CHEM 131
Chemical Principles II
Laboratory Manual

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Synthesis and Characterization of Coordination Compounds

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Introduction

Coordination compounds (also known as complex ions or simply complexes) are formed by the reaction of a Lewis acid (an electron pair acceptor, usually a transition metal) with a Lewis base (an electron pair donor), which is known as a ligand. What is unique about coordination compounds is that they are formed from chemical species that have an independent existence and that this association is often readily reversible (i. e., there is an equilibrium between the solvated metal ion and the ligand). For example, $NiCl_2$ reacts with NH_3 in aqueous solution to form the compound $Ni(NH_3)_6Cl_2$ which contains the complex ion $[Ni(NH_3)_6]^{2+}$. This process is easily reversed (by the addition of H^+) to give back the starting materials. This type of behavior was thought to be very peculiar by chemists in the 1800's. They were familiar with compounds like CO_2, which although it could be made from C and O_2, does not act like it is some loose association of C and O_2. It wasn't until the ground-breaking work of Werner (for which he won the Nobel Prize in chemistry) in the late 19^{th} and early 20^{th} centuries that chemists began to understand these compounds. Werner's work was greatly expanded on in the 20^{th} century especially after it was discovered that coordination chemistry was relevant to the understanding the role of metal ions in biological systems.

You will be preparing a complex of Co^{3+} with ethylenediamine, $NH_2CH_2CH_2NH_2$ (abbreviated: en), and a complex of Fe^{3+} with the oxalate ion, $C_2O_4^{2-}$ (abbreviated: ox^{2-}). Ethylenediamine and oxalate are examples of bidentate ligands, which mean that they have two different atoms that can donate electron pairs to a metal ion. Ethylenediamine does this through lone pairs on its nitrogen atoms, while oxalate donates electron pairs from two of its four oxygen atoms. In these complexes the metal ion is directly bonded to six other atoms in what is called an octahedral geometry (if we connected the six atoms, the resulting solid would be an octahedron, and hence the name of this geometry). There are a number of ways in which the same set of six atoms can be arranged around a central atom in an octahedral geometry, and each of these different arrangements may give rise to compounds with the same chemical formula, but have different arrangements of their atoms (*isomers*). For example, compounds in which the actual connections between atoms (bonds) are different are called *constitutional isomers*. In this exercise you will be synthesizing and studying compounds where the bonds are the same, but the atoms are arranged differently in space (*stereoisomers*). Compounds of this type are classified as either *enantiomers* (the two compounds that are mirror images of each other) or *diastereomers* (the compounds are not mirror images).

Because en is a bidentate ligand, the dichlorobis(ethylenediamine)cobalt(III) complex, $[Co(en)_2Cl_2]^+$, that you will prepare exists as three isomers; one pair of enantiomers and their diastereomer. The isomer where the chlorides are situated on either side of the Co^{3+} (180° from each other) is called the *trans* isomer (Fig. 1), while the isomer where the chlorides are next to each other in the octahedron (90° from each other) is the *cis* isomer. In addition, there are two different ways in which we can put two Cl atoms *cis* to one another, and these are enantiomers (Fig. 2). The tris(oxalato)ferrate(III) ion, $[Fe(ox)_3]^{3-}$, exists as two enantiomers (there is no diastereomer). In one the three oxalates form a right-handed propeller, and in the other they form a left-handed propeller (both are shown in Fig. 3). The enantiomers in *cis*-$[Co(en)_2Cl_2]^+$

and $[Fe(ox)_3]^{3-}$ are distinguished by how the en or ox^{2-} wrap around the metal. This is determined by first placing one the bidentate ligands horizontally at the back of the octahedron defined by the six atoms surrounding the Co. We then look at how the other bidentate ligand (or ligands) cuts across the face of the octahedron. If it does so with a positive slope the enantiomer is designated Λ (lambda), but it does so with a negative slope is designated Δ (delta). Note that what has been presented here is but the briefest introduction to inorganic nomenclature. The interested reader is referred to the publications of the International Union of Pure and Applied Chemistry (IUPAC).[1]

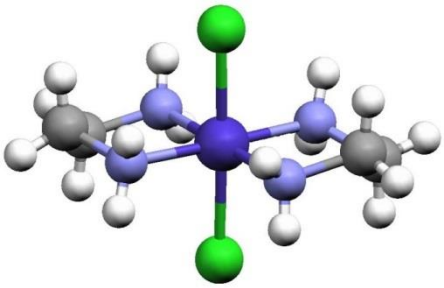

Figure 1. Structure of *trans*-$[Co(en)_2Cl_2]^+$ redrawn from the Cambridge Crystal Structure Database (http://www.ccdc.cam.ac.uk/) entry CENCOS using the Mercury (http://www.ccdc.cam.ac.uk/solutions/csd-system/components/mercury/) molecular visualization software package.

Figure 2. Structures of the two *cis*-$[Co(en)_2Cl_2]^+$ enantiomers redrawn from the Cambridge Crystal Structure Database (http://www.ccdc.cam.ac.uk/) entries CENCOC and CLECOC using the Mercury (http://www.ccdc.cam.ac.uk/solutions/csd-system/components/mercury/) molecular visualization software package. The enantiomer on the left is the Λ enantiomer, while the enantiomer on the right is designated as Δ.

Another interesting property of the transition metals is that their reactivity depends on several factors including the metal ion's charge, the number and type of donor atoms, and the number of d electrons present on the metal ion. It is the later property which we will exploit in this exercise both in the synthesis and then in the reactions of the compounds. The Co^{2+} ion has a $3d^7$ electronic configuration and Fe^{3+} has a $3d^5$ electronic configuration. Metal ions with these electronic configurations rapidly exchange their ligands and are referred to as labile. The $3d^6$ Co^{3+} is an example of an inert ion, that is, an ion that does not rapidly exchange its ligands.

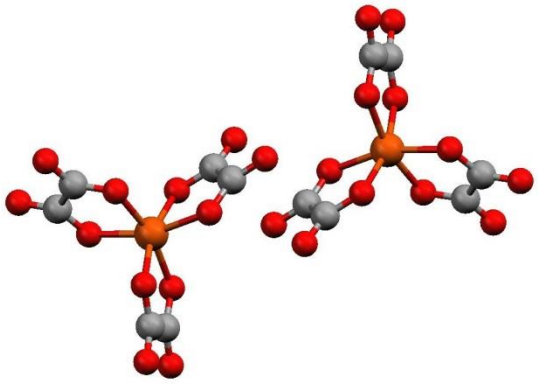

Figure 3. Structures of the $[Fe(ox)_3]^{3-}$ enantiomers redrawn using the Mercury ((http://www.ccdc.cam.ac.uk/solutions/csd-system/components/mercury/) molecular visualization software package from data collected by Professor Russell Baughman at Truman State University on crystals prepared by Truman students. The Λ enantiomer is on the left and the Δ enantiomer is on the right. Unlike the cobalt complex, where both enantiomers can be separated and isolated by crystallization, the enantiomers of the iron complex cannot be separated. This is because there is a rapid pathway available in solution to interconvert the enantiomers.

In this experiment, you will synthesize *trans*-$[Co(en)_2Cl_2]^+$ from $CoCl_2 \cdot 6H_2O$ according to the overall balanced chemical equation given in Scheme 1. In the mechanism by which this compound is formed Co^{2+} is initially chelated by one en and then a second en, with each step being described by an equilibrium constant. Once two, or more, en have become bound to the Co^{2+}, H_2O_2 (or, in some cases, O_2 from the air) is able to oxidize the metal center to Co^{3+}. Since further substitution of a Co^{3+} complex is slow, the reaction will essentially be over at that point. Thus by careful manipulation of the amount of en present and when the oxidant is introduced, we can force the formation of a Co^{3+} complex with either two or three en bound to the metal. Because the Co^{3+} complexes are inert we could subsequently convert *trans*-$[Co(en)_2Cl_2]^+$ to *cis*-$[Co(en)_2Cl_2]^+$ and then separate (resolve) its enantiomers.

$$CoCl_2 \cdot 6H_2O + 2\ en + xs\ H_2O_2 + xs\ HCl \rightarrow \textit{trans}\text{-}[Co(en)_2Cl_2]Cl \cdot HCl + other\ products$$

Scheme 1. Synthetic route to *trans*-$[Co(en)_2Cl_2]Cl \cdot HCl$ starting from $CoCl_2 \cdot 6H_2O$.

Both the *cis*- and *trans*-$[Co(en)_2Cl_2]^+$ complex ions undergo hydrolysis in acidic aqueous solution, as shown in Scheme 2. This reaction can proceed through one of two mechanisms (both are shown in Scheme 3): a dissociative mechanism, where the Cl^- leaves the complex before the H_2O enters, or an associative mechanism, where the H_2O enters the complex before the Cl^- leaves.

$$[Co(en)_2Cl_2]^+ + H_2O \rightarrow [Co(en)_2(H_2O)Cl]^{2+} + Cl^-$$

Scheme 2. The hydrolysis reaction of either *cis*- or *trans*-$[Co(en)_2Cl_2]^+$ under acidic conditions. Note that, in general, starting with the *trans* isomer yields the corresponding *trans* isomer and starting with the *cis* isomer gives the corresponding *cis* isomer of the product.

Associative Mechanism

$$[Co(en)_2Cl_2]^+ + H_2O \rightarrow [Co(en)_2(H_2O)Cl_2]^+$$

$$[Co(en)_2(H_2O)Cl_2]^+ \rightarrow [Co(en)_2(H_2O)Cl]^{2+} + Cl^-$$

Dissociative Mechanism

$$[Co(en)_2Cl_2]^+ \rightarrow [Co(en)_2Cl]^{2+} + Cl^-$$

$$[Co(en)_2Cl]^{2+} + H_2O \rightarrow [Co(en)_2(H_2O)Cl]^{2+}$$

Scheme 3. Possible mechanisms for the acidic hydrolysis of *cis*- or *trans*-$[Co(en)_2Cl_2]^+$.

The problem is further complicated by the interconversion of the *cis*- and *trans*- isomers, as shown in Scheme 4. Luckily, this reaction is known to be much slower than the hydrolysis reaction to be studied, and as long as the reaction temperature is not taken much above 70°C for an extended period of time the *cis*-*trans* isomerization reaction need not be considered.

$$\textit{trans}\text{-}[Co(en)_2Cl_2]^+ \rightarrow \textit{cis}\text{-}[Co(en)_2Cl_2]^+$$

Scheme 4. Reaction converting *trans*-$[Co(en)_2Cl_2]^+$ to *cis*-$[Co(en)_2Cl_2]^+$.

In the second week of this exercise, you will determine the activation energy of the first-order hydrolysis of *trans*-$[Co(en)_2Cl_2]^+$ under acidic conditions. You will be using a quenching method to study the reaction kinetics (compare to the direct measurement method that was used in the CHEM 130 *Kinetics of Crystal Violet Bleaching* exercise. With a quenching method a small portion of the reaction mixture is withdrawn at specific times and the reaction is then stopped by either adding reagent that stops the reaction (usually by rapidly reacting with one of the reactants) or by rapidly cooling or freezing the sample. For the reaction that we are studying, we will use the latter method to quench the reaction. Each lab group will be assigned different temperatures at which to study the reaction, and from the pooled data you prepare an Arrhenius plot and determine the reaction's activation energy.

The overall balanced chemical reaction for synthesis of the $[Fe(ox)_3]^{3-}$ is shown in Scheme 5. It is the sum of three steps, each corresponding to the stepwise reversible binding of ox^{2-} to Fe^{3+}. The metal remains in the labile 3+ oxidation state throughout the reaction, and so by adding a sufficient amount of ox^{2-}, we can force the reaction essentially completely to $[Fe(ox)_3]^{3-}$. Because the complex is labile, we cannot resolve the $[Fe(ox)_3]^{3-}$ enantiomers, but we can use the complex's lability to confirm the 3:1 ox:Fe^{3+} stoichiometry.

$$FeCl_3 \cdot 6H_2O + 3\ K_2C_2O_4 \cdot H_2O \rightarrow K_3[Fe(ox)_3] \cdot 3H_2O + \text{other products}$$

Scheme 5. Synthesis of $K_3[Fe(ox)_3] \cdot 3H_2O$.

In the final week of this exercise, you will confirm the 3:1 oxalate:Fe stoichiometry in your complex in much the same way as Werner did. First you will acidify a solution of $[Fe(ox)_3]^{3-}$ which will force the sequential equilibria that formed the complex back to $Fe^{3+}(aq)$ and $H_2C_2O_4$.

The amount of Fe and oxalate present will then be determined by redox titration against a standard $KMnO_4$ solution.

Experimental

For this exercise it is critical that you read each week's procedure carefully and that you and your lab partner plan what you will do before coming to the laboratory. Each week of this three-week exercise presents different challenges, and unprepared students will find it difficult to finish in the allotted time.

All of the substances that you will be working with this week are moderately toxic if ingested. The 10% H_2O_2, ethylene diamine, $FeCl_3$ $6H_2O$, and concentrated HCl can cause burns if they come in contact with skin. Ethylene diamine is flammable. In addition, you will be working with hot materials. Carefully follow the given instructions and the warnings. **IMMEDIATELY** clean up any spills after consulting your instructor.

Week 1

Each pair of students will need to check out the following items from the stockroom: magnetic stir bar, beaker tongs, Büchner funnel and filter flask.

All work of the first week's work must be carried out in the hood using the two stirring hotplates that will be in each hood. In the cobalt complex synthesis you will use one hotplate **ONLY** for heating, and the other **ONLY** for stirring. The stirring hotplate that you used for stirring will then be used in the synthesis of the iron-oxalate compound (this will allow you to start the synthesis of the iron compound while finishing the cobalt compound's synthesis). There is enough room on each plate for two beakers or two evaporating dishes; work with your hood-mates to assure that everything is done efficiently and safely.

Synthesis of *trans*-Dichlorobis(ethylenediamine)cobalt(III) Chloride Hydrochloride[2,3]

Fill a 600-mL beaker approximately half full with water, and place it on a hot plate in the hood. Place your wire gauze on top of the beaker and heat to boiling.

