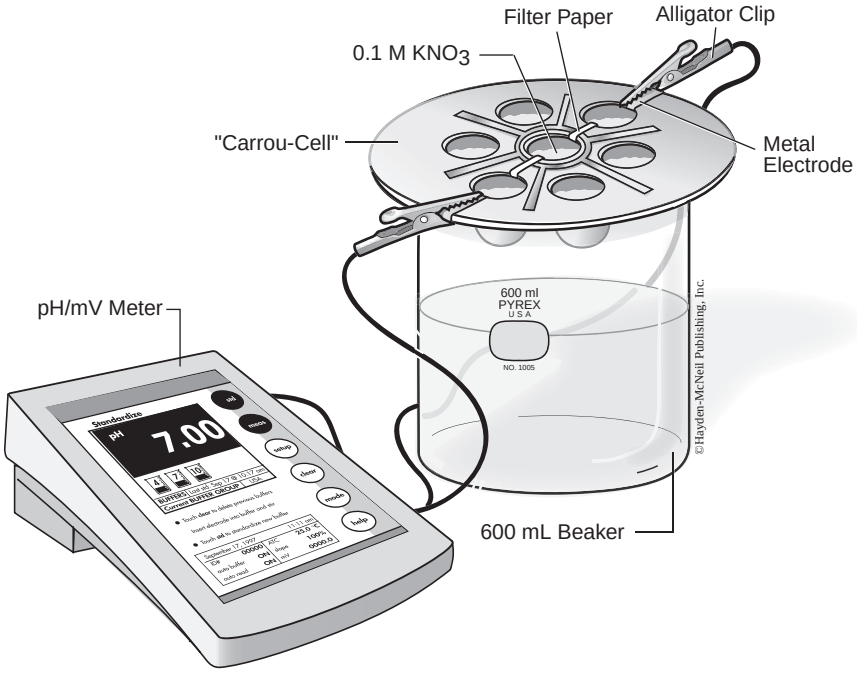


Figure 6.1

1. Fill the center well with 0.1 M KNO_3.

2. Cut several strips of filter paper and wet them with 0.l M KNO_3 on a watch glass.

3. Fill the outer wells with the solutions of interest, then connect the outer wells to the central well with the damp strips of filter paper. Make sure the filter paper does not dry out while you are making measurements.

4. Put the electrodes into the solutions (a metal or platinum as appropriate), and attach the alligator clips from the pH meter to the electrodes.

   The wire with a *black tip is the negative (–) terminal*, at which oxidation occurs for a spontaneous reaction (the overall cell potential will be positive for a voltaic cell).

   The wire with a *red tip is the positive (+) terminal*, at which reduction occurs. Be sure to record which metal/solution is used for the negative and positive terminals for each cell measured—if you don't, you'll get hopelessly lost attempting to do the calculations for the experiment.

   Make sure that the alligator clips do not contact the liquid solutions.

5. Measure the cell potential. Remember that for a spontaneous redox reaction, such as a voltaic cell, the cell potential will be positive. Therefore if the voltage indicated on the meter is not positive, simple reverse the leads (and be sure to note which electrode is positive and which is negative).

A. Cell Potentials

1. At your desk, construct the following electrode systems in four of the outer wells of your Carrou-Cell:

   Ag^+, $Ag_{(s)}$ [electrode = Ag wire]
   Cu^{2+}, $Cu_{(s)}$ [electrode = Cu (s) strip]
   Fe^{3+}, Fe^{2+} [electrode = Pt wire]
   Zn^{2+}, $Zn_{(s)}$ [electrode = Zn (s) strip]

   The solute concentrations may be assumed to be 1 M, and the corresponding cell potentials will be essentially the standard cell potentials.

   Measure the cell potentials for each pair of these cells (six pairs total). Again, make sure that you record which electrode is positive and which is negative in each measurement.

2. The following four electrode systems will be set up in a Carrou-Cell in the hood (the vapors of the halogens are unpleasant):

   Fe^{3+}, Fe^{2+} [electrode = Pt wire]
   Cl_2, Cl^- [electrode = Pt strip]
   Br_2, Br^- [electrode = Pt wire]
   I_2, I^- [electrode = Pt strip]

   Using the same procedure, measure the cell potentials for each pair of these cells (six total). Once again, make sure you record which electrode is positive and which is negative in each measurement.

B. Effect of Concentration on Cell Potentials

1. **Complex ion formation.** At your desk, set up the Cu^{2+}, $Cu_{(s)}$ and Ag^{+}, $Ag_{(s)}$ electrode systems in two of the outer wells, but only half-fill the Cu^{2+} well with about 2 mL of the Cu^{2+} solution. Measure the potential of the cell, with the Ag as the positive electrode. While you are measuring the cell potential, add 2 mL of 6 M NH_3 to fill the well, stirring the solution with a stirring rod. Measure the cell potential when it becomes steady.

   Is the change in the direction that you expected?

2. **Determination of the solubility product of AgCl.** At your desk, set up the Cu^{2+}, $Cu_{(s)}$ electrode system in one of the outer wells. Fill another of the outer wells with 1 M KCl. Add 1 drop of $AgNO_3$ to the well containing KCl, stir the mixture with a stirring rod, insert your Ag wire electrode, and measure the potential of this electrode system relative to the Cu^{2+}, $Cu_{(s)}$ system. Compare the cell potential to that obtained using 1 M Ag^{+} in Part A.

   Is the change in the direction that you expected?

Waste Disposal: Dispose of all solutions in the waste container provided in the laboratory. Make sure you remove all solid material when you clean the Carrou-Cell.

Voltaic Cells 6 Report Sheet

Name _____

Time _____

M T W R F

A. Cell Potentials

	Electrode System Used:	Cell Potential E°_{cell}, volts	Negative Electrode:	Oxidation Reaction:	$E^\circ_{oxidation}$, volts	Reduction Reaction:	$E^\circ_{reduction}$, volts
1							
2							
3							
4							
5							
6							
7							

Calculations

1. Write the oxidation reaction in each of the cells (oxidation occurs at the negative pole in a cell). Write the reduction reaction (other electrode).

2. Assign a value of 0.00 V for $E°_{Ag^+, Ag}$. Enter this value into the table for all of the silver electrode systems you used in your cells.

3. Calculate E°_{cell} for all the electrode systems in which the Ag, Ag^+ system was involved. Exploiting the fact that $E^\circ_{oxidation} = -E^\circ_{reduction}$, complete the table of E° values. The best way to do this is to use one of the E° values you found in another cell with that electrode system. That potential, along with E°_{cell}, will allow you to find the potential of the other electrode.

B. Electrode Potentials

The table above should be complete. Knowing that $E^\circ_{red} = -E^\circ_{oxid}$, find the value for E°_{red} for each system. List those potentials in the left column of the table below *in order of decreasing value*. The usual assumption is that $E°_{H^+,H_2}$ = 0.00 V, under which conditions $E°_{Ag^+,Ag}$. = 0.80V. Add 0.80 V to the values in the first column to obtain $E°_{Ag^+,Ag}$.(third column).

$E°_{reduction}$ ($E°_{Ag^+,Ag}$ = 0.00 V)	Electrode Reaction (in reduction!!!)	$E°_{reduction}$ ($E°_{H^+,H_2}$ = 0.00 V)

Voltaic Cells 6 Report Sheet

Name _____

Time _____

M T W R F

C. Effects of Concentration on Cell Potentials

1. **Complex Ion formation:**

   Potential, E°_{cell} before adding 6 M NH_3 _____ V

   Potential, E_{cell} after $Cu(NH_3)_4^{2+}$ formed _____ V

   Use Equation (4) to calculate the residual concentration of free Cu^{2+} ion in equilibrium with $Cu(NH_3)_4^{2+}$ in the solution. Take $[Ag^+] = 1$ M.

   _____ M

2. **Solubility product of AgCl:**

   Potential, E°_{cell} of the $Cu,Cu^{2+} \parallel Ag^+,Ag$ cell:

   _____ V Negative Electrode: _____

   Potential, E_{cell} with 1 M KCl present:

   _____ V Negative Electrode: _____

Using Equation (4), calculate $[Ag^+]$ in the cell, where it is in equilibrium with 1 M Cl^- ion. E_{cell} in Equation (4) is the *negative* of the measured value if the polarity is not the same as the standard cell.) Take $[Cu^{2+}]$ to be 1 M.

_____ M

Since Ag^+ and Cl^- are in equilibrium with AgCl, find K_{sp} for AgCl from the $[Ag^+]$ and $[Cl^-]$ (which you now know). Write the expression for K_{sp} for AgCl and determine its value.

Expression: K_{sp} = _____

K_{sp} = _____

6 Voltaic Cells

Prelab

Name

Time

M T W R F

A student measures the potential of a cell made up with 1 M $CuSO_4$ in one solution and 1 M $AgNO_3$ in the other. There is a copper electrode in the $CuSO_4$ and a silver electrode in the $AgNO_3$. The student finds the potential of the cell, $E°_{cell}$ to be 0.45 V, and that the copper electrode is negative.

1. At which electrode is oxidation occurring?

2. Write the half-reaction for the oxidation reaction:

3. Write the reaction for the reduction reaction:

4. What is the value of the potential for the oxidation reaction, $E°_{Cu, Cu^{2+}}$, given that the potential of the silver, silver ion electrode, $E°_{Ag^+, Ag}$, is taken to be 0.0000 V?

_____ V

5. If $E°_{Ag^+, Ag}$ equals 0.80 V, what is the value of the potential of the oxidation reaction of copper, $E°_{Cu, Cu^{2+}}$?

_____ V

6. Write the net ionic equation for the reaction that occurs in the cell studied by the student:

7. The student adds 6 M NH_3 to the $CuSO_4$ solution until the Cu^{2+} ion is essentially all converted to $Cu(NH_3)_4^{2+}$ ion. The cell voltage, E_{cell}, increases to 0.92 V and the copper electrode is still negative. Find the concentration of Cu^{2+} ion in the cell (use Equation (4)).