Weigh out approximately 1 g of cobalt(II) chloride hexahydrate, $CoCl_2 \cdot 6H_2O$, measured to the nearest milligram. Place the cobalt salt in your evaporating dish and add 2.5 ml of distilled water. Gently swirl the dish until the cobalt has dissolved.

Once the cobalt chloride has completely dissolved in the water, add 4 mL of 10% ethylene diamine. Place your magnetic stir bar in the solution and set the evaporating dish on a stirring hotplate (**NOT** the hotplate with your water bath). Set the stir control knob so that the stir bar spins but does not splatter solution on the side of the evaporating dish (a setting of "4", or less, on most stir plates is a good starting point). Stir for 10 min. If the evaporating dish rotates, place your triangle between the evaporating dish and the cold hotplate.

After 10 minutes, slowly and carefully add dropwise 1.6 mL of 10% H_2O_2 to the solution while it is still stirring. **CAUTION!** 10% H_2O_2 causes severe skin burns. Gloves are recommended and you should wash your hands after using this solution. Once the H_2O_2 addition is complete, reduce the stir speed (to "3" on most of the laboratory stir plate) and stir for an additional 15 min.

Next, CAREFULLY add 3 mL of concentrated HCl. **CAUTION!** HCl is VERY corrosive and will cause severe burns. Immediately wash off any HCl that comes in contact with skin with copious amounts of water. Turn off the stir plate and remove the magnetic stir bar using the magnetic stir bar retriever, as your instructor will demonstrate.

Place your evaporating dish on top of the wire gauze on the beaker of boiling water. Reduce the solution's volume until there is a thick layer of dark green crystals and very little liquid left. This will take at least 45 min. Be sure to monitor the level of boiling water in your water bath, you will need to gradually add water to the water bath during this time to keep it from boiling dry. **IMPORTANT!** If after about an hour, crystal formation is not evident, consult with your instructor; he/she will have suggestions on how to speed up this process.

This is a good point to start the synthesis of the iron complex.

While you are waiting for the volume to be reduced, you can also set up an ice bath. Obtain ~7 mL of methanol and put it in a small beaker or test tube in your ice bath. You will use the ice cold methanol to rinse your crystals in the final step of this synthesis.

Carefully remove the evaporating dish with the beaker tongs and set it on the bench top in the hood to cool. While your solution is cooling, set up a vacuum filtration apparatus.

Place a piece of filter paper in the Büchner funnel to collect your crystals. Carefully wet the filter paper with a couple drops of methanol BEFORE you add your crystals.

With the aspirator on, transfer the contents of your evaporating dish into the Büchner funnel using a spatula. Add about 2 mL of ice-cold methanol to your evaporating dish, swirl and pour this into the Büchner funnel. This will help remove all of your contents from the evaporating dish. Carefully pour ~5 ml of ice cold methanol over your crystals and filter. Repeat if necessary.

Carefully transfer your crystals to a watch glass or your cleaned evaporating dish, whichever is more convenient. Your instructor will demonstrate how to make this transfer without loss of product. It is not necessary to remove the filter paper at this time. Cover the watch glass with a paper towel and place it in your drawer to dry until next week.

Synthesis of Potassium Tris(oxalato)ferrate(III) trihydrate[4,5]

In your clean, dry 8 inch test tube dissolve 1.6 g $FeCl_3 \cdot 6H_2O$ (measured precisely) in 4 mL of distilled water. It may be convenient to gently heat the solution in a hot water bath on a hot plate to speed the dissolution of larger chunks of the ferric chloride.

Precisely and accurately weight out between 6.0 and 6.5 g $K_2C_2O_4 \cdot H_2O$ and place it in a clean, dry 50-mL beaker. Add 10 mL of distilled water and gently heat on a hot plate with stirring until all of the potassium oxalate has dissolved. It is not necessary to boil the solution.

Once the oxalate salt has dissolved, quickly and carefully pour the hot oxalate-containing solution into the test tube containing the iron solution. Swirl to mix and allow the reaction

mixture to cool slowly to room temperature. Once the test tube is cool to the touch transfer it to an ice bath and continue cooling.

Green crystals of the product may form during the initial cooling to room temperature, but they might not form until the ice cooling step. If crystals do not form after 30 min of cooling, try gently scratching the bottom of the test tube with a stirring rod or add a seed crystal (a crystal of the product obtained from another preparation), which your instructor will provide.

Decant the solution above the crystals and discard. Recrystallize the crude product by adding approximately 5 to 8 mL of hot distilled water to the crystals in the test tube, heat and shake gently to affect total dissolution. Decant the green solution containing the product into a clean, dry beaker and discard any residue that remains in the test tube.

Cover the beaker with a watch glass and set it aside to cool slowly. When the beaker is cool to the touch, transfer it to an ice bath and continue to cool. Green crystals should form within about 20 min. If they do not, consult your instructor for assistance.

Collect the crystals by vacuum filtration. Wash the crystals twice with 2 mL of ice-cold distilled water and then with two 3-mL portions of acetone. **CAUTION!** Acetone is flammable, so do all these manipulations in the hood. Dry the product on the filter and then transfer it to a watch glass. Cover the watch glass with a paper towel and place it in your drawer to dry.

Waste Collection
All waste from this week's experiment is to be placed in the designated receptacle.

Week 2
The cobalt complex should be considered toxic if ingested. Clean up any spills **immediately**. The water baths that you will be using will contain warm to hot water. Take care not to scald yourself.

You will need to bring your own laptop/tablet computer with you to lab this week. While the data analysis described here can be performed on the LabQuest, it is easier to use LoggerPro or Excel on your own computer. It is also more efficient to transfer the data to your own computer so that one data set can be analyzed while the next one is being acquired.

Before beginning any work this week obtain the mass of the dry *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride hydrochloride and the dry potassium tris(oxalato)ferrate(III) trihydrate.

Determination of the Activation Energy for Hydrolysis of *trans*-Dichlorobis(ethylenediamine)cobalt(III) Chloride[6,7]
You will be using a Vernier spectrometer interfaced to a LabQuest device to monitor the progress of the reaction, or if your instructor prefers, you can use your own laptop to acquire the data, but remember that the Chemistry Department is not liable for any damaged incurred. Please review the operation of these spectrometers (see the *Operation of the Vernier LabQuest 2*

section) and the basics of kinetics in the CHEM 130 lab exercise *Kinetics of Crystal Violet Bleaching* (see http://chemlab.truman.edu/chemical-principles/) before coming to lab.

At some point before beginning your kinetics runs you will need to calibrate the spectrometer using a cuvette filled with distilled water. **IMPORTANT!** You must use the same cuvette for both the blank and for the actual measurements. Before inserting the cuvette into the spectrometer, be sure to thoroughly wipe the cuvette's windows with a KimWipe. Any bubbles adhering to the cuvette's windows may be dislodged by **gently** tapping the cuvette with your finger. Do **NOT** tap the cuvette on the table! Be sure that the cuvette's clear windows are aligned perpendicular so that they correspond to the marks on the sample holder. Also be sure that the cuvette is inserted into the spectrometer as reproducibly as possible each time. Many problems that students experience with this exercise can be traced to the cuvette not being cleaned and not being inserted properly into the instrument.

Check out a thermometer and obtain several plastic centrifuge tubes from the stockroom.

Be sure that your large test tube and all of your small test tubes are clean and dry. You will be running the reaction in the large test tube and using the small test tubes to store the aliquots removed from the reaction mixture. Place 3 ml of distilled water in each of your small test tubes and mark the water level; discard the water and dry the test tubes.

Each bench will be assigned two temperatures at which to run the reaction (the pairings are usually 40/65 °C, 45/60 °C and 50/55 °C with two benches in each lab section running the same temperature pairing, but your instructor will inform you of your actual assignments in the laboratory). Water baths set for each of these temperatures will be in the hoods. They will be labeled and your instructor will point out which bath is in which hood. Do **NOT** change the settings on any bath! Use the thermometer to find the actual bath temperature to the nearest 0.1 °C, but do **NOT** leave the thermometer in the water bath between measurements and be careful where you set it between measurements. **Note:** it is not critical that you are exactly at your assigned temperature, as long as the temperature reading is stable and you record and use the actual temperature at which the data were collected.

The actual logistics of how you and your bench mates will accomplish your assigned measurements will depend on the number of groups in the lab and the number of available spectrometers. Your instructor will give you guidance, but it is essential that you and your bench mates develop a plan of attack before coming to the laboratory.

Place 30 ml of 0.01 M HNO_3 in your large test tube and place it in the water bath. Place 1 ml of cold distilled water in a small centrifuge tube (the tubes can contain up to about 3 ml and the volumes are marked on the side). Keep the centrifuge tube cold in an ice bath until ready for use.

To perform a kinetics run, precisely weigh out approximately 0.2 g of *trans*-$[Co(en)_2Cl_2]Cl \cdot HCl$. Place this in the small centrifuge tube containing the cold water, close the tube and shake vigorously to dissolve the solid. Pour the entire contents of the centrifuge tube into your large test tube and mix thoroughly. Do this as quickly as possible; it is best if this can be

accomplished without removing the large test tube from the water bath. Start timing from when the solution is completely mixed.

Remove approximately 3 ml of the reaction mixture immediately upon mixing. Place it in one of your small test tubes and place the tube in the ice bath. Obtain the absorbance spectrum of this sample once it has cooled back to about room temperature and record the absorbance at 505 nm and at 800 nm (this is your data point at $t = 0$). Don't forget to thoroughly wipe the cuvette's windows with a KimWipe before you place it in the spectrometer. Any bubbles adhering to the cuvette's windows may be dislodged by **gently** tapping the cuvette with your finger. Do **NOT** tap the cuvette on the table! If the absorbance measurement at 800 nm is not approximately zero, re-wipe the cuvette's windows and try the measurement again.

You will repeat this process until you have removed a total of nine samples, but make sure ~3mL remains for the 70-°C water bath. The timing between samples will vary with temperature. At 40 °C you must follow the reaction for at least 40 minutes, but at 65 °C you will only need to follow the reaction for 5 minutes. Work out the timing of the sample withdrawals before you start a run. **You must know as precisely as possible how long each sample was in the water bath from when it was mixed until it was placed in the ice bath.** Note that the precision of your time measurement will ultimately affect the precision of your rate constants (you can do the propagation of error analysis to show this, if you wish).

Once you have removed nine samples, place the test tube containing the remaining 3 ml of the reaction mixture in the 70-°C water bath for no more than five minutes. Remove the test tube from the bath and place it in the ice bath. Once the sample has cooled to room temperature, obtain the reaction mixture's absorbance spectrum. Record the absorbance at 505 nm and 800 nm; this is your $t = \infty$ data point.

Prepare a fresh sample and obtain data at the other assigned temperature. Repeat the measurements at the two temperatures as time permits.

All cobalt-containing waste is to be placed in the proper container. Any unused cobalt complex will be saved for later use. Please put it in the container provided, as directed by your instructor.

Week 3

The iron oxalate should be considered toxic if ingested. Potassium oxalate is a poison. Potassium permanganate is a strong oxidant and can cause tissue damage, if hot and concentrated. The permanganate solution used in this exercise is not concentrated, but it will be warm. Take care using these substances.

Before coming to the lab, write balanced chemical equations for the three different redox reactions that you will use in this analysis, all of which take place in acidic aqueous solution. In the first reaction MnO_4^- oxidizes $H_2C_2O_4$ (or $C_2O_4^{2-}$) to give Mn^{2+} and CO_2 as products. In the second Zn reduces Fe^{3+} to Fe^{2+}. In the final reaction, MnO_4^- oxidizes Fe^{2+} to Fe^{3+}, giving Mn^{2+} as the other product. There are other reactants and products (e. g., H^+ and H_2O) that you will need to add to balance the redox reactions.

In this exercise, you will use an approximately 0.01 M MnO_4^- solution as the titrant. A good rule of thumb for a titration is that the optimal amount of titrant should be half the volume of the buret being used. Our burets hold 40 mL, and therefore, we need to know what mass of $K_2C_2O_4 \cdot H_2O$ is needed so that, when it is titrated with a 0.01 M MnO_4^- solution, the equivalence point is reached at 20.00 mL of added titrant. Perform this calculation in your notebook before coming to the laboratory (be sure to show your work). It would also be prudent to set up the other calculations that you will need and to prepare tables to record your titration data.

You are not required to bring your own laptop/tablet computer with you to the laboratory this week. However, you may find it useful for data analysis.

Standardization of 0.01 M Potassium Permanganate Solution

Obtain approximately 75 mL of un-standardized 0.01 M $KMnO_4$ solution. **CAUTION!** Potassium permanganate is a strong oxidizing agent! Immediately wash any spilled on your skin with copious amounts of water.

Wash your buret several times, as your instructor will demonstrate, with no more than 2 mL of the permanganate solution. Each time allow the solution to drain through the buret's tip into a waste beaker. After the final wash, fill the buret to near the 0.00-mL mark such that the upper part of the meniscus is at or below the 0.00-mL mark. Make sure that there are no bubbles in the buret tip. Run some of the solution through to clear any bubbles (gentle taping might help dislodge any recalcitrant bubbles). Refill the buret, if necessary. Record the initial volume of solution in the buret. Because the MnO_4^- ion is so strongly colored, make all your volume readings from the top of the meniscus.

Accurately weigh out (to the nearest 0.001 g) the amount of $K_2C_2O_4 \cdot H_2O$ that you calculated is needed to standardize the MnO_4^- solution (helpful hint: it should be around 0.1 g). Place the oxalate in an Erlenmeyer flask and add about 30 mL of distilled water and 5 mL of 6 M H_2SO_4. Swirl the flask gently to dissolve the solid.

Place the flask on a stirring hotplate in the hood and carefully heat the solution to approximately 60 °C. Do **not** boil! Remove the flask from the hotplate (a folded paper towel makes an excellent hot pad). This titration must be performed fairly quickly so that the solution does not cool too much. Be sure that you swirl the flask as you add the permanganate solution and wash down any solution that splashes on the side of the flask with a small stream of distilled water. If the solution cools too much, reheat. Titrate the sample with the permanganate solution until the slightest purple color persists for at least 30 sec. Record the volume of permanganate used and from it determine the $[MnO_4^-]$. Repeat until three determinations agree with each other within 2%.

Determination of Oxalate in Potassium Tris(oxalato)ferrate(III) Trihydrate

Accurately weigh out about 0.10 g of your $K_3[Fe(ox)_3] \cdot 3H_2O$, place in an Erlenmeyer flask, add 30 mL distilled water and 5 mL of 6 M H_2SO_4. **IMPORTANT!** Be sure that you use **6 M H_2SO_4** and not H_2SO_4 of a lesser concentration; the reaction will not work properly if the acid concentration is not correct. Swirl to dissolve the solid and then heat to 60 °C, again taking care

not to boil the solution. Titrate as described above to the first permanent purple color. Record the volume of titrant dispensed and from it calculate the % $C_2O_4^{2-}$ by mass in the sample.

Do **NOT** discard the solution at this point; proceed to the iron analysis given below.

Determination of Iron in Potassium Tris(oxalato)ferrate(III) Trihydrate
Take your faintly-purple sample from the oxalate analysis above, and set in on a hotplate in the hood (there may be a small amount of brown precipitate forming at this point, but do not be concerned). Gently heat it until it almost boils and add approximately 100 mg of Zn to the hot solution. Cover the flask with a watch glass and continue heating until the yellow color (from Fe^{3+}) disappears (Fe^{2+} is colorless in solution). While you are waiting, perform more oxalate titrations and set up a gravity filtration with fluted filter paper (ask your instructor to demonstrate how to flute filter paper, if you are unsure).

Quickly filter the hot, colorless solution into another Erlenmeyer flask, again using a folded paper towel to handle the hot flask. It is important that this filtration be done quickly to minimize the amount of Fe^{2+} that is re-oxidized to Fe^{3+} by O_2 in the air. Rinse the funnel with several small (approximately 5 mL total volume) portions of distilled water. Titrate this solution with the permanganate solution in your buret until the first faint trace of a persistent pink color. Record the volume of permanganate used and from it determine the % Fe by mass in your sample

Repeat the two titrations until you run out of sample, or when three of the oxalate titrations agree with each other within 2%.

Waste Collection
Excess reagents should be placed in the designated bottles for recycling. The solution that remain after the second titration can be disposed in a laboratory drain with a copious amount of water.

Results and Analysis
Week 1
After you have determined the mass of your dry *trans*-$[Co(en)_2Cl_2]Cl \cdot HCl$ and $K_3[Fe(ox)_3] \cdot 3H_2O$, calculate a percent yield for each compound. In each case assume that the metal salt is the limiting reagent. Note that this is a common practice among coordination chemists because of all the coupled equilibria involved in the synthesis of coordination compounds.

Week 2
Prepare a graph in Excel (see the *Preparing Graphs* and *Guide to Excel* sections) showing absorbance as a function of wavelength in which you overlaid all of the spectra for one run. The scale on the *y*-axis should be 0 to 1 (you may need to set the maximum value on the y-axis to 1.1 or 1.2, depending on your actual concentrations) and the *x* axis scale should be set from 400 to 800 nm. If the data were obtained correctly, the spectra should all have an absorbance of about 0 at 800 nm and there should be two *isosbestic* points (points where the absorbance does not

change as a function of time, indicating that only two species were contributing to the absorbance throughout the reaction).

From the absorbance at 505 nm at each time subtract the absorbance at 800 nm at the same time; this corrects for any baseline drift or other variations that occurred between samples. With the corrected absorbance readings at 505 nm (A_t) and your corrected absorbance at infinite time (A_∞), prepare a first-order integrated rate law graph (i. e., $\ln(A_\infty - A_t)$ as a function of time) for each run. We use $A_\infty - At$ instead of concentration in these graphs because 1) we are following the formation of the product over time and 2) the reactant has a relatively large absorbance at this wavelength.

From each graph determine the value of the rate constant at that temperature. Report each rate constant along with its uncertainty at 95% confidence (see the *Introduction to Statistics in Chemistry* section) and the temperature at which it was obtained to the instructor and the rest of the class. From the class data (rate constant as a function of temperature), prepare an Arrhenius plot, determine the activation energy and its confidence interval at the 95% confidence limit.

Does the fact that the hydrolysis reaction is first-order in the cobalt complex and your value of the activation energy allow you to conclusively rule out one of the possible mechanisms? You will need to derive the rate law predicted by each mechanism for each of the possible cases: 1) the first step is irreversible and rate determining, 2) the first step rapidly goes to equilibrium and the second step is slow, 3) the first step is reversible, but does not come to equilibrium and the second step is slow. What additional experiments could you do to help distinguish between the possible mechanisms?

Week 3

Calculate the average percent oxalate by mass in your $K_3[Fe(ox)_3]\cdot 3H_2O$ and share this with the class. From the class data calculate the average percent oxalate by mass in $K_3[Fe(ox)_3]\cdot 3H_2O$, the standard deviation and the confidence interval at the 95% confidence limit. Be sure to perform a Q-test on the class data first to exclude any suspect point. Calculate the true percent oxalate by mass and determine a percent error for both your data and the class data. See the *Introduction to Statistics in Chemistry* and *Guide to Excel* sections to review how to perform these calculations.

Calculate the average percent iron by mass in your $K_3[Fe(ox)_3]\cdot 3H_2O$. Share this with the class, and calculate the average percent iron by mass in $K_3[Fe(ox)_3]\cdot 3H_2O$, the standard deviation and the confidence interval at the 95% confidence limit from the class data. Perform a *Q*-test on the class data first to exclude any suspect point. Calculate the true percent iron by mass and determine a percent error for both your data and the class data.

Conclusions

This exercise contains elements of both a **synthesis** exercise and a **measurement** exercise. Your instructor may have you treat all three weeks as one exercise for the purposes of writing your Discussion of Conclusions, or he/she might have you treat each week separately. If you are unsure, ask! In addition to the points covered in the **synthesis** and **measurement** outlines, be sure to address the questions raised in the *Results and Analysis* section above.

Summary of Results

In your *Summary of Results* you should have tables that summarize the results for each week: Week 1, the percent yield of *trans*-$[Co(en)_2Cl_2]Cl \cdot HCl$ and $K_3[Fe(ox)_3] \cdot 3H_2O$; Week 2, the average rate constants at each temperature that you determined and the activation energy that was determined from the class data (along with a 95% confidence interval for each, if possible); and Week 3, the statistical (average, standard deviation and confidence interval) results for the $K_3[Fe(ox)_3] \cdot 3H_2O$ analyses.

References

1. The IUPAC's comprehensive guide to inorganic nomenclature (the *Red Book*) is available online at http://old.iupac.org/publications/books/rbook/Red_Book_2005.pdf (accessed, August 24, 2016). This book is 377 pages long and is not light reading. The IUPAC also has a brief guide (https://www.iupac.org/cms/wp-content/uploads/2016/07/Inorganic-Brief-Guide-V1-1.pdf, accessed August 24, 2016), which is only four pages long, but is still, for the most part, beyond the scope of this course. Both of these links will work from Truman computers because of agreements between the university and the publisher, but may not work off-campus.

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3. Bailar, J. C., Jr. *Inorg. Synth.* **1946**, *2*, 222-225.

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5. Marcus, S.; Sienko, M. J. and Plane, R. A. *Experimental General Chemistry*; McGraw-Hill: New York, 1988.

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7. Herrick, R. S.; Mills, K. V. and Nestor, L. P. *J. Chem. Educ.* **2008**, *85*, 1120-1122. This article is available as a PDF file at http://pubs.acs.org/doi/pdf/10.1021/ed085p1120 for Truman addresses and *J. Chem. Educ.* subscribers.

Molecular Modeling 1: Classic Molecular Modeling

J. M. McCormick

Introduction

Dalton's Atomic Theory revolutionized chemistry by explaining chemical properties in terms of small, indivisible pieces of matter called atoms that are linked together to form polyatomic species (both ions and molecules). As chemists explored the properties of the polyatomic species, it became clear that they have size and shape and that shape is particularly important in explaining their physical properties and why and how chemical reactions occur.[1-5] A summary of some of the commonly observed polyatomic shapes (also known as structures or geometries) are shown in Table 1 arranged by the number of atoms around the "central atom."

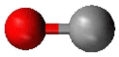
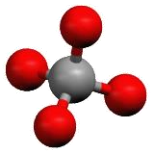
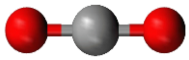
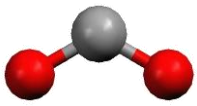
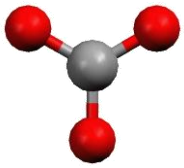
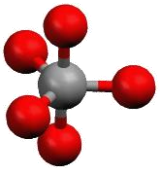
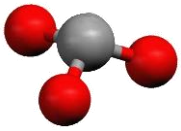
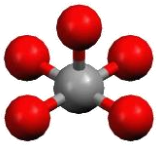
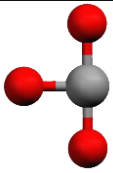
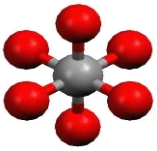
Atoms Around "Central Atom"	Shape	Atoms Around "Central Atom"	Shape
1	 Linear	4	 Tetrahedral
2	 Linear		 Square planar
	 Bent		 Bisphenoid (see-saw)
3	 Trigonal planar	5	 Trigonal bipyramidal
	 Trigonal pyramidal		 Square pyramidal
	 T-shape	6	 Octahedral

Table 1. Summary of idealized common structures of molecules and polyatomic ions.

The structures shown in Table 1 are idealized structures; real molecules seldom exhibit these idealized shapes. However, the ideal shapes are good starting points toward understanding how the spatial arrangement of atoms in polyatomic species affect their properties and chemistry.

Chemists often find it convenient to build a model of a molecule or polyatomic ion to help them visualize its actual shape, much in the same as an architect will build a model of a building to help him or her see its structure. The complexity of the model a chemist will use is dictated by the answer sought. And the explanation as to why a molecule or polyatomic ion has a certain structure depends on the theory used.

The simplest model is a Lewis dot structure (see the *How to Draw Lewis Structures* section for a brief overview of Lewis dot structures) which gives us an approximate picture of the bonding interactions that hold the polyatomic species together. It does not, however, give an accurate picture of structure or the electrons' energies. Because Lewis dot structures assume that all valence electrons are paired and a chemical bond requires two electrons, it is limited to simple compounds of the main group elements (s and p blocks) and some transition metal ions (those with d^0 and d^{10} configurations). A Lewis dot structure can be used to obtain a rough picture of structure by using Valence Shell Electron Pair Repulsion (VSEPR) theory (see the *Valence Shell Electron Pair Repulsion Theory* section for a brief overview of VSEPR theory).

In VSEPR theory we assume that the electron pairs, whether in bonds or in lone pairs, take up space and repel each other. The final arrangement of the atoms is determined in VSEPR theory by the jostling of the electrons for space. VSEPR theory gives reasonable predictions of structure and can explain why certain polyatomic species are distorted relative to an ideal geometry. It suffers from the same limitations as Lewis dot structures. And the structures that VSEPR predicts are really only valid in the gaseous state because it ignores interactions between species.

VSEPR theory only predicts structure and cannot be used, by itself, to describe the places where electrons are allowed to be (i. e., the molecular orbitals). Valence Bond theory allows us to take a VSEPR structure (or a real structure) and get a rough idea of how the electron density is distributed in bond. As with the other models a number of simplifying approximations have been made and we still cannot get energies for a polyatomic species. The hybrid orbitals that are used to explain bonding in Valence Bond theory do give us a reasonable approximation of how the electrons distribute themselves for many chemical species (the molecular orbitals). For relatively simple systems, like compounds formed by elements of the first two periods, the combination of Lewis dot, VSEPR and Valence Bond theories is sufficient to explain most of their chemistry.

The most complete theory is Molecular Orbital (MO) theory which considers the energies of the atomic orbitals and how well the atomic orbitals on different atoms overlap. In MO theory it is the balance between orbital energy and overlap that ultimately determines structure. MO theory can give a very accurate description of structure, electron arrangement and molecular energies, but it is neither quick nor simple to apply. So unless a detailed picture of molecular structure is required, one of the simpler models is used.

This exercise will give you practice in using Lewis dot structures, VSEPR and Valence Bond theory models. We will also be exploring the ramifications of molecular shape and how to describe shape in mathematical terms. **NOTE!** Your instructor may use this exercise in any one of a number of ways. Be sure that you understand what he or she wants you do before coming to laboratory.

Experimental

Do **not** write this exercise up in your notebook. There are worksheets for the eight groups of molecules and ions (click on one of the links below to jump to the worksheet in this document, print each out and bring them to laboratory).

In this exercise you will be using a traditional model kit to build models of a number of molecules and polyatomic ions. Most of the balls in the kit have only one hole drilled in them. These are used to model atoms that have only one connection to another atom where we can ignore the disposition of any lone pairs (i. e., terminal atoms). There are balls drilled for the ideal angles for tetrahedral, trigonal bipyramidal and octahedral geometries. Your kit may have red balls, representing oxygen, drilled with only two holes instead of four because the positions of the lone pairs have already been taken into account. See Table 2 for the correspondence between ball color and element.

Color	Number of Holes	Element Represented
White	1	Hydrogen
Green	1	Chlorine
Orange	1	Bromine
Purple	1	Iodine
Red	2	Oxygen
Yellow	2	Sulfur
Blue	4	Nitrogen
Black	4	Carbon
Brown	5	Any element with an expanded octet
Silver	6	Any element with an expanded octet

Table 2. Key to the atoms in the molecular model kit. Any color may be used to represent any element not listed, as long as the number of bonds and the disposition of the lone pairs match.

The stiff, gray connectors are used for single bonds and the flexible, gray connectors are used for multiple bonds. Do not use the short white connectors (they are hard to get out). Because the connector representing bonds are the same size and the balls used to model the atoms are not to scale, the models give inexact representations of the molecules and ions. But, they are useful for observing the connectivity and the three-dimensional arrangement of atoms in space.

If directed by your instructor, before coming to laboratory draw Lewis dot structures for each of the species on the worksheets (use a pencil!). Show all contributing resonance structures, where appropriate (use the back of the page, if necessary), and consider formal charges as needed. See the *How to Draw Lewis Structures* section to review Lewis dot structures.