_____ M

8. In part (7) the $[Cu(NH_3)_4^{2+}]$ is about 0.05 M and $[NH_3]$ is about 3 M. Given these values and the $[Cu^{2+}]$ from part (7), calculate K for the reaction:

$$Cu(NH_3)_4^{2+}{}_{(aq)} \rightleftharpoons Cu^{2+}{}_{(aq)} + 4\ NH_{3(aq)}$$

K = _____

Experiment 7

7

Complexes of Cu(II) Ion

REFERENCE: Ebbing, pages 1011–1019.

In aqueous solution, typical cations, particularly those produced from atoms of the transition metals, do not exist as free ions but rather consist of the metal ion in combination with some water molecules. Such cations are called complex ions. The water molecules, usually two, four, or six in number, are bound chemically to the metallic cation, but often rather loosely with the electrons in the chemical bonds being furnished by one of the unshared electron pairs from the oxygen atoms in the H_2O molecules. Copper ion in aqueous solution may exist as $Cu(H_2O)_4^{2+}$ with the water molecules arranged in a square around the metal ion at the center.

If a hydrated cation such as $Cu(H_2O)_4^{2+}$ is mixed with other species that can, like water, form coordinate covalent bonds with Cu^{2+}, those species, called ligands, may displace one or more H_2O molecules and form other complex ions containing the new ligands. For instance, NH_3, a reasonably good coordinating species, may replace H_2O from the hydrated copper ion, $Cu(H_2O)_4^{2+}$, to form $Cu(H_2O)_3NH_3^{2+}$, $Cu(H_2O)_2(NH_3)_2^{2+}$, $Cu(H_2O)(NH_3)_3^{2+}$, or $Cu(NH_3)_4^{2+}$. At moderate concentrations of NH_3, essentially all the H_2O molecules around the copper ion are replaced by NH_3 molecules, forming the copper ammonia complex ion $Cu(NH_3)_4^{2+}$.

Coordinating ligands differ in their tendencies to form bonds with metallic cations, so that in a solution containing a given cation and several possible ligands, an equilibrium will develop in which most of the cations are coordinated with those ligands with which they form

the most stable bonds. There are many kinds of ligands, but they all share the common property that they possess an unshared pair of electrons that they can donate to form a coordinate covalent bond with a metal ion. In addition to H_2O and NH_3, other uncharged coordinating species include CO and ethylenediamine; some common anions that can form complexes include OH^-, Cl^-, CN^-, SCN^-, and $S_2O_3^{2-}$.

When solutions containing metallic cations are mixed with other solutions containing ions, precipitates are sometimes formed. When a solution of 0.1 M copper nitrate is mixed with a little 1 M NH_3 solution, a precipitate forms and then dissolves in excess ammonia. The formation of the precipitate helps us to understand what is occurring as NH_3 is added. The precipitate is hydrous copper hydroxide, $Cu(OH)_2(H_2O)_2$, formed by reaction of the hydrated copper ion with the small amount of hydroxide ion present in the NH_3 solution. The fact that this reaction occurs means that even at very low OH^- ion concentration $Cu(OH)_2(H_2O)_2(s)$ is a more stable species than $Cu(H_2O)_4^{2+}$ ion.

Addition of more NH_3 causes the solid to redissolve. The copper species then in solution cannot be the hydrated copper ion. (Why?) It must be some other complex ion and is, indeed, the $Cu(NH_3)_4^{2+}$ ion. The implication of this reaction is that the $Cu(NH_3)_4^{2+}$ ion is also more stable in NH_3 solution than is the hydrated copper ion. To deduce in addition that the copper ammonia complex ion is also more stable in general than $Cu(OH)_2(H_2O)_2(s)$ is not warranted, since under the conditions in the solution $[NH_3]$ is much larger than $[OH^-]$, and given a higher concentration of hydroxide ion, the solid hydrous copper hydroxide might possibly precipitate even in the presence of substantial concentrations of NH_3.

To resolve this question, you might proceed to add a little 1 M NaOH solution to the solution containing the $Cu(NH_3)_4^{2+}$ ion. If you do this you will find that $Cu(OH)_2(H_2O)_2(s)$ does indeed precipitate. We can conclude from these observations that $Cu(OH)_2(H_2O)_2(s)$ is more stable than $Cu(NH_3)_4^{2+}$ in solutions in which the ligand concentrations (OH^- and NH_3) are roughly equal.

The copper species that will be present in a system depends, as we have just seen, on the conditions in the system. We cannot say in general that one species will be more stable than another; the stability of a given species depends in large measure on the kinds and concentrations of other species that are also present with it.

Another way of looking at the matter of stability is through equilibrium theory. Each of the copper species we have mentioned can be formed in a reaction between the hydrated copper ion and a complexing or precipitating ligand; each reaction will have an associated equilibrium constant, which we might call a formation constant for that species. The pertinent formation reactions and their constants for the copper species we have been considering are listed here:

$$Cu(H_2O)_{4\,(aq)}^{2+} + 4\ NH_{3\,(aq)} \rightleftharpoons Cu(NH_3)_{4\,(aq)}^{2+} + 4\ H_2O \qquad K_1 = 5 \times 10^{12} \qquad (1)$$

$$Cu(H_2O)_{4\,(aq)}^{2+} + 2\ OH^-_{(aq)} \rightleftharpoons Cu(OH)_2(H_2O)_{2\,(S)} + 2\ H_2O \qquad K_2 = 2 \times 10^{19} \qquad (2)$$

The formation constants for these reactions do not involve $[H_2O]$ terms, which are essentially constant in aqueous systems and are included in

the magnitude of K in each case. The large size of each formation constant indicates that the tendency for the hydrated copper ion to react with the ligands listed is very high.

In terms of these data, let us compare the stability of the $Cu(NH_3)_4^{2+}$ complex ion with that of solid $Cu(OH)_2(H_2O)_2$. This is most readily done by considering the reaction:

$$Cu(NH_3)_4^{2+}{}_{(aq)} + 2\ OH^-{}_{(aq)} + 2\ H_2O \rightleftharpoons Cu(OH)_2(H_2O)_{2\ (S)} + 4\ NH_3\ (aq) \qquad (3)$$

We can find the value of the equilibrium constant for this reaction by noting that it is the sum of Reaction 2 and the reverse of Reaction 1. By the Law of Multiple Equilibria, K for Reaction 3 is given by the equation

$$K = \frac{K_2}{K_1} = \frac{2 \times 10^{19}}{5 \times 10^{12}} = 4 \times 10^6$$

$$\frac{[NH_3]^4}{[Cu(NH_3)_4^{2+}]\ [OH^-]^2} \qquad (4)$$

From the expression in Equation 4 we can calculate that in a solution in which the NH_3 and OH^- ion concentrations are both about 1 M.

$$[Cu(NH_3)_4^{2+}] = \frac{1}{4 \times 10^6}$$

$$2.5 \times 10^{-7}\ M \qquad (5)$$

Since the concentration of the copper ammonia complex ion is very, very low, any copper(II) in the system will exist as the solid hydroxide. In other words, the solid hydroxide is more stable under such conditions than the ammonia complex ion. But that is exactly what we observed when we treated the hydrated copper ion with ammonia and then with an equivalent amount of hydroxide ion.

Starting now from the experimental behavior of the copper ion, we can conclude that since the solid hydroxide is the species that exists when copper ion is exposed to equal concentrations of ammonia and hydroxide ion, the hydroxide is more stable under those conditions, and the equilibrium constant for the formation of the hydroxide is larger than the constant for the formation of the ammonia complex. By determining, then, which species is present when a cation is in the presence of equal ligand concentrations, we can speak meaningfully of stability under such conditions and can rank the formation constants for the possible complex ions, and for precipitates, in order of their increasing magnitudes.

Experimental Procedure

(Wear your safety goggles while performing all experiments.)

In your lab notebook, prepare a data table identical to the one in the Report Sheet.

1. Obtain two plastic well plates (6 × 8).

2. Position the two plates side-by-side on top of a piece of white paper, so that there are 12 columns and 8 rows.

3. Add 6 drops of 0.1 M $Cu(NO_3)_2$ to every other well in the first six rows. This will leave every other column of wells empty to aid in avoiding contamination of adjacent wells.

4. Be careful when adding solutions to the well plate, to avoid spilling any into an adjacent well.

5. To all of the odd-numbered wells in row 1, add 6 drops of 1 M NH_3.

6. To all of the odd-numbered wells in row 2, add 6 drops of 1 M NaCl.

7. To all of the odd-numbered wells in row 3, add 6 drops of 1 M NaOH.

8. To all of the odd-numbered wells in row 4, add 6 drops of 1 M $K_2C_2O_4$.

9. To all of the odd-numbered wells in row 5, add 6 drops of 1 M Na_2HPO_4.

10. To all of the odd-numbered wells in row 6, add 6 drops of 0.1 M Na_2S.

11. For each of the following steps, indicate a change by placing a C in the data table followed by the solution's color. Indicate if a precipitate is present and note its color. If no change occurs, indicate this by placing an NC in the data table.

12. To all the wells in **column 1, add 6 drops of 1 M NH_3**. Mix each well using a stirring rod. *Be sure to clean the stirring rod before placing it in a new well.* Note whether the solution changes color or a precipitate forms upon this addition. Record observations and the formula of the stable copper complex in the data table.

13. To all the wells in **column 2, add 6 drops of 1 M NaCl**. Mix each well using a stirring rod. *Be sure to clean the stirring rod before placing it in a new well.* Record observations and the formula of the stable species (copper complex) in the data table.

14. To all the wells in **column 3, add 6 drops of 1 M NaOH.** Mix each well using a stirring rod. *Be sure to clean the stirring rod before placing it in a new well.* Record observations and the formula of the stable species in the data table.

15. To all the wells in **column 4, add 6 drops of 1 M $K_2C_2O_4$**. Mix each well using a stirring rod. *Be sure to clean the stirring rod before placing it in a new well.* Record observations and the formula of the stable species in the data table.

16. To all the wells in **column 5, add 6 drops of 1 M Na_2HPO**. Mix each well using a stirring rod. *Be sure to clean the stirring rod before placing it in a new well.* Record observations and the formula of the stable species in the data table.

17. To all the wells in **column 6, add 6 drops of 1 M Na_2S**. Mix each well using a stirring rod. *Be sure to clean the stirring rod before placing it in a new well.* Record observations and the formula of the stable species.