Predict the electron pair geometry (also known as the "stereochemical formula"), and the molecular geometries for each chemical species using VSEPR. Below the picture of each molecule write the name of the geometry (e. g. linear, trigonal planar, etc.). Although you do not need to name the molecular shape for molecules and ions with more than one "central atom", you should be able to indicate the molecular geometry about each "central atom" (see the *Valence Shell Electron Pair Repulsion Theory* section to review VSEPR theory)

During lab construct a molecular model, using the kit provided, for each species listed in the tables. Do not make models for species where resonance is important (e. g., species in Group B and Group E) because these models will mislead you into thinking that there are double and single bonds in these species where there are not. Verify that your predicted geometries are the same as what you obtain with the models. Correct any errors in your table, and use the models as an aid to fill in any blank spaces. When writing the electron pair or molecular geometry for a species with a double or triple bond, just draw two or three straight lines, not curved lines.

After you have made a model check to see if it is included in Group H. If it is, examine its symmetry and use the table in Group H to find the different ways the molecule or ion can be rotated, reflected or inverted to give a configuration that is identical to the starting configuration. Fill in the Group H table.

Predict whether the molecule is "polar" or "non-polar". You do not need to indicate polarity for species with an entry of "---" in the polarity column. For ions this is because the electrostatic forces involved are much stronger than forces involving dipoles.

Results and Analysis

See the *Molecular Models Post-Lab Questions* section for questions to consider after completing this exercise. Your instructor will inform you whether he/she wants you to turn in these questions and what to do with the worksheets.

Conclusions

There are no conclusions to write for this exercise, unless your instructor informs you otherwise.

References

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Group A: Simple Lewis Dot Structures

Species	Lewis Dot Structure	Electron Pair Geometry	Molecular Shape	Polarity
F_2				
O_2				
N_2				
HF				
CO				
CO_2				

Species	Lewis Dot Structure	Electron Pair Geometry	Molecular Shape	Polarity
NO_2^+				----------
CH_4				
SiH_4				
NH_3				
PH_3				
H_2O				
H_2S				

Group B: Resonance

Species	Lewis Dot Structure	Electron Pair Geometry	Molecular Shape	Polarity
O_3				
N_2O				
NO_2^-				----------
NO_3^-				----------
CO_3^{2-}				----------
OCN^-				----------

Species	Lewis Dot Structure	Electron Pair Geometry	Molecular Shape	Polarity
CNO^-				----------
HNO_3				
HCO_3^-				----------
$C_3H_5^+$				----------

Group C: Expanded Octet

Species	Lewis Dot Structure	Electron Pair Geometry	Molecular Shape	Polarity
PCl_5				
PF_6^-				--------
SF_4				
SF_6				
ClF_3				
I_3^-				----------

Species	Lewis Dot Structure	Electron Pair Geometry	Molecular Shape	Polarity
IF_4^-				---------
IF_5				
XeF_2				
XeF_4				

Group D: Radicals and Electron-Deficient Species

Species	Lewis Dot Structure	Electron Pair Geometry	Molecular Shape	Polarity
BH_3				
NO				
NO_2				
B_2H_6				
BF_3				
Al_2Br_6				

Group E: Expanded Octet and Resonance

Species	Lewis Dot Structure	Electron Pair Geometry	Molecular Shape	Polarity
SO_2				
SO_3				
SO_4^{2-}				--------
HSO_4^-				--------
$POCl_3$				
ClO_4^-				--------

Group F: Organic Functional Groups

It may be easier to construct the models for C_2H_2, C_2H_4, and C_2H_6 if you consider them to have the structural formulas CHCH, CH_2CH_2, and CH_3CH_3, respectively.

In stable compounds carbon always forms four bonds and these may be distributed as four single bonds, a double bond and two single bonds, two double bonds, or one triple and one single bond. Accordingly, compounds of carbon are classified by the bonds formed between carbon atoms: compounds that contain only carbon-carbon single bonds are called *alkanes*, compounds with carbon-carbon double bonds are *alkenes* and compounds with carbon-carbon triple bonds are called *alkynes*. These groupings of atoms, which can occur individually or together in a molecule, are examples of *functional groups*.

You should also note that even when several carbon atoms are strung together, each carbon atom retains a distinct geometry that is dictated by its bonding, and the same is true when other atoms replace the hydrogen in the parent molecules.

There is an alternate way of writing structural formulas that may help you build some of these models. In this method if more than one oxygen atom appears next to a carbon, parentheses are placed around the oxygen or around both the oxygen and carbon when the carbon and the oxygen are attached to each other. So we can write HCOOH as HC(O)OH, or as H(CO)OH, and HCOH as H(CO)H to emphasize the connectivity. These compounds contain functional groups that involve oxygen: -OH (*alcohol* or *hydroxyl*), C-O-C (*ether*), C-(CO)-H (*aldehyde*), C-(CO)-C (*ketone*), and C-(CO)-OH (*carboxylic acid*). Again we see that carbon only forms four bonds, no matter what else is attached to it. Note the similarity of the alcohol and ether functional groups to H_2O. There are two other functional groups found in the table C-N (*amine*) and C-(CO)-N (*amide*). Note the similarity of the amine functional group to NH_3.

Species	Lewis Dot Structure	Electron Pair Geometry	Molecular Shape	Polarity
C_2H_2				
C_2H_4				
C_2H_6				
$CH_3CH_2CH_3$				
CH_3Cl				
CH_2Cl_2				

Species	Lewis Dot Structure	Electron Pair Geometry	Molecular Shape	Polarity
$CHCl_3$				
CH_3OH				
CH_3NH_2				
H_2CO				
$HCOCH_3$				
HCOOH				

Species	Lewis Dot Structure	Electron Pair Geometry	Molecular Shape	Polarity
CH_3OCH_3				
$HCONH_2$				
C_6H_6				

Group G: Isomers

Isomers are chemical compounds with the same chemical formula, but which have different chemical and physical properties. In this part of the exercise we will consider three types of isomers of the many that exist. These are *constitutional isomers* (compounds where the bonds are different, but the atoms are the same), *geometric isomers* (the bonds are the same, but their arrangement in space is different) and *rotational isomers* or *rotamers* which arise by the rotation about a bond.

The chemical formula for the molecule CH_3CHClF is a structural formula (attempts to show how the atoms are connected). There are two different ways in which this molecule can be constructed without changing the nature, or the number, of the chemical bonds. These compounds <u>are</u> different, and are examples of a class of geometric isomers called *enantiomers*. Examine the models to determine how enantiomers are related to each other.

The chemical formula for the molecule $C_2H_2Cl_2$ is <u>not</u> a structural formula. There are three ways in which to construct molecules with this chemical formula. Two of them have the atoms connected in the same way, but differ only in how the atoms are arranged in space. They are examples of geometric isomers called *diastereomers*. In the third molecule the atoms are connected differently, and so it is a *constitutional isomer* of the other two. From your models can you tell how diastereomers differ from enantiomers?

Take your models of C_2H_2, C_2H_4 and C_2H_6 from Part E, and holding one of the carbon atoms, <u>gently</u> try to rotate the other carbon atom. The carbon atoms of C_2H_6 can be rotated relative to each other, but the others can not. Why can this rotation occur? As you rotate about the carbon-carbon bond in the molecule for which this is possible you will notice two limiting arrangements of the atoms relative to each other. Draw these two rotamers.

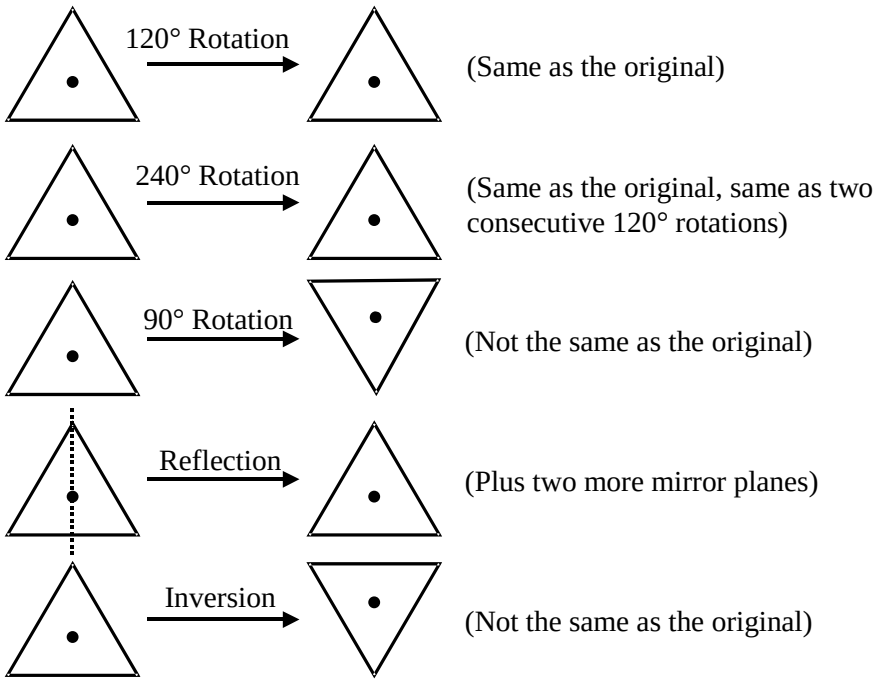
Species	Lewis Dot Structure	Electron Pair Geometry	Molecular Shape	Polarity
CH_3CHClF (first way)				---
CH_3CHClF (second way)				---

Species	Lewis Dot Structure	Electron Pair Geometry	Molecular Shape	Polarity
$C_2H_2Cl_2$ (first way)				---
$C_2H_2Cl_2$ (second way)				---
$C_2H_2Cl_2$ (third way)				---
CH_3CH_3 (first rotamer)				---
CH_3CH_3 (second rotamer)				---

Group H: Symmetry

To understand bonding in molecular orbital (MO) theory one must describe a chemical species mathematically. The first step in this mathematical description is to describe the symmetry of ions and molecules. While a full description of MO theory is well beyond the scope of this course, we can begin to appreciate symmetry as it relates to chemical species.

Mathematically symmetry is described by what physical operations can be performed on an object such that it is brought to a new position that is indistinguishable from the original. These operations are rotation about a line (a rotation axis), reflection through a plane (a mirror plane), inversion through a point and the improper rotation (a rotation followed by a reflection in a plane perpendicular to the rotation axis). The geometric features of a point, a line and a plane are called *symmetry elements*, about which a *symmetry operation* (reflection, rotation, inversion, or improper rotation) is performed. For example, a triangle has rotational and mirror symmetry, but not inversion symmetry. Inverting the triangle through the center does not give us the same configuration. Note that a triangle has only one rotation axis, but we can do two rotations about it (120° and 240°, which is the same as a 120° rotation done twice). We cannot do a 90° rotation of a triangle and get a configuration that is the indistinguishable from the original. Objects that have more symmetry elements are more symmetrical and are said to have higher symmetry.



For the molecules listed in the table, determine what symmetry elements, and how many of each, are present. Differentiate the rotations by how many degrees you must rotate about the axis to obtain a configuration that is identical to the original. Be as descriptive as possible in describing the location of the different symmetry elements.

Species	Rotations					Mirror Planes	Inversion
	30°	60°	90°	120°	180°		
F_2							
HF							
NH_3							
H_2O							
BH_3							
CH_4							
SF_4							
XeF_4							
PCl_5							
SF_6							

How to Draw Lewis Structures

The following is a general procedure for drawing Lewis structures. It will also work with more complex molecules and ions, if you recognize that individual atoms will have the same arrangement of bonds and lone pairs as they do in the simple structures. It is this similarity that allows us to understand the chemistry of complex molecules (especially organic molecules).

Remember that a Lewis dot structure is an approximation of the actual arrangement of electrons in a molecule or polyatomic ion, much in the same way a cartoon of a cat is an approximation of the actual animal. Our cartoon picture of a molecule is limited, but can give us a rough idea the bonds that hold a polyatomic chemical species together, which is why it is useful.

1. Determine type of compound.

Remember that Lewis dot structures

- only give reasonable results for covalent compounds and polyatomic ions of the main group (s and p block) elements,

- cannot predict the structure of ionic compounds,

- they are not useful for compounds (molecules or polyatomic ions) involving transition metal ions except those which have a d0 or d10 electronic configuration, for which they do work.

2. Identify the arrangement of the atoms.

- Identify the central atom.
  - Usually this is the least electronegative atom (example: in CF_4, C is the central atom).

- In simple compounds the central atom is the element that appears only once in the formula (example: H_2O, there are two H and only one O, so O is the central atom, even though it is the most electronegative atom).

- H and F are almost always terminal. The primary exception to this rule is where H is bonded to more than one other atom. Examples of this are hydrogen bonding, and a family of compounds called boranes (e. g., B_2H_6). In these cases hydrogen is said "to bridge" the other atoms or is said to be "bridging." Compounds of this type are rarely encountered in introductory chemistry, but you should be aware of their existence because they are not uncommon.

- All other halogens can be either the central or a terminal atom.
  - The easiest way to tell which is which is to go by electronegativity or by the number of atoms.

  - The terminal atoms when a halogen is in the center are usually O or another halogen.

-All halogens, except F, can form bridges, just like hydrogen. Like the other bridged structures discussed above, bridging halogens are not often encountered in introductory chemistry classes, but you should know that it is possible. An example of bridging halogens occurs in aluminum bromide (Al2Br6) where two Br bridge the Al and the other four Br are bound terminally.

- Unless it is clearly the central atom, oxygen is a problem, because it can be a terminal atom (as in CO_2) or a central atom (as in H_2O). The best course of action is to leave it until last. Some of the most vexing examples are organic compounds where oxygen is bound to carbon. Examples of these are:

  -Ethers (O is the central atom between two C),

  -Alcohols (O is the central atom between C and H),

  -Aldehydes, ketones and amides (O is attached terminally to one C, in an amide the C is also bonded to an N),

  -Esters and carboxylic acids (two O are attached to one C, one O is terminal and the other is attached to another atom).

- When all else fails, go with the arrangement that gives the most symmetric structure.

3. Determine the total number of valence electrons.

- Add up the number of valence electrons from all atoms.

- For anions add a number of electrons equal to the negative charge.

- For cations subtract a number of electrons equal to the positive charge.

4. Place one electron pair between each pair of adjacent atoms (as determined from the framework found in step 2) to form a single bond.

5. Place electron pairs around each terminal atom (except H) to complete octets.

6a. If not all of the electrons have been placed and all terminal atoms have complete octets, place the remaining electrons pairs on the central atom.

- Be sure to recognize the elements that violate the octet rule by having more than 8 electrons (elements of the third and higher periods).

- If you have electrons left over and the central atom cannot violate the octet rule, then there is a mistake somewhere. Common errors include: wrong number of valence electrons, wrong framework (central atom is incorrect) and simple math/counting errors.

6b. If the central atom doesn't have a complete octet, move a lone pair from a terminal atom to a position between the terminal and central atoms. This gives a double bond. Repeat as needed to form other double bonds using other terminal atoms, or a triple bond if no other terminal atoms are available.

- Hydrogen never forms a double or triple bond.

- Carbon, oxygen, nitrogen and sulfur are the most commonly encountered atoms that will form multiple bonds. So, look for these first when you need to form multiple bonds.

- Halogens seldom form multiple bonds when they are not the central atom.
  - The primary exception is where the central atom can't complete its octet (e. g., BF_3).
  - Use the Electroneutrality Principle (see point 8, below) to guide you. If it violates the Electroneutrality Principle, then forming the extra bonds is probably not a good idea.
  - Halogens that are central atoms can form multiple bonds with the atoms around it because they can expand their octet (see points 7 and 8).

- Langmuir's Rule can also help you decide whether you should form multiple bonds. Langmuir's Rule states that for a molecule or polyatomic ion where n atoms complete their octets, the number of covalent bonds is given by the equation shown below. Note that this rule does not work for compounds containing hydrogens or that have atoms that have expanded octets.

$$number\ of\ covalent\ bonds = \frac{8n - (number\ of\ valence\ electrons)}{2}$$

7. Consider resonance.
Resonance is an attempt to show bonds that do not involve a pair of electrons being shared by two atoms. The keys to spotting resonance are:

- atoms that have a single bond on one side and double or triple bond on the other,

- atoms with a double bond adjacent to an atom with lone pairs,

- atoms that can exceed the octet bonded to an atom with lone pairs.

- Langmuir's Rule is sometimes useful in spotting resonance, too.

8. Calculate formal charges and use the Electroneutrality Principle to determine which Lewis dot structure is the best, or which resonance structure makes the largest contribution to the resonance hybrid.

The Electroneutrality Principle states:

- electrons are distributed so that charges on atoms are as close to zero as possible,
- best structures are those that minimize formal charge and don't separate formal charge,
- if charges must be placed on an atom, a negative charge should sit on the most electronegative atom or a positive charge should sit on the least electronegative atom,
- structures with more covalent bonds are better Lewis dot structures (as long the above rules are also satisfied).

Valence Shell Electron Pair Repulsion Theory

Valence Shell Electron Pair Repulsion (VSEPR) theory is a convenient way to turn a Lewis dot structure into a three-dimensional representation of a polyatomic chemical species in the gaseous state. Because Lewis dot structures do not give a highly accurate model for bonding in most molecules, VSEPR structures are limited in the same ways that Lewis dot structures are limited. In addition, VSEPR only gives an accurate prediction of structure in the gaseous state because there are no interactions between particles in a gas, which can have a significant influence on structure in liquids and solids.

1. Start from the Lewis dot structure and count areas of electron density around the central atom.

In VSEPR a lone pair, a single unpaired electron and any bond (single, double or triple) each count as one area of electron density. For species with more than one "central atom," treat each "central atom" separately.

2. From the number of areas of electron density around the central atom determine the electron pair geometry.

In VSEPR there are only five electron pair geometries that maximize the distance between areas of electron density. These are given in Table 1.

Areas of Electron Density	Electron Pair Geometry
2	linear
3	trigonal planar
4	tetrahedral
5	trigonal bipyramidal
6	octahedral

Table 1. VSEPR's electron pair geometries.

3. Place the bonds (and their associated atoms), lone pairs and unpaired electrons around the central atom in the correct electron pair geometry.

There are two special cases:

- in the trigonal bipyramidal geometry, the lone pairs are always placed in one of the three equatorial positions, and

- in the octahedral geometry when there is a single lone pair, it is always shown in the bottom "axial" position by convention, and when there are two lone pairs they are placed across from each other in the "axial" positions.

4. Convert the electron pair geometry to the molecular structure (more commonly referred to simply as the structure) by omitting the lone pairs and unpaired electrons.

NOTE! Omit does not mean that we redraw the structure (this is the most common error in converting the electron pair geometry to an actual structure). The placement of all bonds and atoms does not change! We, in essence, go from the electron pair geometry to the structure by covering up the lone pairs and draw everything that remains in exactly the same position as in the electron pair geometry.

There are several new structures that derive from the presence of lone pairs in electron pair geometries. They are shown in Table 2.

Structure	Where does It come from?
Bent	A trigonal planar electron pair geometry and one lone pair, or a tetrahedral electron pair geometry and two lone pairs
Trigonal pyramidal	A tetrahedral electron pair geometry and one lone pair
Bisphenoid/See-saw	A trigonal bipyramidal electron pair geometry and one lone pair
T-shaped	A trigonal bipyramidal electron pair geometry and two lone pairs
Square pyramidal	An octahedral electron pair geometry and one lone pair
Square planar	An octahedral electron pair geometry and two lone pairs

Table 2. Structures arising from electron pair geometries due to the presence of lone pairs.

A linear structure can be obtained from some electron pair geometries because of the presence of lone pairs. These cases are: a tetrahedral electron pair geometry with three lone pairs, and a trigonal bipyramidal electron pair geometry with three lone pairs.

5. Predict or Explain Deviations from Ideal Structures.

VSEPR can also be used to predict how a polyatomic species will distort relative to the idealized structure. However, it is best used as a tool to explain why a given structure is distorted rather than as a predictive tool. In explaining why the distortions occur we need to balance three competing influences:

- lone pairs take up more space than bonds. Repulsion between electrons in a lone pair and the other electrons (either in bonds or other lone pairs) may cause distortions in the structure.

- triple bonds are fatter than double bonds, which are fatter than single bonds. The amount of electron-electron repulsion experienced between a bond and lone pairs or other bonding pairs decreases in the order: triple > double> single. Therefore, we expect that a triple bond may cause more distortions in the structure than either a double or single bond and that a double bond will cause more distortion when compared to a single bond.

- bonds which involve a significant difference in electronegativity between the atoms in the bond will have the electrons in the bond distorted toward the more electronegative atom. This will decrease electron density near the central atom and lessen the repulsion between this bonding pair and other electron pairs in the molecule.

Molecular Models Post-Lab Questions

1. Why can we ignore the disposition of the lone pairs on terminal atoms?

2. How does the bonding change for O_2, N_2 and F_2? How do you expect this to affect the chemistry of these substances? Why?

3a. Describe the structural changes that occur for BH_3, CH_4, NH_3, H_2O, HF as the central atom changes. According to the Lewis/VSEPR theory of bonding why do these changes occur?

b. What are the ideal bond angles in each compound? Which ones are expected to be distorted?

c. Give the hybridization of the central atom in each molecule.

4. Borane, BH_3, actually exists as diborane, B_2H_6, but the bonding in diborane cannot be adequately described by a Lewis dot structure. Why?

5a. Compare the structures in Group A where the central atoms are in the same group of the periodic table (i. e., SiH_4 and CH_4, NH_3 and PH_3, and H_2O and H_2S). What structural <u>similarities</u> do you see for elements in the same group?

b. Now consider the compounds containing P and S in the Group C worksheet. What structural <u>differences</u> do you observe for compounds where the central atoms are in the same group in the periodic table? How are these differences explained in Lewis theory? In valence bond theory?

c. How do you expect the chemistry of the elements to change descending a group, given the different structures available to the heavier elements?

6a. Calculate the formal charges and oxidation numbers on each atom for the following chemical species CO, CO_2, CO_3^{2-}.

b. Describe the structural and electronic changes that occur when oxygen atoms are sequentially added to CO. According to VSEPR theory why must the structure change?

7. Describe the structural and electronic changes that occur when oxygen atoms are sequentially added to SO_2 to give SO_3 and then SO_4^{2-}.

8. What structural and electronic changes accompany protonation (adding an H^+ to) CO_3^{2-} (to form HCO_3^-) and SO_4^{2-} (to form HSO_4^-)?

9. Describe the structural and electronic changes that occur when an electron is removed from NO_2^- to give NO_2 and then another electron is removed to give NO_2^+.

10a. Classify the molecules you have constructed in part F by their functional group.

b. Identify the hybridization about each carbon atom.

Molecular Modeling 2: Computational Chemistry

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Introduction

Computational chemists use the principles of quantum mechanics, classical physics and thermodynamics to answer questions about chemical processes. Since its birth in the 1960's, the growth of computational chemistry has generally followed advances in computer technology and it has become an essential tool in chemical research. It is used both as a guide to new avenues of research and as a way to understand fundamental chemical processes. Computational chemistry is used in areas as diverse as materials science to pharmaceutical research where most companies have a computational chemistry division that helps guide the development of new drugs. Of all the areas in computational chemistry, calculations that solve Schrödinger's equation are the most prevalent. Almost any property associated with where electrons are in the molecule, and how those electrons behave can be calculated. For example, molecular geometries, the polarity of a bond, the molecular orbitals, or the visible spectrum of a molecule can all be calculated using quantum calculations. Schrödinger's equation is written succinctly as

$$\hat{H}\psi = E\psi$$

where $\hat{H}$ is the Hamiltonian operator, ψ is the wavefunction, and E, the energy, is the eigenvalue of $\hat{H}$. The Schrödinger equation is a type of problem called an eigenvalue problem and you may not have encountered in your study of mathematics yet. As an example of how an eigenvalue problem works, if you have the function e^{5x} and the operator is to take the derivative, d/dx, then our eigenvalue equation would be d/dx (e^{5x}) = 5 e^{5x} where 5 is the eigenvalue since you apply the operator to the function and get back the function multiplied by a value which we call the eigenvalue. Only some operators and some functions are eigenvalue problems and that fact that quantum mechanical systems are described by eigenvalues is of deep significance.

In quantum chemistry methods, Schrödinger's equation is solved to give the electron density and the allowed electronic energies in a molecule (among other things). Solving Schrödinger's equation is dependent upon two primary considerations: 1) the form of the Hamiltonian and 2) the space electrons are allowed to occupy.

The level of theory describes the type of Hamiltonian and the basis set describes the space electrons are allowed to occupy. In general, the Hamiltonian for a molecule must include terms that take into account the kinetic energy of the electrons, the kinetic energy of the nuclei, electronic-nuclear attraction, electron-electron repulsion and nuclear repulsion. The full Hamiltonian is impossible to solve exactly for systems with more than one electron. Therefore we must make some approximations in order to solve the Schrödinger equation, and we must take an iterative approach which is facilitated by computers. In this exercise we will use three different levels of theory (essentially different approximations) to solve Schrödinger's equation: Austin Model 1 (AM1), Hartree-Föck (HF) and Density Functional Theory (DFT).

The AM1 level of theory is based upon a semi-empirical theory where certain portions of the molecule's energy are approximated empirically (determined experimentally). In semi-empirical methods, only valence electrons are considered explicitly, while paired core electrons are

approximated. In addition, the space the electrons are allowed to occupy is restricted to the bare minimum (H –1 set of s orbitals; C, O, N – 1 set of s, 3 sets of p orbitals).

HF is what is termed an *ab initio* (Latin: from the beginning) method because the Hamiltonian is based upon fundamental principles. The Hartree Hamiltonian is written so that the last term is a single potential that describes an average electron-electron repulsion energy or an interaction potential of electron *i* with all other electrons *j*. A general term for electron-electron repulsion and neglect of electron-electron correlation is needed to make the calculation more feasible. Methods that account for electron-electron correlation are available but computationally expensive and are usually restricted to molecules with unpaired electrons.

DFT is similar to HF in that all electrons are considered. However, in DFT the electron density ($|\psi|^2$) rather than the explicit ψ is solved for. In addition, electron-electron correlation is empirically parameterized based upon the density. DFT levels of theory are named to give specific information about them, but since these can be long, they are abbreviated (e. g., B3LYP, BPW91, mPWPW91) and often look like a bowl of alphabet soup.

In this exercise you will be using WebMO,[1] which is a web-based, user-friendly interface to the program Gaussian,[2] to calculate orbital energies and other properties of a series of molecules.

Experimental

General Instructions

The most recent version of WebMO that we are using no longer uses Java, and therefore should run under all current web browsers. However, if one web browser does not work, try a different one, and please report the problem to your instructor.

Go to the Truman WebMO website https://pyrite2.truman.edu/~webmo/cgi-bin/webmo/login.cgi. Clicking on this link will open your default browser, and take you to the site. If it does not, copy and paste the link into the browser's address field.

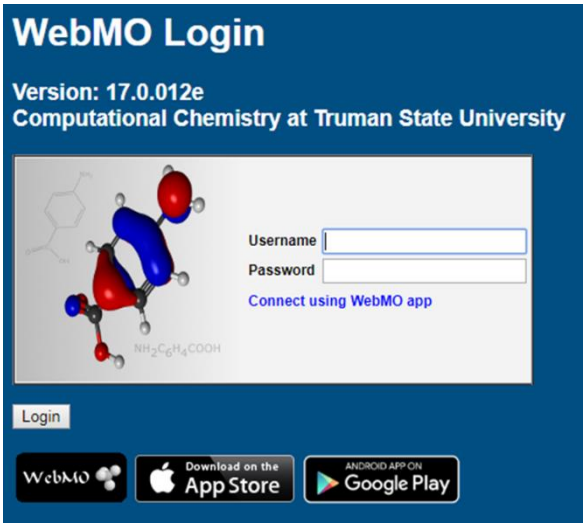

Figure 1. WebMO *Login* screen.

The WebMO ***Login*** screen shown in Fig. 1 will be displayed. Enter your username and password which will be given to you by your instructor. Click the *Login* button (or just hit enter) and the ***Job Manager*** screen (Fig. 2) will be displayed. You are now ready to set up your first calculation. Note that if more than one person is using the same account at the same time, WebMO will behave erratically.