18. Given your entries in the table, you should be able to decide on the relative stabilities of the six Cu(II) species studied in this experiment. List the six species, in order of increasing stability.

19. Obtain an unknown from your TA. Your unknown will contain a ligand which is not present in any of the known solutions. The ligand will form a soluble complex or a precipitate when combined with Cu(II) ion. You will be asked to determine the stability of the resulting complex or precipitate compared to the known complexes.

20. To every other well in the **7th row**, place 6 drops of 0.1 M $Cu(NO_3)_2$ and 6 drops your unknown ligand. Mix the contents of each cell thoroughly. Record the color of the solution and any precipitate that may form. The remainder of this procedure refers to the wells of the 7th row ONLY.

21. To the **first well, add 6 drops of 1 M NH_3.** Mix thoroughly using a stirring rod. *Be sure to clean the stirring rod before placing it in a new well.* Record observations in the data table in your notebook.

22. To the **third well, add 6 drops of 1 M NaCl.** Mix thoroughly using a stirring rod. *Be sure to clean the stirring rod before placing it in a new well.* Record observations in the data table in your notebook.

23. To the **fifth well, add 6 drops of 1 M NaOH.** Mix thoroughly using a stirring rod. *Be sure to clean the stirring rod before placing it in a new well.* Record observations in the data table in your notebook.

24. To the **seventh well, add 6 drops of 1 M $K_2C_2O_4$.** Mix thoroughly using a stirring rod. *Be sure to clean the stirring rod before placing it in a new well.* Record observations in the data table in your notebook.

25. To the **ninth well, add 6 drops of 1 M Na_2HPO_4.** Mix thoroughly using a stirring rod. *Be sure to clean the stirring rod before placing it in a new well.* Record observations in the data table in your notebook.

26. Finally, to the **eleventh well add 6 drops of 1 M Na_2S.** Mix thoroughly using a stirring rod. Record observations in the data table in your notebook.

27. From the data obtained from the unknown, determine its position in the stability list.

28. **Empty the contents of all of the wells into the waste container. Be sure to rinse any remaining residues with water and pour the rinse into the waste container. The well plate should be placed in the appropriate container.**

7 Report Sheet

Complexes of Copper(II) Ion

Name

Time

M T W R F

A. Table of Observations (summarized from your notebook data)

	NH_3	Cl^-	OH^-	$C_2O_4^{2-}$	PO_4^{3-}	S^{2-}
NH_3						
Cl^-						
OH^-						

A. Table of Observations (continued)

	NH_3	Cl^-	OH^-	$C_2O_4^{2-}$	PO_4^{3-}	S^{2-}
$C_2O_4^{2-}$						
PO_4^{3-}						
S^{2-}						
Unknown						

7 Report Sheet

Complexes of Copper(II) Ion

Name

Time

M T W R F

B. Relative Stabilities of Copper(II) Complexes

In each row of your table of observations you can compare the stabilities of species involving the ligand in the horizontal row with those of the species containing the ligand initially added. For example, in the first row of the table, the copper (II)–NH_3 species is observed to be more stable than some of the species obtained by addition of other ligands, and less stable than others. After examining each row, make a list of all the complex ions and precipitates you have in the table, in order of increasing stability and formation constant.

		Reasons
Lowest ↓		
Highest		

C. Stability of Unknown

Indicate the position your unknown would occupy in the above list.

Reasons:

Unknown no. _____

Complexes of Copper(II) Ion

7

Prelab

Name

Time

M T W R F

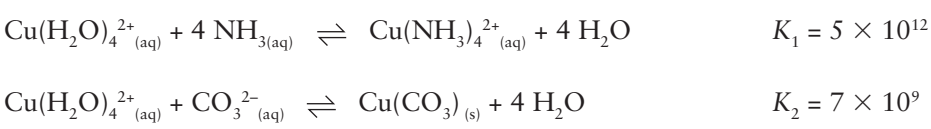
1. In testing the relative stabilities of Cu(II) species a student adds 2 mL of 1 M NH_3 to 2 mL of 0.1 M $Cu(NO_3)_2$. She observes that a light blue precipitate initially forms, but that in excess NH_3 the precipitate dissolves and the solutions turns deep blue. Addition of 2 mL of 1 M NaOH to the dark blue solution results in formation of a light blue precipitate.

   a. What is the formula of the Cu(II) species in the dark blue solution?

   b. What is the formula of the light blue precipitate present after addition of 1 M NaOH?

   c. What species is more stable in equal concentrations of NH_3 and OH^-, the one in Part a or the one in Part b?

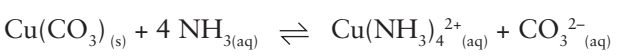
2. Given the following two reactions and their equilibrium constants:



$$Cu(H_2O)_4^{2+}{}_{(aq)} + 4\ NH_{3(aq)} \rightleftharpoons Cu(NH_3)_4^{2+}{}_{(aq)} + 4\ H_2O \qquad K_1 = 5 \times 10^{12}$$

$$Cu(H_2O)_4^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightleftharpoons Cu(CO_3)_{(s)} + 4\ H_2O \qquad K_2 = 7 \times 10^{9}$$

a. What is the equilibrium constant for the reaction (see discussion):



$$Cu(CO_3)_{(s)} + 4\ NH_{3(aq)} \rightleftharpoons Cu(NH_3)_4^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)}$$

K_3 = _____

b. If 1M NH_3 were added to some solid $CuCO_3$ in a test tube containing 1M Na_2CO_3, what, if anything, would happen? Explain your reasoning.

Appendix **A**

A

The Laboratory Notebook and Reports

One of the major objectives of the chemistry laboratory program is for you to observe events and to record your observations accurately and concisely in a laboratory notebook. For this course, you will use a bound laboratory notebook with tear-out carbons or carbonless duplicate pages (available from the campus Bookstore). This laboratory manual has Report Sheets for each experiment. However, you are not to write on the Report Sheet during lab. ENTER ALL DATA IN YOUR LABORATORY NOTEBOOK.

Guidelines for keeping a good lab notebook:

(a) Leave a few pages at the beginning for an index. Keep the index current.

(b) Put your name and the date at the top of each page.

(c) Use a ball point pen when making lab notebook entries (ordinary ink can be made illegible by a water spill; pencil does not provide a valid record because it can be erased). Always make a carbon copy.

(d) Make corrections by drawing a single line through the entry. Never obliterate a lab notebook entry–even wrong data may be useful later.

(e) Do not attempt to keep data on loose sheets of paper for later, leisurely entry into your notebook. Such papers will be confiscated and destroyed by your TA. Many students seem to feel it is really important to have a neat, tidy lab book. This they might try to

accomplish by entering data on random bits of paper to be recopied (wrongly?) after the lab period. At UCR we want data entered immediately and correctly in the lab book during the lab. We aren't concerned with prettiness; we want accurate, readable data where they belong. This is your record of your work.

What Is Required in the Notebook?

To judge what should go into the notebook, ask yourself, "If two years from now I should find this experiment had results which anticipated a patent worth $\$1.0 \times 10^9$, could I understand and reproduce all that I did two years before and prove in court that I had prior rights to the ideas?"

Using this criterion and remembering the purposes of keeping the lab notebook, namely,

(a) to be properly prepared for doing the lab safely and efficiently through your pre-lab write-up,

(b) to have a self-contained complete record of what you did so you can complete your report, and

(c) to have an understandable record of how you analyzed your data and came to your conclusions, you will need to have at least the following in your lab notebook:

(1) Before the lab–a statement in your own words of the goal of the experiment (*Purpose*), an outline of the *Procedure* you expect to follow, quantities of reagents you will need, and the precautions to observe. This should be complete enough so that you can use it as your plan in the lab rather than using the laboratory manual. You should also have a table of the data and observations you will need to record.

(2) During the experiment–you need to take down all the information and comments you will need to calculate and interpret your results without relying on memory, notes on scraps of paper, or your partner's help later. You will probably be writing comments about changes in procedures, observations, color changes, temperature changes, or things which went wrong in addition to filling in blanks with *data*. (If it's not in your notebook, it's not to be used in your report.) Important: do not fill in the Report Sheet(s) during the lab period; record all data directly in the lab notebook. **Turn in the copy of your *data* page(s) at the conclusion of the period; you will not receive any credit for the experiment if your *data* is not received.**

(3) After the lab–your notebook must show the actual reasoning and *Calculation* setups you used to get to your results and conclusions, that is, how you analyzed the data. It should also contain your explanations of what went wrong, and *Results and Conclusions*–your analysis of the results and a concluding statement. Attached to these will be the Report Sheet(s).

Your TA will periodically inspect your lab notebook and will make suggestions as needed. Your TA will form definite impressions of you as a student from what he or she sees in your notebook.

Laboratory Reports

The report for your experiment is due at the beginning of the next lab meeting and will be collected by the TA. The laboratory report on an experiment will consist of the following, stapled together:

(a) Filled-out Report Sheets for the experiment from the laboratory manual. You must tear out the pages and hand them in to your TA. You may also make photocopies of the blank Report Sheets and turn in the filled-in copies.

(b) Carbon copies of the pages in your laboratory notebook in which you carried out the *Calculations* and an analysis of the *Results* of the experiment, including an overall statement of *Conclusion* for the experiment.

Example Notebook Pages Including Purpose, Procedure, and Data

Page 1

Experiment 29: Density of a Metal

Ava Gadro
7/3/2003
Partner: John Dalton

PURPOSE: The purpose of this experiment is to determine the density of an unknown metal by measuring the mass and volume.

PROCEDURE:

A. Determining Volume of Flask

1. Weigh dry 25-mL flask and stopper to nearest 0.001 g.
2. Fill flask with distilled water to top of flask.
3. Stopper flask carefully to exclude air bubbles.
4. Dry outside of flask and reweigh (nearest 0.001 g).
5. Record temperature of water in the flask.

B. Determining Volume of Unknown Metal

1. Record number of unknown metal.
2. Dry flask used above and place metal sample in flask.
3. Weigh flask, stopper, and metal to nearest 0.001 g.
4. Fill the flask with distilled water.
5. Turn and gently tap flask to remove any air bubbles on surface of metal.
6. After bubbles are removed, stopper flask as above to exclude air bubbles.
7. Dry outside of flask and reweigh (nearest 0.001 g).
8. Record temperature of water in the flask.
9. Dry the flask and return it to the TA.