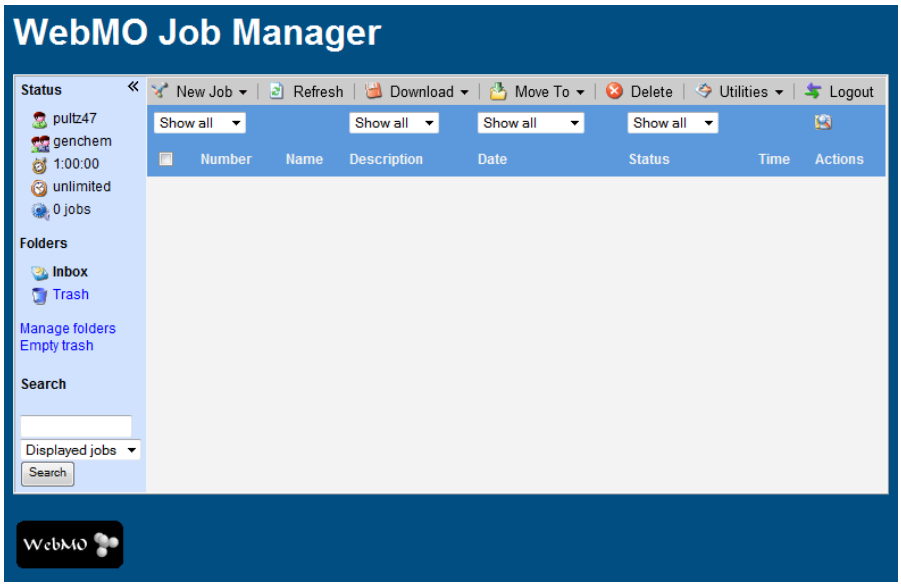

Figure 2. WebMO *Job Manager* screen.

Before performing any calculations you will need to input information about the molecule, what calculations to do and what level of theory that you want the program to use. The steps are 1) building the molecular framework, 2) selecting the calculation to do (geometry optimization, energy level calculation, etc.), 3) selecting the level of theory, 4) choosing a basis set, and 5) specifying the charge and number of unpaired electrons (multiplicity) on the molecule. With WebMO you are guided through the configuration process; start it by going to "New Job" and clicking on "Create New Job". This will take you to the *Build Molecule* screen shown in Fig. 3.

WebMO assumes that you want to create a new molecule when you create a new job, so *New Job: Create New Job* takes you straight to the editor. The function of each button that appears on the left side of the editor is given in Table 1.

Click on the *Periodic Table* button,  , to display a pop-up periodic table and click on the element you want to add. Then click in the gray space to add that atom. If you want additional atoms of the same element, click to place them in appropriate spots, being guided by VSEPR as best you can. For a new element, go back to the *Periodic Table* button and repeat the process until all the atoms you need for your molecule have been added. To draw bonds between atoms, click and drag the mouse from one atom to another. It is not usually necessary to specify any bond over a single bond because the program will determine the number of bonds that are needed.

Table 1. WebMO Editor Buttons.

Button	Name	Function
	Build	Allows placement of atoms in the display window.
	Periodic Table	Allows user to choose the atom to be placed when build button is active.
	Rotate	Allows the molecule to be rotated by clicking and holding the left mouse button and then dragging.
	Translate	Click and hold the left mouse button and then drag to move molecule within the display window.
	Zoom	Zooms in or out.
	Adjust/Select	When selected, you can click on any atom of bond in the molecule and changes its properties. Hold the *shift* key and click on atoms to select more than one atom. In the View Job screen this button allows you select atoms to determine bond lengths and angles.
	Adjust Charge	Select an atom and then push this button to set the atom's formal charge.
	Comprehensive Clean Up	Performs a comprehensive clean-up of the drawn molecule. Program takes its best guess as to what you really meant to draw. You can choose to clean up only certain parts of the molecule using the *Clean-Up* tool on the menu bar.
	Clean Up using Mechanics	Same as the comprehensive clean up, except that the program uses molecular mechanics to determine the best bond angles and lengths.
	Molecular Symmetry	This button appears dulled until something is drawn. The program will then display its best guess of the molecule's symmetry. The symmetry will change after a comprehensive clean up or after the molecule is symmeterized (*Calculate, Symmetry, Symmeterize* from the menu bar)
	Display Symmetry Elements	Will show where the molecule can be rotated, reflected, etc. to give a configuration that is identical to the starting configuration (see *Group H: Symmetry* in the *Molecular Modeling 1: Classic Molecular Modeling* exercise for more information.
	Huckel Orbitals	Displays the molecular orbitals derived from Hückel theory, and their energies, for molecule in its current geometry.
	Undo	Undoes the last action.
	Redo	Repeats the last action
	Preferences	Allows editing of some of the settings.

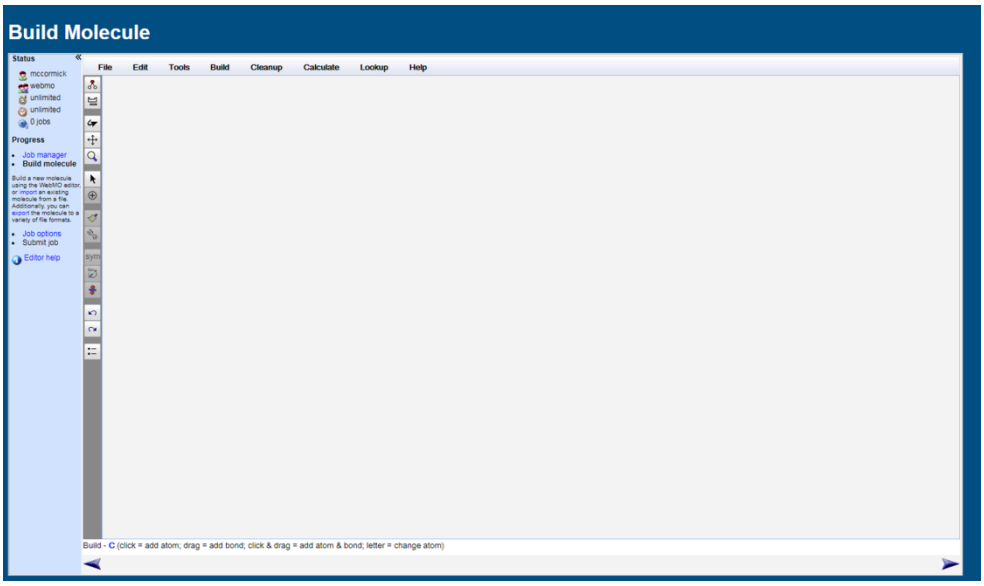

Figure 3. WebMO *Build Molecule* screen.

Comprehensive Cleanup adds hydrogen atoms to bonded atoms you have already drawn so that the octet rule is usually followed or zero formal charges are achieved. If you do perform a *Comprehensive Cleanup* on a molecule after you have drawn it, make sure the number of atoms agrees with the molecular formula and your starting geometry is still what you want. Unless otherwise directed to do so, do **not** perform a *Comprehensive Cleanup*.

When you are done drawing the molecule, click on the blue right arrow in the lower right corner. This will take you to the ***Configure Job Options*** screen shown in Fig. 5.

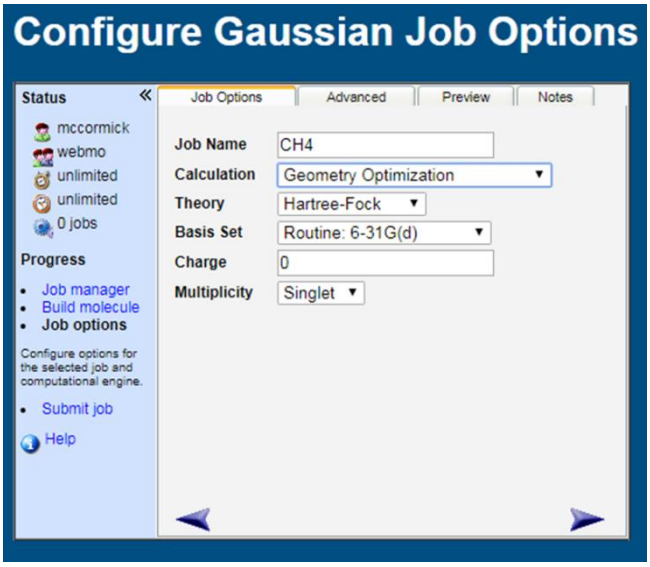

Figure 5. WebMO ***Configure Job Options*** screen.

The program will give your job a name based on the molecule that you drew. Be sure that your job has a unique name (it helps if the name is somewhat descriptive of what the calculation was about, like "H2 Hartree-Fock 3-21G"). Choose the type of calculation to do from the *Calculation Pulldown* menu; your initial calculation will never be the default in this exercise. Choose a theory from the *Theory Pulldown* menu and then select a basis set from the *Basis Set Pulldown* menu. If you are performing a calculation on an ion, enter its charge. For molecules the charge is 0. Leave the multiplicity as a singlet (this means that there are no unpaired electrons). Verify what you have entered and then start the calculation by clicking the right hand blue arrow head or "Submit job."

WebMO returns to the ***Job Manager*** screen. The ***Job Manager*** lists all the jobs you have submitted to be calculated along with pertinent information about them (from left to right this is job number, job name, type of job, the date you submitted it, job status, the length of the job). In the far right column (*Actions*) there will be displayed one of several icons (*View*, *Kill*, *Restart*) that you can use to control how the computer handles your job. If you made a mistake, one of two things usually happens; the program terminates your job and your results file contains nothing (or gibberish) or the program runs for a long time. If you want to stop a job for any reason, click the *Kill* icon ( ). You can restart a stopped job by clicking on the "Restart" icon ( ) which is displayed whenever a job is terminated abnormally. When your job is finished, its status will be *Complete* and the "View job" icon ( ) will be displayed to the right of the job. After you have submitted a job it is a good idea to occasionally click on the "Refresh" button on the WebMO Job Manager screen to get the most up to date information about your jobs; this is not the web page refresh button.

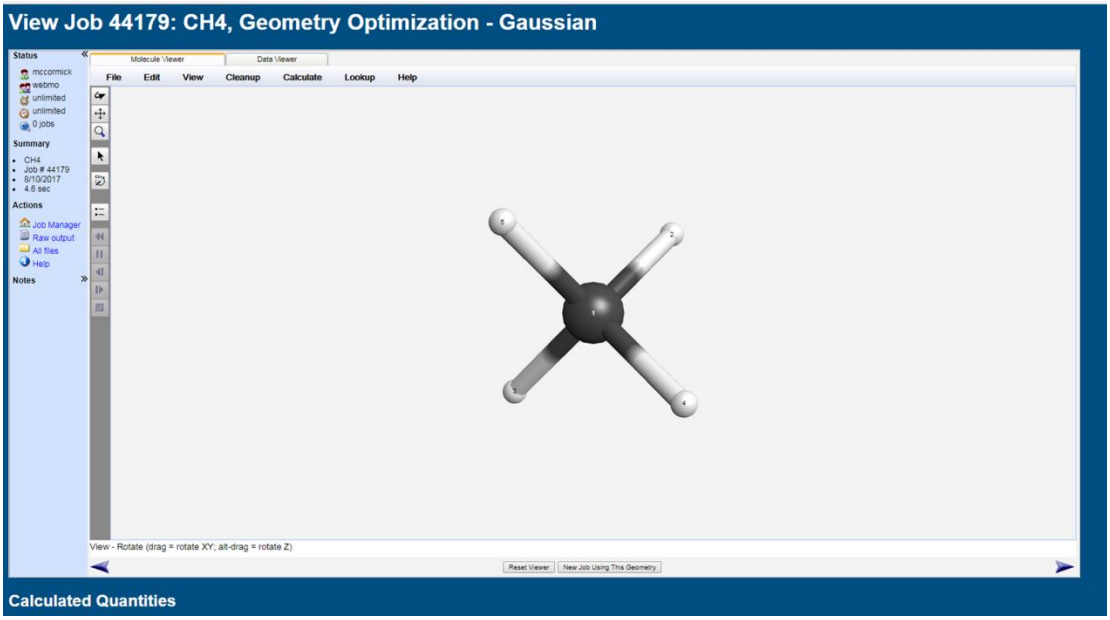

Figure 6. A portion of the View Results screen.

Important: If a calculation fails, click on the "View job" icon under Actions for the job. If you see the message "Optimization not converged (too many iterations)" and if the molecule looks

okay (the molecule may be rotated from how you initially drew it), click on the button New Job Using This Geometry. The next screen is Build Molecule. Click on the right hand blue arrow head to go to the "Configure Gaussian Job Options" screen. You probably should modify your job name to distinguish it from the previous failed job. Verify that the entries for Calculation, Theory, Basis Set, Charge, and Multiplicity are the same as specified in this exercise, and if they are not, correct them. Click on the right hand blue arrow head to submit your job again.
When you click on the "View job" icon, the results of your calculation will be displayed on the *View Job* screen like the one shown in Figure 6. At the top of the screen will be displayed the job number, the name you gave the job and what calculations were performed. Below this will be the *Viewer*, which is similar to that on the *Build Molecule* screen, but with some new buttons and actions that are listed in Table 2.

Table 2. Buttons on the WebMO *Viewer* that are active in the *View Results Screen*.

Button/Actions	Function
Job Manager	Returns to the *Job Manager* screen.
Raw Output	Shows the program's main output file.
All files	Allows the user to view all of the output files and change whether they are text or binary (if you select binary, the program will download the file to your computer, so don't do it).
Reset Viewer	Returns the Viewer to how it was when you entered the *View Results* screen.
New Job Using This Geometry	Starts a new job using the results of this job as a starting point (very useful).
Export Molecule	Allows user to take structures that you have created and pass them to other programs for viewing or additional calculations.

Below this will be a listing of the calculated quantities, which vary depending on what you told the computer to calculate. Be sure to scroll all the way to the bottom of this screen.