Experiment 29: Density of a Metal

Ava Gadro
7/3/2003
Partner: John Dalton

DATA:

A. Mass of empty flask + stopper	30.210 g
Mass of flask + stopper + liquid	60.602 g
Temperature of water	23.5°C
B. Unknown metal number	612
Mass of flask + stopper + metal	82.305 g
Mass of flask + stopper + metal + water	106.873 g

Appendix **B**

B

Preparation for Laboratory

It is essential that you come to the laboratory prepared for the experiment. If you are not prepared, it is likely that you will not finish the experiment and will receive little or no credit for it. You should read through the experiment before the lab period, and plan what you will do in the lab.

As part of your preparation for the laboratory work, you are required to do the following before coming to lab:

A. At the beginning of each lab period, you are to be prepared for a brief ***Quiz*** which will be given and graded by your TA. The quiz may cover:

   (1) The principles behind or the objectives of the day's experiment.

   (2) The principles behind the previous experiment.

   (3) The procedure for the day's experiment.

B. The *Purpose and Procedure* for the experiment will be outlined in your laboratory notebook. The *Purpose* consists of a brief (usually one or two sentences) statement, in your own words, of the goal of the experiment. The *Procedure* consists of the detailed steps you plan to follow in lab, written in the form of an outline. The level of detail in your outline must be sufficient to enable you to carry out the experiment *without the aid of your lab manual*. However, it is not acceptable to copy the procedure verbatim from the lab

manual. Anyone who has not completed the *Purpose and Procedure* prior to class will not be allowed to attend lab (and will not be allowed to make up the missed period).

C. The *Prelab Exercise (Prelab)* for the experiment. You may either fill out the Prelab and tear it from your lab manual, or make a photocopy of the blank Prelab and fill it out before submitting it to your TA.

At the beginning of lab, give your TA the Prelab and the carbon copies of the Purpose and Procedure from your lab notebook. At the end of lab period, hand in the carbon copies of your data and observations for the period from (your lab notebook). NOTE: photocopies or facsimiles of any of your lab work will not be accepted.

The table below summarizes the different components required for a complete experiment.

What	Where	When
Prelab Exercise	Prelab page(s) from lab manual	beginning of lab period
Purpose and Procedure	written in your lab notebook	*copy* turned in at the beginning of the lab period
Data	recorded in your lab notebook	*copy* turned in at the end of the lab period
*Report (*includes *Calculations* and *Results and Conclusions)*	Report Sheet(s) from lab manual; Calculations and Conclusion written in your lab notebook	the following lab period

Appendix C

Laboratory Equipment

You will be assigned a workstation in the laboratory. You are responsible for keeping the glassware and equipment clean and in good condition. This includes making certain that all items are put away at the end of the lab period. In addition to your station, you are responsible for keeping the common areas (those used by all students) of the lab clean. If you spill something at the balance, you should clean it up immediately. When using reagents, be sure to replace the caps on the containers when you are done. Paper towels should be disposed of in the trash bins, and not left on the benches, floor, or in the sinks. Broken glass should be discarded in the designated containers. If you are unsure what to do about something, bring it to the attention of your TA. Keeping the lab safe and in good order requires the cooperation of everyone in the class. Part of your grade (refer to the lab syllabus) will be based on how well you keep your lab area clean and safe.

Laboratory Equipment List

Refer to the equipment list to make sure you have the proper equipment in your drawer or locker.

Student Locker

6 - Beakers, 1 ea. 800, 600, 400, 250, 100, 30 or 50 mL
2 - brush, test tube, 1 x 1 3/8", 1 x 1/2"
2 - cylinders, graduated, 1 x 10 mL, 1 x 50 mL
4 - flasks, Erlenmeyer, 2 x 250 mL, 2 x 125 mL
1 - forceps
1 - funnel, short stem, 65 mm
1 - pipet, graduated, 10 mL (0.1 mL divisions)
1 - rack, test tube

1 - scoopula
1 - spatula (flat ends)
1 - stirring rod, glass w/policeman
2 - test tubes, Pyrex, 25 x 200 mm
6 - test tubes, 16 x 125 mm
6 - test tubes, 12 x 100 mm
1 - test tube holder, 5"
1 - thermometer, -20° to 110°C (alcohol)
2 - watch glasses
1 - wash bottle
1 - weighing boat
1 - safety goggles

Community Equipment

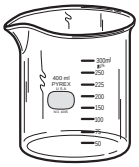
bunsen burners
buret clamp (on benchtop rod)
clamp
clamp holders
crucible tongs
"hot hands", hot glassware grip
ring, iron, 3"
tubing, flexible, amber (for burner)
tubing, flexible, black (for filtration)
wire gauze, 6" x 6"

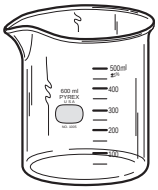
STUDENT LOCKER

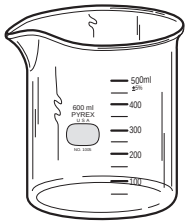

30ml or 50ml Beaker

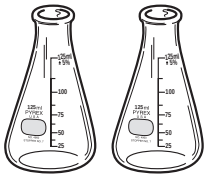

100ml Beaker

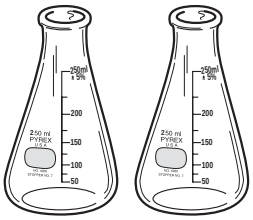

250ml Beaker

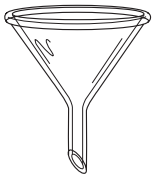

400ml Beaker

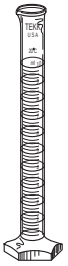

600ml Beaker

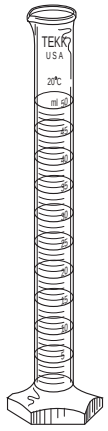

800ml Beaker


125ml Erlenmeyer Flask

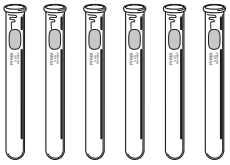

250ml Erlenmeyer Flask

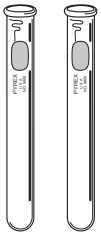

65 mm Short Stem Funnel

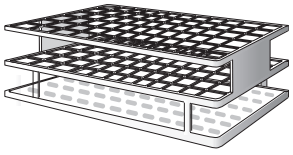

10ml Graduated Cylinder

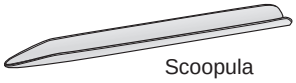

50ml Graduated Cylinder


Test Tubes 12 x 100 mm


Test Tubes 16 x 125 mm


Test Tubes Pyrex, 25 x 200 mm


Test Tube Rack


Scoopula


Test Tube Brush


Wash Bottle

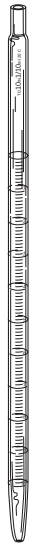

Test Tube Holder, 5"


Spatula


Glass Stirring Rod with Rubber policeman


Forceps


Weighing Boat

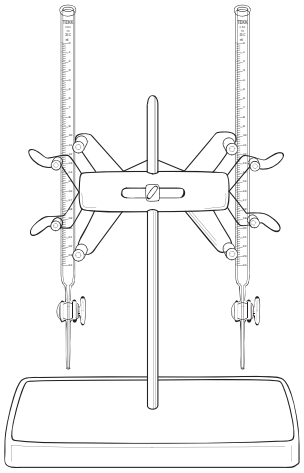

10ml Graduated Pipet


Watch Glass

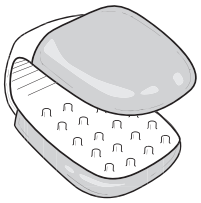

Safety Goggles


-20° to 100° C (alcohol) Thermometer

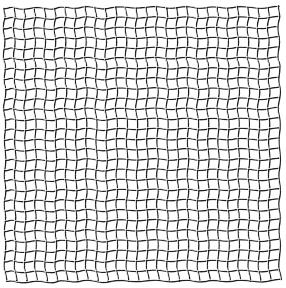
COMMUNITY EQUIPMENT



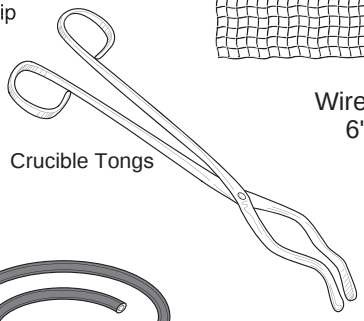
Buret Clamp



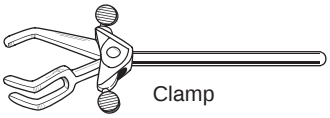
"Hot Hands"
Hot Glassware Grip



Wire Gauze
6" x 6"

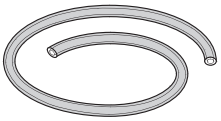


Crucible Tongs

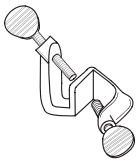


Clamp

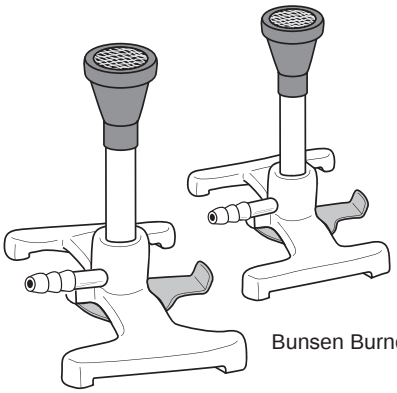
Flexible Tubing
Black (for filtration)



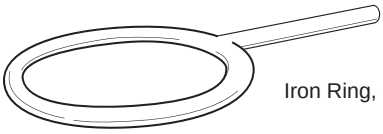
Flexible Tubing
Amber (for burner)



Utility Clamp
Holder



Bunsen Burners



Iron Ring, 3"

Appendix **D**

D

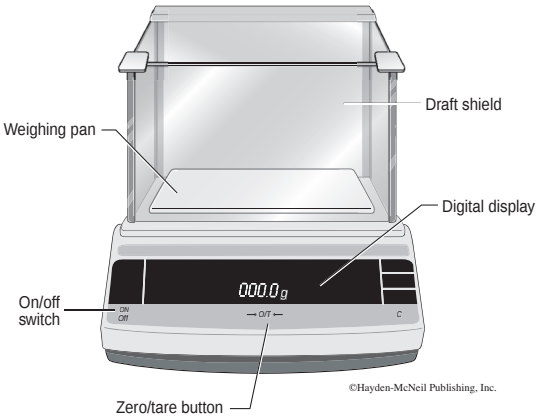
Laboratory Techniques

Using an Electronic Balance

An electronic balance, such as the one shown on the following page, directly measures the mass of an object placed on the weighing pan. The type of balance you will be using has a capacity of 200 g measurable in increments of 0.001 g.