H_2 Geometry Optimization and Molecular Orbital Calculations
In the *Job Manager* screen go to the "New Job" tab and click on "Create New Job" to open the *Build Molecule* screen. Specify the element H by using either the Periodic Table button on the left side of the screen or the Build tab at the top. Put two H atoms in the window. Click on one H atom and drag the mouse to the second to create a bond between them. Continue to the next screen by clicking on the right hand blue arrow head. WebMO defaults to "Job Options" which is where you want to be for this exercise. Perform a "Geometry Optimization" calculation (not the default option) using "Hartree-Fock" theory and the "3-21G" basis set. Leave the charge as "0" and the multiplicity as "Singlet." Give your job a name. What you have told the computer to do is to repeatedly solve Schrödinger's equation each time adjusting bond angles and lengths (in this case, only the bond length) until it finds the lowest energy structure. Verify that you will do a geometry optimization and use the specified basis set. After the job is complete, click on the "View job" button in the *Job Manager* screen to look at the output.

Open a new Word document to record your molecule. Format the "2" as a subscript in H_2. Copy and paste the Route line (found under "Calculated Quantities") to have a succinct record of the

theory, basis set, and type of calculation, and the route line is useful in determining why you may have obtained unexpected results. Record the RHF energy, including sign and units, and again it may be easiest to copy and paste. Compare your value to the value calculated by classmates. You should converge to almost the same value; if there are significant differences, discover the reason and fix the problem.

Once the H_2 geometry is set, we can perform a molecular orbital calculation on H_2. In a molecular orbital calculation, you will specifically ask the program to render the shapes of the molecular orbitals from what is known about the wavefunction. From the *View Job* screen, click on "New Job Using This Geometry". You should now be in the *Build Molecule* screen. Click on the blue right hand arrow head or "Job Options". For this new job the *Calculation* is "Molecular Orbitals," *Theory* remains "Hartree-Fock," the *Basis Set* is "3-21G," the *Charge* is "0" and the *Multiplicity* is "Singlet." Give the job a name. Click either the right hand blue arrow head or "Submit Job." When the job is complete, click on the *View Job* button and scroll down to the section called "Molecular Orbitals". To view a molecular orbital, click the "View" button to the right of the molecular orbital. For H_2, the two lowest-energy molecular orbitals are labeled "1" and "2". These are the σ (bonding) and σ* (antibonding) molecular orbitals, respectively. A screen may appear asking you what to do. Click "Open" to open the MOViewer file (*.mo). One issue that you might encounter when viewing the molecular orbitals is that the program may clip the pictures (the MOs will look like sections were shaved off). This can be fixed by clicking on the *Preferences* button  and then on the *Isosurfaces* tab. Set the *MO isosurface value* to 0.08 and click OK.

The default view for molecular orbitals often does not allow you to see where the nuclei are located. Put the cursor on the molecular orbital picture and drag to rotate it so that you can see both nuclei. There should be holes or windows in the solid surface so that you can see inside to the nuclei. You could also modify the display by right clicking in the display window, point to the *Opacity* option and then select *Transparent* or *Mesh* from the sub-menu that appears.

In the" View Job" screen, click on the molecular orbital, then Ctrl-C to copy, go to your Word document, and press Ctrl-V to paste. (Alternatively, you could click File and Save Image, then import the file into your Word document.) Label the MO and record its energy. **Do not close MOViewer when you are finished with this orbital since you will use it several more times.** Also copy MO # 2, label it, and record the energy. Note that in the "View Job" screen there will now be a second tab labeled "job####_mo2" where the job number replaces ####, and you can switch between the MOs. Everything you record for H_2 should fit on one page.

N_2 Molecular Orbital Calculation

Build N_2 and perform a "Geometry Optimization" using Hartree-Fock theory and the 3-21G basis set (remember that N_2 is a singlet and has no charge). When the job is complete, record N_2 in your Word document and paste the Route line and RHF Energy, again including the sign and unit. On the optimized structure, perform a "Molecular Orbitals" calculation. View molecular orbitals 3 through 7. They are σ_{2s}, σ_{2s}*, the two π_{2p} orbitals, and σ_{2p}, respectively. In your Word document make a table with headings **Molecular Orbital Number**, **Unrotated**, and **Rotated**. Copy the five molecular orbitals (without rotation). How do the π molecular orbitals differ?

Then rotate each of the five molecular orbitals to see both nuclei, and copy the rotated molecular orbitals. Also record the energy and occupancy for the first ten molecular orbitals.

Structure of N_2O

There are two potential isomers of N_2O: one with a N-N-O framework and another with a N-O-N framework. Build both frameworks for N_2O (an uncharged singlet) in the *Build Molecule* screen, each as a separate job, using only single bonds. It is important that the N-O-N calculation start with a linear geometry. (The N-N-O framework can also be set to start with a linear geometry, but it usually turns out to be very close to linear as the result of the calculation. If your NNO calculation fails or your energy is significantly different from classmates, try building NNO again and impose a linear geometry.) To start with an exactly linear geometry, click on the "Select" button,  , and then click on one of the end atoms in the structure. While depressing the shift key, click on the central atom (the bond length will be displayed in the lower left corner of the window) and then the third atom (the bond angle, which should be around 180°, will be displayed). From the menu bar at the top of the *Build Molecule* screen, select *Adjust* and then *Bond Angle*. Enter 180 in the pop-up window and then select *OK*.

Perform a geometry optimization on each structure (be sure to give each a <u>different</u> name) using Hartree-Fock theory and the 6-31G(d) basis set. When each job is complete, click on the *View job* button. In your Word document, type your structure, either NON or NNO, and paste the Route line and RHF Energy, including unit, from the WebMO screen. Copy just the value, starting just before the negative sign and ending just before the unit, into Excel. Repeat the recording in Word and Excel for the other structure. In Excel calculate the magnitude of the energy difference in Hartree and record the result to four significant figures in Word, including the unit. Typical bond energies are given in kJ/mol, so convert the energy difference from hartree to kJ/mol (see http://physics.nist.gov/cuu/Constants/index.html for the hartree to joule conversion).

Once you have converted the RHF Energy's units, find the energy difference (in kJ/mol) between the lowest energy structure (i. e., the one that actually exists) and the highest energy structure. Report the difference to four significant figures. Compare your RHF energies and energy difference to those of your classmates.

Now scroll down to the section called "Partial Charges." The partial charge on each atom is listed by atom number and element. Click on the "View" button (magnifying glass in the *Partial Charges* section) to graphically display the partial charges on each atom in the viewer at the top of the page. The values should be in close agreement with values calculated by other students. Copy the three atoms of each N_2O structure in your Word document and show the calculated partial charges on each atom. (To copy in Windows, press the *PrtScn* button, press *Ctrl-C* to copy, open Paint and press *Ctrl-V* to paste. In Paint, click on Select, then Rectangular Selection, and use the mouse to put a rectangle around the molecule. Press *Ctrl-C* and then paste into your Word file.)

Bond Orders of N_2O

Return to the results for the <u>lower energy</u> structure. Below the picture of the molecule click on "New Job Using This Geometry" to return to the *Build Molecule* screen. Select "Job Options"

(or click the right hand blue arrow head) and set up a "Bond Order" calculation using Hartree-Fock theory and the 6-31G(d) basis set. The charge is again 0 and the multiplicity is singlet. Name the job and submit it. **Note:** you do not need to run the higher energy structure, but you may if you are interested and time permits.

When the job is complete, view the results. In the *Viewer*, click on the "Select" button,  . Then click on the central N (atom will be highlighted) and then while depressing the shift key, click on the other N. The N-N bond length will be displayed in the *Viewer*'s status window; record this number (the units of bond length used here are Ångstroms, symbol Å, 1 Å = $1x10^{-10}$ m). Unselect the terminal N by holding the shift key and clicking on it. Now select the O and record the N-O bond length. Determine the N-N-O bond angle by highlighting all three atoms, starting at an end atom; the angle should be 180°.

Note the number on the central N and scroll down to the section called "Bond Order". The numbers with four digits after the decimal indicate the bond order between the atom listed in the row heading (on the left) and the column heading (on the top). The bond order of an atom with itself is zero. Record the calculated N-N and N-O bond orders between <u>adjacent</u> atoms.
You may wish to include a picture.

Structure of ClF_3
Draw the Lewis electron dot structure for ClF_3 and predict its molecular shape with VSEPR theory. Use this as the starting point to build ClF_3 in WebMO. Perform a "Geometry Optimization" on ClF_3 using the semi-empirical theory AM1. The *Basis Set Pulldown*, will no longer be active because an AM1 calculation does not require a basis set (do not be concerned that there is an entry in the pulldown, the program will ignore it). **Note:** this calculation may fail because it exceeds the default maximum number of iterations. If this happens, simply restart the job, although you may have to select the "Other ()" option in the *Basis Set Pulldown*.
While this is calculation is running, set up another geometry optimization calculation for ClF_3 using the VSEPR geometry as the starting point. This time use the theory B3LYP and the basis set 6-31G(d).

Copy the structures predicted by each calculation. Be sure to include the starting geometry and which theory was used. Determine the Cl-F bond lengths (there are three of them) and the F-Cl-F angles (there may be several) and include these on your sketches.

Now perform a "Geometry Optimization" on the ClF_3 structure predicted by AM1 theory, but using the theory B3LYP and the 6-31G(d) basis set. Record the results of this calculation in your report, again specifying the starting geometry and theory.

Bond Polarity
Create separate jobs for the following molecules: CH_4, CH_3BH_2, CH_3NH_2, CH_3OH and CH_3F. After you draw each molecule in the *Build Molecule* screen, do a *Comprehensive Cleanup* to get better results. (For CH_4 you only need to put in a C atom and the *Comprehensive Cleanup* will enter the four H atoms in a tetrahedral arrangement. For the other four molecules, enter atoms other than hydrogen and connect them with a bond. *Comprehensive Cleanup* will then add the

hydrogen atoms.) Perform a geometry optimization on each using HF theory and the basis set 6-31G(d). All of these molecules are singlets and have no charge.

When the jobs are complete, go to the *View Job* screen for each molecule. Scroll down to the section called "Dipole Moment" and record the dipole moment value (the unit of dipole moment is the Debye). Click on the "View" icon and scroll back to the top to see the direction of the dipole (i. e., which direction are the electrons pulled in the bond). You may need to rotate the molecule to see the arrow. Put a picture of each molecule with the dipole moment in your report.

Results and Analysis

H_2 and N_2

Make a molecular orbital energy-level diagram for H_2 which is to scale; an Excel scatter chart may be the easiest approach. The program assumes the atomic H 1s orbitals are at 0.000 Hartree. You may wish to include in your MO diagram the pictures of the σ and σ* molecular orbitals.

Make a molecular orbital energy-level diagram for N_2 which shows the ten lowest-energy MOs (use occupancies to help place the electrons). You may wish to make two diagrams, one which emphasizes the difference between the MOs formed from n=1 atomic orbitals and n=2 atomic orbitals. The second diagram could then zoom in on the MOs formed from the valence atomic orbitals. Both of these diagrams must be to scale, not the caricatures shown in textbooks.
In the Lewis dot structure of N_2 we would predict three bonds and two lone pairs arising from the valence electrons. Is this consistent with the MO picture? How does MO theory describe the bonds and lone pairs in N_2?

According to Valence Bond theory, what hybridization would you expect each N atom to have? How does this compare to the MO description? (Hint: think about the following: how are the bonds described? how are the lone pairs described? do the valence bond orbitals look like the molecular orbitals?).

N_2O

Draw the two best resonance structures for NNO and calculate the formal charges on each atom in both cases. Draw the best Lewis dot structure for NON and calculate the formal charges on each atom. Based on formal charges and electronegativity, which connectivity is predicted to be more stable? Does this prediction match the structure which you calculated to have the lowest energy? Based upon your MO calculation, which resonance structure for NNO is slightly dominant? Why is this resonance structure dominant?

The N-N bond length in N_2O has been measured to be 1.128 Å and the N-O bond length has been measured to be 1.184 Å.[3] Given the <u>average</u> bond lengths shown in Table 3, are the measured bond lengths and the calculated bond lengths consistent with the bond orders? How well did the calculation do in obtaining the true values of the bond lengths?

Table 3. Average bond lengths for different N–N and N–O bonds.[4]

Bond	Bond Length (Å)
N-N single bond	1.45
N-N double bond	1.25
N-N triple bond (in N_2)	1.10
N-O single bond	1.40
N-O double bond	1.21
N-O triple bond	1.08

ClF_3

On your VSEPR-predicted structure of ClF_3 indicate the predicted distortions from the ideal angles caused by the repulsion of the bonding pairs by the lone pairs. Do your predictions (using different levels of theory) match that predicted by VSEPR? Which theory can give a better match to the VSEPR model? Why?

The structure of ClF_3 has been determined at -120 °C using X-ray crystallography,[5] and is shown in Fig. 7. Also shown in Fig. 7 are the measured bond angles and bond lengths. Which of the models considered (VSEPR, AM1 or B3LYP) always gives a better qualitative agreement to the actual structure of ClF_3? Which can give a better quantitative agreement to the actual structure?

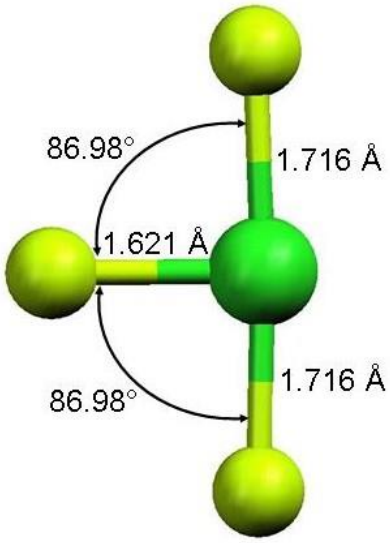

Figure 7. Structure of ClF_3 as determined by X-ray crystallography at -120 °C showing the relevant bond angles and bond distances.[5] Here the fluorines are represented by yellow-green balls and the chlorine by a darker green ball.

With ClF_3 you should have found that the AM1 calculation gave the wrong answer and that when you start from a structure that is not close to the "true" structure, you are not guaranteed that you can arrive at the "true" answer. These illustrate two important considerations in computational chemistry (and anywhere where we use computer models): the appropriateness of the model and the problem of "local" versus "global" minima. The AM1 result is an example of the first consideration because AM1 theory ignores important aspects of bonding, which are

included in the B3LYP model, that lead to an incorrect predicted structure. The trigonal planar structure predicted by AM1 theory is a local minimum (it is a structure that has a low energy, but not the lowest energy) from which the program cannot escape even using a better model. Although computers are very good at performing calculations, they have no chemical intuition, which is why the human element is an essential component of computational chemistry.