To weigh a chemical, set the balance to zero and place a clean weighing vessel (weighing boat, beaker or flask) on the weighing pan. The mass of the empty vessel is called the *tare*. You can either record the tare so that it can later be used to calculate the mass of the chemical, or you can press the zero/tare button to set the tare to zero. Add the chemical to the vessel and read its new mass. If you used the tare button, the mass of the chemical will be displayed directly on the front display panel. Otherwise, subtract the mass of the vessel from the new mass to obtain the mass of the chemical you added.

In order to protect the sensitive components of the balance, *chemicals should never be placed directly on the weighing pan*. To weigh solids, use a spatula or scoopula to carefully add the material to the weighing vessel. Liquids should be weighed by transferring to the vessel with a pipet. Spills should be cleaned up immediately. Also, be sure to wear gloves or use forceps to handle any objects that you are weighing. If you don't, the oils from your fingertips will change the mass of the object - thus introducing errors in your measurements.

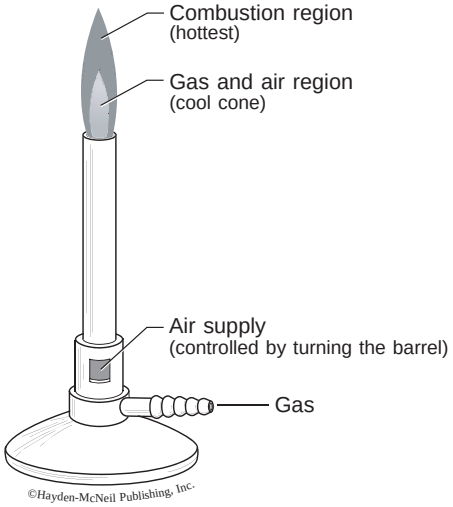


An Electronic Balance

Using a Bunsen Burner

Most heating in the laboratory is done with a Bunsen burner, in which natural gas (mostly methane, CH_4) is mixed with air and then burned.* The temperature of the flame and the total amount of heat produced are regulated by the supply of air and gas. The best flame for most laboratory purposes is relatively hot with a large proportion of air; it is blue and often makes a rustling noise.

*The burning reaction is
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ (+heat)



A Bunsen Burner

To light a Bunsen burner, simply turn on the gas supply (the burner may not light if the flow of gas is too great) and light the burner with a match. If it will not light, close the air-supply valve most of the way and light it. Adjust the air and gas supply to give the desired flame.

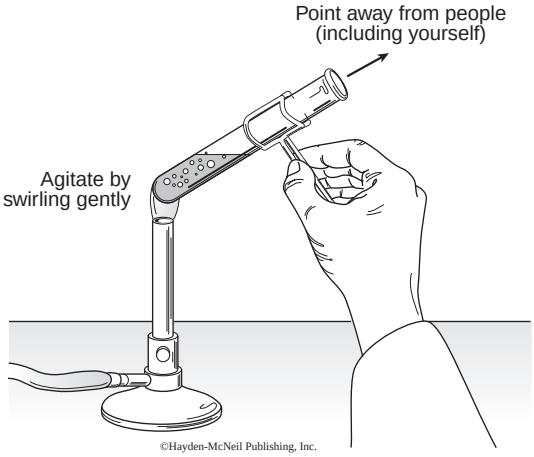
Heating Things

1. Test tubes

It is very difficult to heat liquids in a test tube without having them spatter. Hence a test tube that is being heated should never be pointed at anyone, and you should never look down into a hot test tube. The test tube to be heated should be no more than 1/4 full. Hold it at an angle, shake it, and hold the flame at the upper part of the solution, not at the base of the test tube. See the illustration below.

2. Flasks and beakers

Solutions may bump or spatter when boiled in a beaker or flask on a piece of wire gauze. The chance of this happening can be minimized by applying the flame beneath a glass rod placed in the beaker or flask.



Safely Heating a Test Tube

Volumetric Equipment

Using clean, accurately calibrated volumetric equipment–volumetric flasks, pipets, and

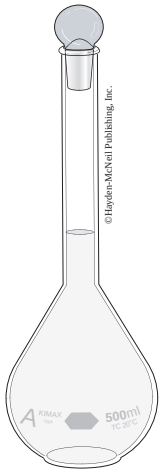
burets–it is routinely possible to carry out experiments with an accuracy of one part in a thousand (0.1%). However, attention must be paid to cleanliness, calibration, and techniques for using the equipment.

To give reproducible results, volumetric glassware must be ridiculously clean; water must drain evenly from the walls leaving no droplets. Note that one drop of water is 1/30 to 1/20 mL; a single extra drop of liquid in a 25-mL pipet will eliminate its 0.1% accuracy.

Volumetric glassware is made either to contain (TC) or to deliver (TD) a fixed volume of liquid.

Volumetric Flasks

Volumetric flasks are calibrated to contain a fixed amount of liquid. When the flask is filled to the calibration mark on its neck, it contains the volume given on the flask. Volumetric flasks are used to prepare solutions of known concentration: a given amount of a substance is dissolved or diluted in the flask, and the resulting solution diluted to the mark.



Volumetric Flask

Volumetric flasks do not have to be as clean as burets and pipets, since one is not concerned about drops of water left on the walls (most of what will be put in it the next time will be water, anyway). To clean the flask, pour some detergent solution into it, slosh it around, and use a brush to clean the neck. Rinse three or more times with tap water to remove the detergent and several times with distilled water. Store volumetric flasks filled with distilled water.

Volumetric flasks are easy to use. Just pour the solution to be diluted or the solid to be dissolved into the flask (making sure all of it is transferred), fill the flask about halfway, swirl to mix the solutions or dissolve the solid, then gradually fill the flask close to the calibration mark, swirling it occasionally. Make sure no excess water remains in the neck of the flask above the mark (remove it with a tissue or a strip of filter paper if necessary), and use a dropper to fill the flask to the mark with water and read the meniscus. Insert the ground-glass stopper, and invert and shake the flask several times to be sure the contents are thoroughly mixed.

The only precaution one has to make with volumetric flasks is to be sure the contents are well mixed and at room temperature while diluting them, since there are volume and temperature changes associated with dilution. For example, if one were to put 50 mL of 40% sucrose solution in a 100-mL volumetric flask, dilute to the mark, and <u>then</u> mix it, the volume at the end would be significantly less than 100 mL.

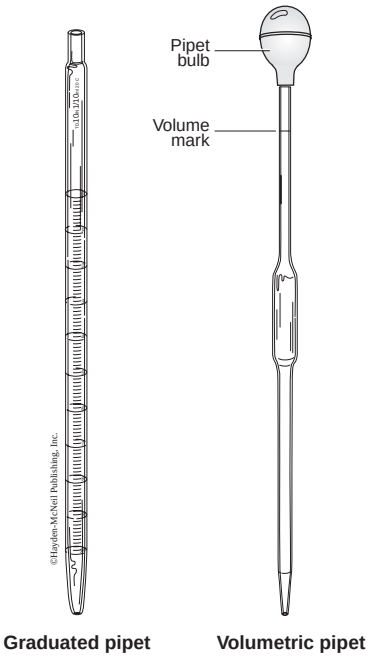
Pipets

Transfer pipets are made to deliver a fixed volume when filled to the calibration mark. Measuring pipets are convenient for delivering varying amounts of liquid, but are not especially accurate.

To clean a pipet, use a pipet bulb (see next page) or pipet pump to draw up detergent solution into the pipet and slosh it around inside. After doing this 2-3 times check that water flows freely down the walls without leaving streaks or droplets. If it does not, ask for a new pipet.

Rinse the pipet out several times with water, then rinse with distilled water.

Any time you use a pipet, rinse it immediately with distilled water.



Pipets

Unfortunately, the proper use of a pipet involves an arcane procedure that requires considerable practice. To use a pipet (the following directions are for right-handed people):

(a) Before transferring a liquid, rinse the pipet with the liquid to be pipeted to remove any water in it. First, squeeze the pipet bulb (mouth-pipetting is forbidden).

(b) With the tip of the pipet in the liquid to be transferred, hold the bulb against the end of the pipet firmly enough to make an airtight seal, as illustrated. Do not attach the bulb to the pipet; it is difficult to get it off. Also, hold the upper part of the pipet with your right hand, as illustrated: Do not grasp the pipet at its wide part or its bottom; it is likely to break and stab both your left hand and right wrist.

(c) Maintaining the seal, release the bulb, and hold the pipet as illustrated. Note that the pipet is held with the fingers, not grasped in the palm; and that the index finger, not the thumb, maintains the seal. Slosh the liquid around in the pipet to wet all the walls. Release the seal and allow the liquid to drain–not back into the container it came from. Repeat this rinsing.

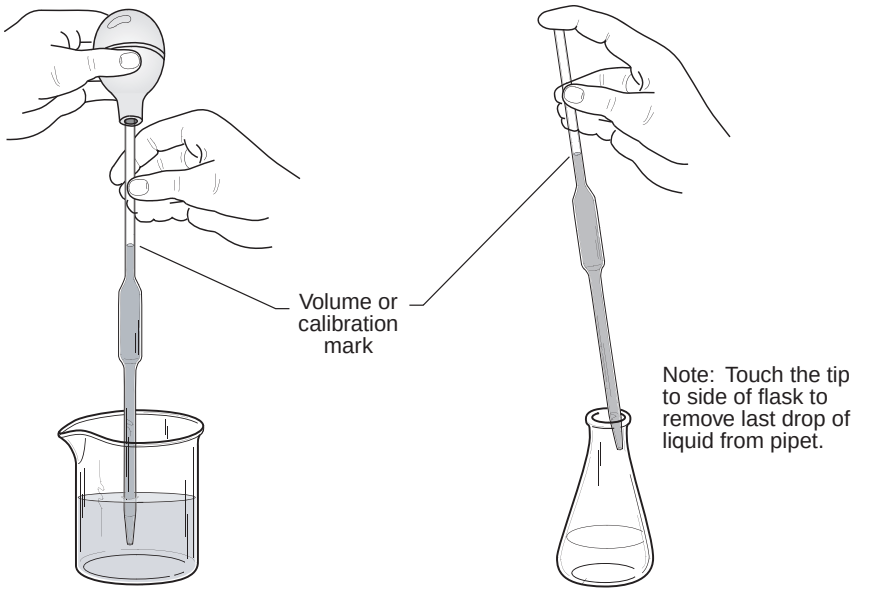
(d) Using the same technique, suck the liquid to be transferred about 2-3 cm above the calibration mark. Remove the bulb and hold the pipet as before. Be patient if you didn't catch the liquid before it fell below the calibration mark; the technique requires practice.

(e) Holding the pipet vertically, allow the solution to drain so that the bottom of the meniscus is exactly at the calibration mark. (This takes practice, too.)

(f) Wipe the tip of the pipet free of any extra drops; be sure the liquid level doesn't fall below the calibration mark.

(g) Hold the pipet vertically over the container into which the solution is to be transferred; release your finger and allow the pipet to drain.

(h) After all the liquid has apparently drained out, touch the tip to the wall of the container to remove any hanging drops. Hold the pipet away from the wall for fifteen seconds, then touch the tip to the wall again.



Using a pipet

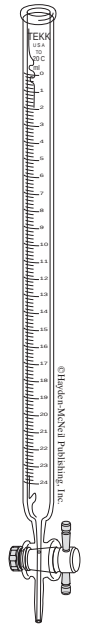
This last step insures delivery of liquid that temporarily clings to the walls of the pipet. Using this procedure it is possible (though seldom necessary) to obtain a reproducibility of 0.001 mL–about 1/50 of a drop.

(i) Do not blow the remaining liquid out of the pipet. The amount of liquid left in the tip is reproducible (part of the pipet's calibration) and not meant to be blown out.

(j) Be sure to rinse the pipet with distilled water (three times) after use.

Burets

Burets are cylindrical glass tubes with a delivery tip at one end and a valve (usually a stopcock) to control or stop the flow. They are used to deliver measured volumes of liquid.



Buret

To add liquid to a buret, place a small funnel in the top of the buret. Pour the liquid carefully through the funnel into the buret. (If you don't use a funnel, the liquid will probably run down the outside of the buret; if you don't pour the liquid slowly and carefully, it will probably overflow the buret.)

To clean a buret, wash it with detergent, using a "buret brush," until water drains evenly from the walls without leaving streaks or droplets. If you are unable to get the buret clean, or if there is grease in the tip, ask for a new one. The washed buret should be rinsed with tap water several times to remove the detergent, then rinsed with distilled water.

The buret should be rinsed and filled with distilled water when it is to be stored. Put a small cork or rubber stopper in the top to prevent leakage.

To use a buret also see the section on titration techniques.

(a) Rinse the buret with the solution to be delivered: Pour about 5 mL of solution into the buret; remember to use a funnel. Rotate and invert the buret (with a stopper in the top) to wet all the walls. Drain the solution through the stopcock and tip. Repeat this rinsing twice.

(b) Close the stopcock and fill the buret nearly to the top with the solution; continue to use a small funnel to help prevent spills. Open the stopcock to fill the tip; tapping the tip helps to remove air bubbles.

(c) Drain the buret close to (but it doesn't need to be exactly on) the 0.00 line; allow the liquid to drain off the wall for 30 seconds, and check that there are no air bubbles in the tip (i.e. in the part below the stopcock). If an air bubble is present, open the stopcock fully and let the solution run out until the bubble is gone. This shouldn't take more than about 5mL. Take the reading from there as your "Initial Buret Reading."

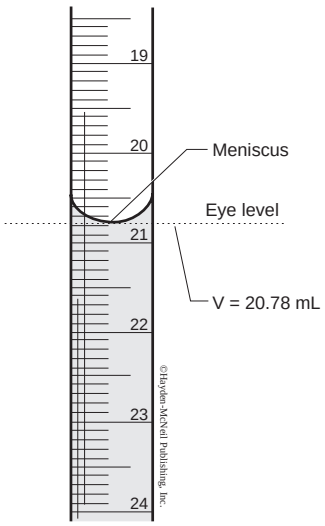
(d) Adjust the liquid to the line and touch a glass surface to the tip to remove any hanging drop. (Note that it isn't important that the liquid be right at the line, but only that it be read exactly and that the initial reading be subtracted from the final reading.)

(e) Deliver the desired amount from the buret–a given volume, enough to produce a slight color change in an indicator, etc.

(f) Allow the liquid to drain from the walls (i.e., wait) 30 seconds, touch the receiver wall to the tip, and read the buret (see below).

Reading a buret

It is trivial to read a buret to the nearest 0.1 mL. However, one part in a thousand accuracy requires estimation of the reading to the nearest 0.01-0.02 mL; this requires some practice. An example is given below.



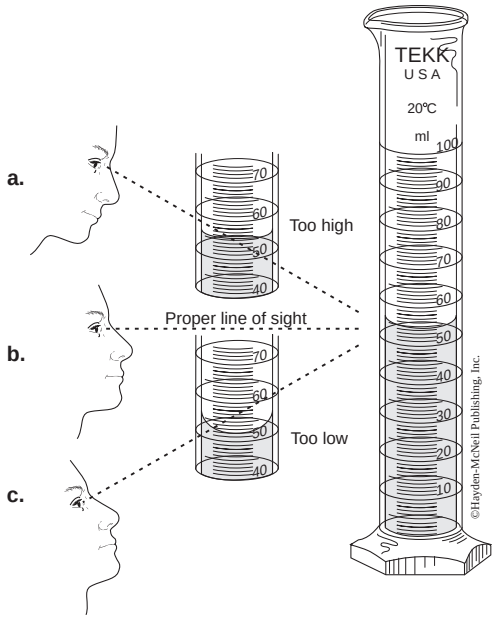
Reading a Buret to the Nearest 0.02 mL

Meniscus

The meniscus is the curved surface that appears at the top of a liquid in a container. For reasons that won't be clear until you study thermodynamics, liquids that "wet the walls" (e.g., water on glass) form a concave meniscus, while those that don't (e.g., mercury) form a convex meniscus.

Because they are more reproducible, readings with volumetric glassware and transparent aqueous solutions are always made at the bottom of the meniscus. Taking consistent and reproducible readings requires the following:

(1) Keeping your line of sight at a constant angle to the calibration mark. The easiest angle is 90°; that is, perpendicular to the glass. With volumetric flasks, pipets, and the mL and half-mL marks on burets this angle is easy to attain: the calibration mark goes all around the cylindrical surface and you will see only a single straight line when the angle is correct. Interpolation on a buret requires some practice.



Reading a Meniscus

(2) Defining the bottom of the meniscus. The apparent position of the meniscus will vary with lighting conditions; to convince yourself, try looking at the meniscus of a buret with (a) nothing behind it, (b) a piece of white paper behind it, and (c) a piece of dark paper behind it. A simple and effective way to take care of this problem is to make a black stripe on a white index card, then hold the black line exactly at the bottom of the meniscus.

Titrations

In a titration, one solution (called the titrant) is added from a buret to a second solution until (usually) a color change is observed. This color change (called the end point of the titration) is an indication that all the reactant in the second solution has been consumed. If one knows

(a) the concentration of the titrant, one can calculate the number of moles (more precisely, equivalents) of reactant that was titrated from the relation

moles = volume x concentration

(b) the number of moles being titrated, one can calculate the concentration of the solution:

$$\text{concentration} = \frac{\text{moles}}{\text{volume}}$$

Volumetric methods are popular (at least with instructors) because they are conceptually simple, rapid, and accurate.

In order for a titration to be a practical way to carry out a given analysis,

(a) *The reaction must go to completion rapidly*–acid-base reactions clearly do–a reaction that requires 24 hours, or even several minutes, would not be suitable.

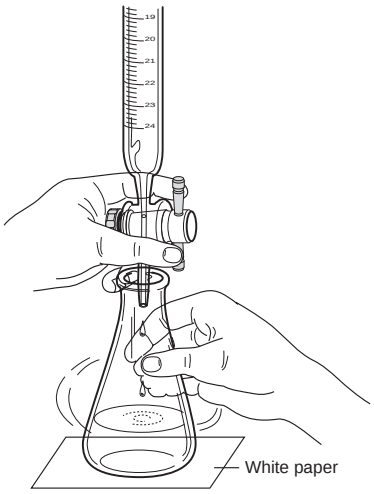
(b) *There must be a way to recognize the completion of the titration.* For acid-base reactions, one can use phenolphthalein indicator, a pH meter, or even a piece of litmus paper.

(c) *There must be some way of standardizing the titrant.* For acid-base titrations, it is difficult to make up solutions of NaOH of known concentration because solid NaOH absorbs water and CO_2 from the air. In practice, one titrates a known number of moles of a so-called "primary standard" acid, usually either an HCl solution of known concentration or potassium hydrogen phthalate (sometimes called potassium acid phthalate) with the base, then calculates the concentration of the base solution.

(The chemical formula of potassium hydrogen phthalate is $KC_8H_5O_4$. Its molar mass is 204.23 g, the same as its equivalent mass.)

Titration techniques

(1) ***Holding the buret:*** One should control the flow from the buret with one hand and swirl the flask with the other. The recommended method is illustrated on the next page; it requires practice. This method has the advantage that the stopcock is constantly pushed into the buret, which prevents leakage of titrant around the stopcock.



Delivery of liquid from a buret

Titrating

(2) ***Reading the buret:*** Use the white-card-with-a-black stripe technique described on page 101. Be sure to wait 30 seconds to make a reading.

(3) ***Avoiding overshooting the end point the first time you do a titration:*** Take a long dropper and suck about 1/2 mL of the solution being titrated into it; when you pass the end point, simply squirt the liquid back into the flask and finish the titration. To be sure you get all the acid (or whatever) out of the dropper, rinse it into the titration flask several times with distilled water. This dropper is known as a titration thief.

(4) ***Being careful near the end point:*** When you approach the end point–you can usually tell because it will take longer for the transient indicator color change to disappear–add titrant very slowly, a drop at a time, swirling the solution after each drop. Since you

usually want half-drop accuracy, at the very end you should allow a small drop to swell at the tip of the buret (but don't let it fully form), touch the tip to the wall of the flask (as far down in the flask as possible to minimize error) to get rid of the drop, then wash it into the titration flask with water from a wash bottle.

If you know you are within 1/2-drop of the end point, read the buret both before and after delivering the half-drop and average the two readings; doing this guarantees accuracy to 1/4-drop.

(5) ***Determining when you're at the end point:*** When the indicator changes from colorless to a color, the end point is usually taken to be the point at which the faintest tinge of color persists, NOT the point where the color is the darkest. Consequently, one usually carries out the titration over a piece of white paper.

For a titration of potassium hydrogen phthalate with NaOH, when an equal number of moles of each is present, the solution is essentially one of $KNaC_8H_4O_4$. Consequently, the indicator in a solution of $KNaC_8H_4O_4$ (or $Na_2C_8H_4O_4$) should have the same color as the end point.

Preparing Solutions

Solutions of known concentrations can be prepared from solids by two methods. Either method may be used to prepare solutions for general chemistry labs.

Direct Method

In the direct method, the solid to be dissolved is weighed out on weighing paper (or in a small container). This solid is then added *directly* to a volumetric flask. A funnel may be used to aid the addition of the solid into the slim neck of the volumetric flask. A small quantity of deionized water (commonly called "D.I." water) is then added to rinse the solid from the funnel and neck of the volumetric flask. More D.I. water is added until the meniscus of the liquid reaches the calibration mark of the volumetric flask. The stopper is then placed on the flask, which is inverted several times until the solid material is completely dissolved.

Disadvantages of the "direct" method:

1. Some of the weighed solid may adhere to the weighing paper, container, or funnel.

2. Transfer of the solid into the slim neck of the volumetric flask without spilling may prove challenging.

3. The solution may be contaminated if the beaker, stirring rod, funnel, or flask have not been washed carefully.

Transfer Method

In the transfer method, the solid is first weighed in a small beaker. Enough D.I. water is added (while stirring the solution) to completely dissolve the solid. This solution is then transferred to the volumetric flask. A funnel may be used to aid in the transfer of this solution to the volumetric flask. Before additional water is added to bring the meniscus to the calibration mark, the beaker, stirring rod, funnel, and flask *must* be rinsed carefully and the washings added to the volumetric flask. After all remaining washings have been added to the volumetric flask, additional water is added to the flask until the meniscus reaches the calibration mark on the neck of the volumetric flask. The stopper is then placed on the flask, which is inverted several times until the solid material is completely dissolved.

Disadvantages of the "transfer" method:

1. Some of the solution may adhere to the beaker, stirring rod, or funnel if not washed thoroughly.

2. The solution may be contaminated if the beaker, stirring rod, funnel, or flask have not been washed carefully. The disadvantages of each of these techniques may be minimized with careful lab techniques and practice.

Expressing Concentrations

There are many ways to express the concentration of a solution: molarity (M), molality (m), mass percent (%m/m), part per million (ppm), etc. In general chemistry we commonly use molarity as the concentration unit:

Molarity = (moles of solute / liters of solution)

This equation is often more useful by replacing the *moles of solute* with, by definition, *(grams of solute / molar mass of solute)*. The equation above then becomes:

Molarity = (grams of solute) /
(molar mass of solute x liters of solution)

Note: The *solute* is defined as the substance to be dissolved and the *solvent* is defined as the substance in which the solute is dissolved. A *solution* is defined as a homogeneous mixture of solute and solvent.

Diluting a Solution of Known Concentration

Dilution occurs when additional solvent is added to a solution. While the molarity of the resulting solution decreases, the number of moles of solute in the new solution remains the same:

$$(\text{moles of solute})_{\text{before dilution}} = (\text{moles of solute})_{\text{after dilution}}$$

The *moles of solute* is equal to the *molarity* times the *volume* (notice how the volume units cancel):

moles of solute = M x V = (mol / liter) x liter

A very useful equation can be derived by combining these two equations:

$$M_1V_1 = M_2V_2$$

(where "1" refers to the solution *before dilution* and "2" refers to the solution *after dilution*). Again, this equation basically states that the *moles of solute before dilution (Solution 1)* is equal to the *moles of solute after dilution (Solution 2)*.

Safety Note:

When diluting concentrated acids and bases, *always add the acid or base to the water* (one way to remember this is that alphabetically acid or base comes before water). The dilution of concentrated acids and bases is usually accompanied by release of a large amount of heat and splattering of the corrosive solution. By slowly adding the acid or base solution (which is more dense than water and tends to sink) to a relatively large excess of water, the heat is dissipated and splattering is minimized.

Appendix **E**

E

Significant Figures

Most students are first introduced to the concept of significant figures in General Chemistry. Pay close attention to your instructor when this material is covered in lecture. Learning significant figures correctly initially will prevent a lot of confusion (and lost points on exams and labs).

Every time you make a measurement in the laboratory you must be concerned with the precision and significant figures involved. In General Chemistry Laboratory we are usually more concerned, however, in what an experiment reveals. When quantitative values are being reported, but their exact values are less important than the qualitative results are, the following simple system can be employed to determine the number of significant figures:

1. To determine the number of significant figures in an individual measurement, read the number from left to right, counting all the digits starting with the first one that is non-zero:

   100. 3 significant figs.
   1.00 3 significant figs.
   0.10 2 significant figs.

2. When adding or subtracting, the number of *decimal places* in the answer should be equal to the number of *decimal places* in the number with the fewest places. The number of significant figures is not relevant:

0.12	2 sig. figs.	2 decimal places
1.6	2 sig. figs.	**1 decimal place**
11.490	5 sig. figs.	3 decimal places
Sum: 13.2	3 sig. figs.	**1 decimal place**

When multiplying or dividing, the number of significant figures in the answer should be the same as that of the quantity with the fewest significant figures. The number of decimal places is not relevant:

	1.365	x	2.63	/	3.0	= 1.2
sig. figs.:	4		3		**2**	**2**

Appendix F

Experimental Errors and Statistical Analysis

1. Experimental Errors

Every measurement has some uncertainty, which is called *experimental error*. Experimental errors can be classified as either *systematic* or *random*.

Systemic error arises from a flaw in experimental design or equipment. This error is reproducible and in principle, can be identified and corrected by utilizing a different experimental design or instrument. This type of error is not easily studied by statistical analysis.

Random error arises from natural limitations in our ability to make physical measurements (e.g., uncertainties in reading an interment scale or due to instrumentation noise). Random error has an equal chance of being positive or negative around the true value. This error is always present and cannot be completely eliminated. The statistical analysis discussed below provides a useful method for analyzing the random errors.

2. Statistical Analysis

If an experiment is repeated many times, and if the errors are purely random, the results tend to distribute symmetrically about the average value (see Figure F.1). When the number of measurements approach infinite, the distribution follows an ideal smooth curve called the Gaussian (Normal) distribution. In practice, we can carry out only limited number of measurements in the laboratory, but from this small set of data, we can estimate the statistical parameters and statistical behavior that describe a large set of data.

The Gaussian distribution can be characterized by two parameters: mean and standard deviation.

For a data set of n measurements of value x: x_1, x_2, x_3, ..., x_n, the ***mean*** or the *average* is defined as:

$$\bar{x} = \frac{x_1 + x_2 + x_3 + \ldots + x_n}{n} = \frac{\sum_{i=1}^{n} x_i}{n}$$

The mean gives the best estimate of the "true" value based on the set of experimental data. The standard deviation, s, measures how closely the data are scattered about the mean or the width of the Gaussian distribution. The smaller the standard deviation, the more closely the data are clustered about the mean.

$$s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}}$$

A series of measurements that produce a small standard deviation is more *precise*, but not necessarily more *accurate*, than one which produces a large standard deviation. An example of mean and standard deviation:

For a set of experimental measurements of the mass of a chemical sample (in grams), 5.1, 5.0, 4.9, 5.4, 5.2, the mean of the masses is

$$\bar{x} = \frac{\sum x}{n} = \frac{5.1 + 5.0 + 4.9 + 5.4 + 5.2}{5} = 5.\underline{1}2$$

(Recall that the underline indicates that the result should be rounded to that number of significant digits. Review Appendix E for the rules for determining the number of significant figures in calculation.)

The standard deviation is

$$s = \sqrt{\frac{(5.1 - 5.\underline{1}2)^2 + (5.0 - 5.\underline{1}2)^2 + (4.9 - 5.\underline{1}2)^2 + (5.2 - 5.\underline{1}2)^2}{5 - 1}} = 0.19.$$

The mean and standard deviation should both end at the same *decimal place*. Therefore, the mass of the sample would be reported as 5.1 ($\pm$0.2).

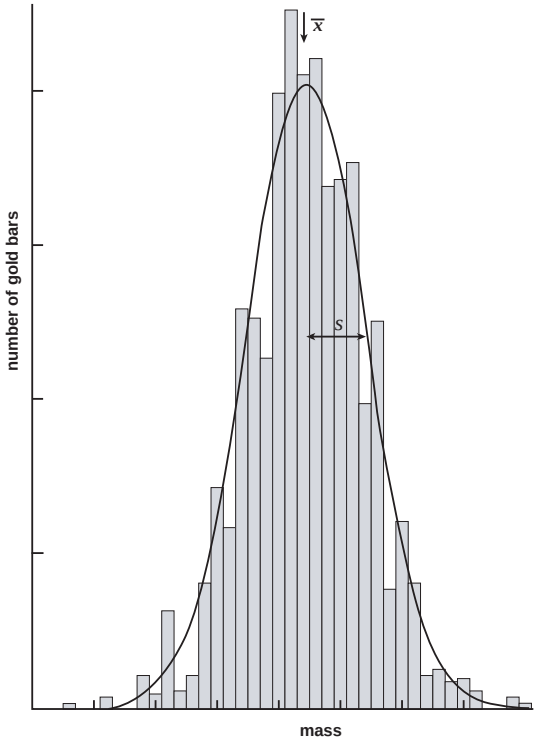


Figure F.1. Bar graph and Gaussian curve describing the masses of a hypothetical large collection of gold bars. A finite set of data will differ from the bell-shaped curve. The more measurements that are made, the closer they will come to the smooth curve.

Appendix G

Graphing Techniques

Several experiments will require graphing of data collected during the experiment. Graphing of experimental data allows us to visualize trends in data, as well as enable us to calculate additional variables without performing extra experiments. Also, information for data points that would be difficult to achieve in the laboratory (*i.e.* very high or low pressures or temperatures) can be extrapolated from graphs. The following paragraphs provide important information about proper graphing techniques. Review these points each time you prepare a graph from your experimental data.

The Abscissa and the Ordinate

A graph of two variables consists of two axes at right angles. The horizontal axis is referred to as the x-axis, or the *abscissa*. The vertical axis is called the y-axis, or the *ordinate*. Normally the x-axis is chosen to represent the variable that the student purposely manipulates during an experiment (*i.e.* the "independent" variable). The y-axis is chosen to represent the "dependent" variable, which changes as a result of the experiment. Example: A student wishes to measure the relationship between volume and temperature. The student decides to increase the temperature and measure the resultant change in volume. Therefore the student should graph the temperature values on the x-axis and the resulting measured volumes on the y-axis.

Choosing an Appropriate Scale

Choose a scale for the abscissa and ordinate so that the maximum portion of the graph is used. The data should not be restricted to one small region of the graph. The scales do not have to begin with zero.

Titles and Labelling Axes

The title should describe the variables measured, chemicals used, and any special conditions (see examples). Each axes should be clearly labelled with the name (or symbol) of the variable. Units (if any) should also be included.

Data Points & Extrapolations

If you are using data from several sources (such as another student's data), use a different symbol for that data. Be sure to reference the source of this additional data in your report.

Drawing Lines or Curves

Draw a smooth curve through data points; do not use "dot-to-dot" connections. For data points in a linear graph, draw a "best-fit" straight line through the data points. This is accomplished by drawing a line in which an equal number of data points lie an equal distance above and below the line. Use a dashed line to extrapolate a line beyond the data that is graphed.

Computer Generated Plots

Most students have access to computer graphing programs. Plots from computer programs are acceptable only if they can perform all of the aforementioned requirements. Computers and graphing software will be used for certain experiments.

Appendix **H**

H

Using a Spectrophotometer

How a Spectrophotometer Works

A schematic representation of a simple spectrophotometer, the Spectronic 20, is shown in Figure H.1. White light from the lamp is diffracted by the dispersion grating (that is, the colors are spread out), and a cam (turned by the wavelength control) is used to turn the grating so that light of the desired wavelength is passed through the exit slit. Light of this selected wavelength then passes through the sample, and the intensity of the light is measured by the photocell and its associated electronics.

When there is not a cuvet in the sample compartment, the light is blocked and 0% transmittance is then set using the electronics. With a blank cuvet containing only solvent, 100% Transmittance is set by using the "0 ABS/100% T" button to adjust the amount of light which reaches the sample.

You will note in the lab that the display on the Spectronic 20 (Figure H.2) can be set to show either absorbance or percent transmittance. The relationship between absorbance and percent transmittance is explained in detail in the discussion for Experiment 3.

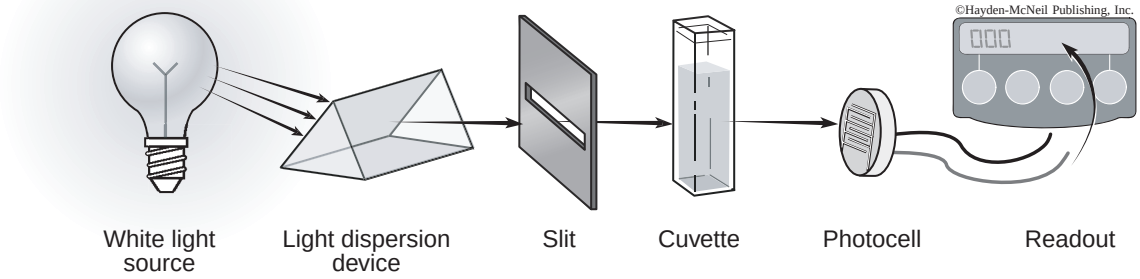


Figure H.1. Schematics of a Spectronic 20 spectrophotometer

Operating a Spectronic 20 Spectrophotometer

The instructions here apply to the Spectronic 20 Genesys spectrophotometer with the digital LCD display.

1. Turn instrument on at the beginning of the lab period (① in the figure below). Allow 10 minutes of warm-up time.

2. Set the wavelength to the proper wavelength in nanometers (nm) using the **nm▲** and **nm▼** buttons (② keypad).

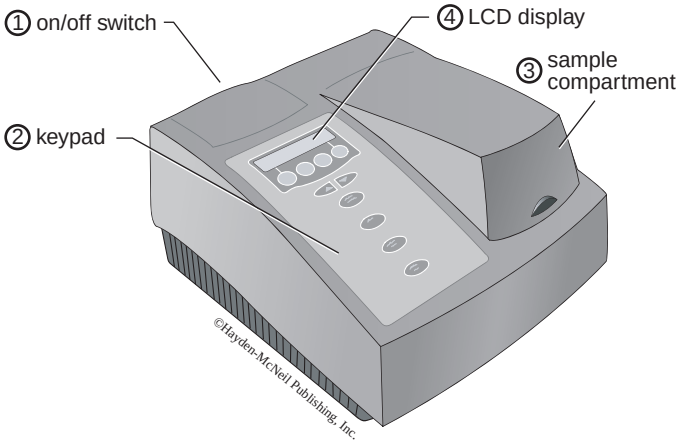


Figure H.2. Spectronic 20 spectrophotometer controls

3. **a.** Rinse a cuvet with a small amount (2–3 mL) of the blank solution or distilled water if a particular blank is not specified. Then fill the cuvet about one-half full (about 4 mL should be required) of the blank solution. Wipe the cuvet with a Kimwipe tissue (regular paper towels may scratch the glass). Open the sample compartment (③ below) and insert the cuvet in the sample holder.
   b. Close the sample compartment and set the instrument to read zero absorbance (100% transmittance) by pressing the **0 ABS/100 %T** button (② keypad).

4. Remove the cuvet for the blank. Using the same procedure as in **3a**, rinse and fill a matched, second cuvet with the solution whose absorbance is to be measured. Insert this cuvet as above, and read the absorbance value from the LCD display (④ in the figure to the right).

5. After your measurements are complete, wash the cuvets with distilled water and return them as directed by your TA. Remember that these cuvets are fragile and expensive, and should not be confused with ordinary test tubes.

Appendix I

Using a pH Meter

An illustration of the accumet AR15 pH meter is shown in Figure I.1. In combination with a pH electrode (also shown), this meter can measure and display the pH of various aqueous solutions. The meter can also be used to measure the electrical potential of electrochemical cells.

Figure I.1. The accumet AR15 pH meter and electrode

Standardization of the pH Meter

Every pH electrode is unique, so the pH meter must be standardized for each electrode. Even for a given electrode, the standardization will change over time. Therefore it is usually necessary to standardize the meter before each use.

To standardize the meter, use the following procedure:

1. Rinse a test tube with about 10 mL of pink-colored pH 4.00 buffer. Add enough buffer solution to fill the tube approximately halfway. Prepare two more test tubes—one with yellow pH 7.00 buffer and one with blue pH 10.00 buffer.

2. The pH electrode should have been left with the tip immersed in a yellow buffer solution. Make sure the white plastic ring on the upper part of the upper part of the pH electrode to the open position. The opening in the ring should line up with the opening in the side of the electrode.

3. Remove the electrode from the solution and rinse the tip in a 100-mL beaker half-filled with distilled water. Remove the electrode from the water and gently blot the tip dry with a Kimwipe.

4. Immerse the electrode about 1/4 of the way in one of the buffer solutions. You are now ready to standardize the meter at the pH of this particular buffer.

5. On the main (Measure) screen of the pH meter, press **std**. The display will change to the **Standardize** screen as shown in Figure I.2. Touch **clear** to remove any previous standardization values. If the screen says "Not Standardized", then it is not necessary to press the **clear** button.

6. Touch **std** again to standardize the meter The word **MEASURING** will flash until the signal is stable. The word **STABLE** appears when the meter has recognized the buffer. An icon of a beaker labeled with the pH value will appear on the screen. The display will then return to the Measure screen.

7. Repeat steps 2 through 6 to standardize with the remaining buffers. After the last buffer has been entered you may begin using the meter to take pH measurement. It is only necessary to standardize the meter once per lab period.

Measuring the pH of a Solution

Once the meter has been standardized, you may measure the pH of a sample using the following procedure:

1. Remove the electrode from the buffer solution it is stored in and rinse the tip with distilled water. Gently blot the tip dry with a Kimwipe.

2. Immerse the electrode in the sample solution.

3. Touch **meas** to begin measuring the sample. When the reading has stabilized, **STABLE** will appear on the display.

4. When all measurements have been performed, rinse the electrode and return it to the storage solution.

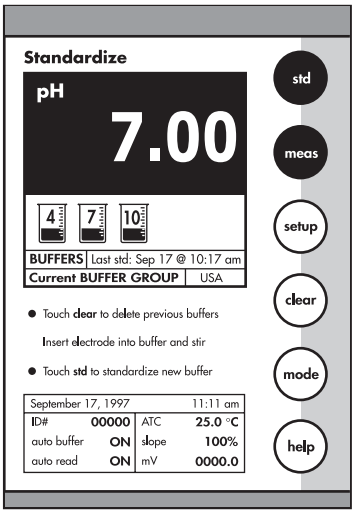


Figure I.2. The accumet AR15 pH meter standardization screen

Measuring the Voltage of an Electrochemical Cell

From the main screen, press the **mV** button. Record the voltage once **STABLE** is indicated on the display.