Bond Polarity

The experimentally determined dipole moments for compounds considered here are given in Table 4.[6] Note that there is no entry for CH_3BH_2. Qualitatively rationalize the calculated dipole moment's direction and magnitude with what you know about electronegativity. How do the calculated dipole moments quantitatively compare with the actual values? If we were able to measure the dipole moment of CH_3BH_2, predict how it would compare to the calculated value?

Table 4. Experimental dipole moments measured in the gas phase.[6]

Substance	Dipole Moment (D)
CH_4	0.00
CH_3BH_2	-----
CH_3NH_2	1.31
CH_3OH	1.70
CH_3F	1.85

Conclusions

Devise your own conclusions for this exercise (helpful hint: the questions in the *Results and Analysis* section, above, will be particularly helpful, and it you construct your answers to them in a logical fashion, you will be well on your way to a good *Conclusions* section for this exercise).

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Gas Chromatography: Identifying Unknown Compounds

V. M. Pultz

Introduction[1]

Most materials are mixtures of some kind. This includes everything from food to gasoline, car tires to sea water and even animals. Chemists often need to know how to determine the composition of a mixture. A common and logical approach is to separate the components of the mixture and identify them one at a time. Finding the identity of the components of a sample is very desirable information (qualitative identification), but quantification of the amount of a component in a mixture (for example, the amount of residual pesticide contamination a food item) is often critically important as well.

The problem that chemists face is then how to separate the components of a mixture? One simple way to do this is by distillation where the mixture is heated until the random kinetic motion of the molecules can overcome the attractive intermolecular forces holding molecules together at the surface of the liquid. Depending on the volatility of the mixture's components (i. e., their boiling points, which is determined to a large extent by the intermolecular interactions), the composition of the vapor will be rich in the more volatile component (the one with the lower boiling point). Condensing the vapor thus formed would give a liquid that is richer in the more volatile component. Repeating the boiling/condensing process multiple times, in a procedure called fractional distillation, would result in separation of the low-boiling point components of the mixture from the high-boiling point components. Therefore, one factor that is important in separating a mixture by distillation is the length of the distillation column. The longer the column the more times the boiling/condensing process can occur, and the more efficient the separation can be. With a sufficiently long column, even substances with very similar boiling points can be separated. Fractional distillation how crude oil is refined into gasoline and other products, albeit on a much larger scale than we would do in the laboratory. There are several problems with separating mixtures by fractional distillation, one of which is that some compounds decompose upon heating. Another problem is that some mixtures form *azeotropes*, which boil as the mixture at a set boiling point, and cannot be separated by distillation (azeotropes are quite interesting, but beyond the scope of this exercise). Because of these problems, and others, chemists need more additional methods by which to separate the components of a mixture.

These other methods are grouped under the name chromatography, and even though they have slightly different names, they are all based, at least in part, on the strength of intermolecular forces. Some examples of chromatographic methods used by chemists are gas chromatography (GC), thin layer chromatography (TLC), and high-pressure liquid chromatography (HPLC). Whereas distillation typically requires a minimum ~10 mL of sample, sample sizes for chromatography can be as small as 0.1 μL (but can range all the way up to liters). The different chromatographic methods are physically different. For example, TLC is usually performed on thin glass or plastic plates, while GC and HPLC separations are usually performed in hollow tubes called columns, and this can also affect how the components of a mixture can be separated.

One advantage of chromatography over distillation is that, because the mixture is not heated in many of these methods, thermal instability is not a problem. It is also possible to separate

azeotropes, because of the way that we use the intermolecular interactions to our advantage in chromatography. In distillation the intermolecular interactions were only between the different components of the mixture. However, in chromatography there is another interaction. All chromatographic methods have two parts: the *stationary phase* which is a solid (or a liquid coating a solid), and the *mobile phase* (either a gas or a liquid) that sweeps past the stationary phase. The key to most chromatographic separations is the polarity difference between the mobile and stationary phases and how the molecules in the mixture interact with the two different phases.

When a compound moves with the mobile phase over the stationary phase, the compound experiences an intermolecular attraction to stay in the mobile phase, and a competing attraction to adsorb onto the stationary phase. The molecules of the different components in the mixture will, thus, partition themselves between the mobile and stationary phases differently, with those components that interact only weakly with the stationary phase move spending more time in the mobile phase. Because the mobile phase is moving, mixture components that interact more strongly with it will tend to move over/through the stationary phase more quickly, while components that interact more strongly with the stationary phase will move more slowly. The amount of time that a compound is retained on the column is called the *retention time*. Ideally, the individual components of the mixture have sufficiently different retention times so that they reach the end of the device individually (that is one component at a time).

In this exercise you will be using a Vernier Mini-GC to separate organic compounds and explore the factors that affect this separation in the gaseous state. The Vernier Mini-GC uses an 11-meter-long steel column with an inner diameter of 0.53 mm that is coated with a nonpolar silicone polymer that serves as the stationary phase. A sample, consisting of one or more compounds, is injected into the column and is carried by atmospheric air, which is the mobile phase. As each component of the mixture exits the chromatography column, it will be detected to give a *chromatogram*, such as the one shown in Fig. 1. Note that in a chromatogram the

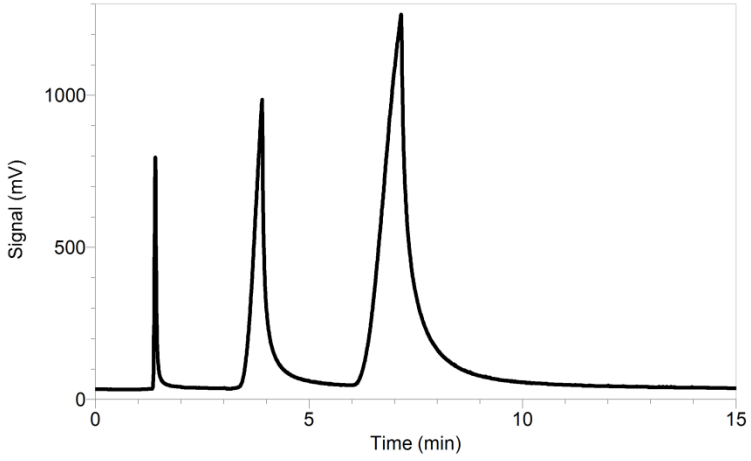


Figure 1. An example of a gas chromatogram showing good separation of three analytes.

signal intensity (instrument response) is proportional to the amount of the substance present and if the separation were perfect the *peaks* in the chromatogram would be very sharp, with no tailing, as evident in the peaks in Fig. 1.

The time it takes for a specific compound to exit the column after it is injected is called the *retention time*, and which should be constant for a particular compound under a particular set of experimental conditions. Note that retention times are highly dependent on the factors, such as the gas flow rate, the temperature of the GC column and the stationary phase used. This means that we must clearly specify the conditions when reporting and comparing retention times. This also means that using a GC, a compound may only tentatively be identified from a mixture of compounds by its retention time, because two different substances can have the same retention times. Thus, it is easier to prove the absence of a compound than its presence, but this problem can be partially overcome by establishing a library of known retention times by testing known substances first under the same set of conditions. You will build such a library as part of this exercise and use it to identify unknowns.

We will also examine the effect that molecular polarity and polarizability have on the separation in this exercise. Because we will keep the stationary phase, gas flow rate, and the temperature profiles the same in each run, the retention time should allow us to make comparisons between molecular polarity and polarizability. To understand why polarizability is important in the separation, consider the organic compounds ethanol (boiling point 78 °C) and ethyl acetate (boiling point 77 °C). It is very difficult to separate these two solvents by distillation because of the very similar boiling points. However, they <u>can</u> be separated easily by gas chromatography, because of differences in polarizability. When a molecule being analyzed (the *analyte*) is introduced onto a GC column, there are likely negligible interactions between it and gas phase atmospheric molecules (N_2, CO_2, and O_2), since the density of gas molecules is very low, so the focus is on the interactions between the analyte and the nonpolar stationary phase. The only possible intermolecular interaction of ethanol with a nonpolar stationary phase is dipole-induced dipole. Ethyl acetate interacts with the nonpolar stationary phase via dipole-induced dipole forces that are enhanced by the greater polarizability of the larger ethyl acetate molecule. Thus, ethyl acetate molecules tend to spend more time adsorbed on the stationary phase than ethanol molecules do, which sweeps them to the detector slower than the ethanol molecules. While we may be able qualitatively predict retention times based on basic rules of polarity and polarizability, we can get better results using the computational chemistry methods introduced earlier in the semester.

Experimental

The compounds used in this exercise, and some pertinent information about them, are shown in Table 1. Draw Lewis electron dot structures for each of these compounds, and based on these Lewis structures, predict the order in which these compounds will exit the GC column (known as *elution order*). Assign the number 1 to the compound that you expect to elute first, 2 to the one that you feel would elute next, and so on until have assigned the last compound to elute a 9. You may also wish to consider the molar mass, a combination of boiling point and molar mass in coming up with your predictions.[2]

Table 1. The compounds used in this exercise, their chemical formulas, boiling points and molar masses.

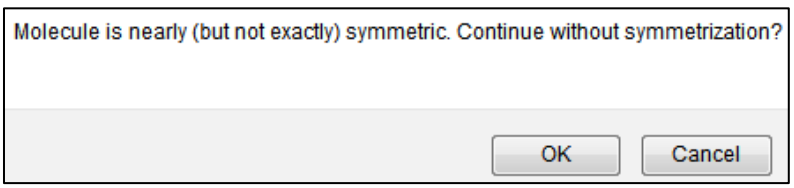
Compound	Formula	Boiling Point (°C)	Molar Mass (g/mol)
Acetone	CH_3COCH_3	56	58.080
2-Butanone	$CH_3COCH_2CH_3$	80	72.107
2-Pentanone	$CH_3COCH_2CH_2CH_3$	102	86.134
4-Methyl-2-pentanone	$CH_3COCH_2CH(CH_3)_2$	117	100.161
2-Heptanone	$CH_3COCH_2CH_2CH_2CH_2CH_3$	151	114.188
Methanol	CH_3OH	65	32.042
Ethanol	CH_3CH_2OH	78	46.069
Ethyl acetate	$CH_3COOCH_2CH_3$	77	88.106
Acetic acid	CH_3COOH	118	60.052

Computational Chemistry Procedure

The following procedure will show you how to calculate the polarizability of each compound in Table 1 using computational chemistry package that we introduced to you previously.[3, 4] With the calculated polarizabilities you can then predict the elution order for these compounds (which may, or may not, be the same as what you predicted from the Lewis dot structures). You will then compare the elution order that you predicted qualitatively based on polarity with the elution that you predicted from the calculated polarizability with the experimentally determined elution order. **NOTE:** your instructor may have you perform the computational part of the exercise before coming to the laboratory, or during the laboratory itself. Please check with him or her to determine how you are to complete this exercise.

Log on to the WebMO server by clicking on the link https://pyrite2.truman.edu/~webmo/cgi-bin/webmo/login.cgi, or by copying and pasting this link into your browser. If one browser does not work, try a different one. Login using the username and password that was previously assigned to you. Upon successfully logging in, the **WebMO Job Manager** screen should appear.

Initiate a calculation on acetone by going to the "New Job" tab (it will show "Create new job") and click. If you get a security warning, accept the risk and click on *Run*. This will take you to the **Build Molecule** screen. In the **Build Molecule** screen put in all C and O atoms, use single or double bonds to connect them as appropriate (see the *Molecular Modeling 2: Computational Chemistry* section to review how to build a molecule in WebMO). Perform a *Comprehensive Cleanup*, which will enter the H atoms and set bond angles and distances to their appropriate values. Once the molecule has been created and cleaned-up, click on the blue right arrow in the lower right corner. You may get the warning



You may click on *OK* to continue, or you may press *Cancel* and then click on **Symmetry** at the top of the **Build Molecule** screen. This will bring up **Symmetrize Molecule…**, click on it and then press **Symmetrize**. The point group will probably be C2, but another possibility is Cs, in either case click OK.[5] Click on the blue right arrow in the lower right corner again.

Now you should be at the **Configure Gaussian Job Options** screen. The program gives your job a name based on the molecule that you drew; you might want to add to the name that this is acetone. Choose the type of calculation to do from the *Calculation Pulldown* menu. Select the fourth one down which is "Optimize + Vib Freq" This will tell the program to first do a "Geometry Optimization" followed by a calculation of the vibrational frequencies which also includes a calculation of the polarizability. Keep the theory as "Hartee-Fock" and choose the basis set "Basic: 3-21G." Leave the charge as "0" since your molecule is neutral. Leave the multiplicity as a singlet (this means that there are no unpaired electrons). Verify what you have entered and then start the calculation by clicking the right hand blue arrow head or "Submit job." WebMO returns to **WebMO Job Manager** screen which lists all the jobs you have submitted.

While this job is running, start jobs for the remaining molecules listed in Table 1. Set up and run the calculation for each of the molecules as described above for acetone.

Once you have started calculations for all of the molecules, the acetone calculation should be finished, and its status will be *Complete* and the "View job" icon () will be displayed to the right of the job. Click on the "View job" icon and, if necessary, accept the risk and Run. Your molecule should be displayed on the screen. At the left side of the screen, click on *Raw output* which is immediately below *Job Manager*. Depending on the browser, you may have to click on *Edit* at the very top of the screen to open it. Search for **isotropic polarizability** (Ctrl-f). Record the value immediately before the units Bohr**3 which stands for $Bohr^3$ or a_0^3 (the volume in atomic units).

Close the *Raw Output* tab and scroll down to the *Vibrational Modes* section. Click on  to animate a vibrational mode. Watch what happens if you choose one with a frequency over 3000 cm^{-1} compared to one around 1900 cm^{-1} compared to one around 1500 cm^{-1} and finally compared to one with an even lower frequency. Note that these calculated frequencies are higher than the experimentally determined frequencies.

Repeat the process for the other molecules and record all of the polarizabilities in your notebook. For fun, you may wish to animate the vibrational modes for some of the other molecules, especially for methanol or ethanol, being sure to at least view the highest frequency mode for them.

When molecules are put into a gas chromatography column which has a nonpolar coating, their primary interaction with the column coating will be based on their polarizability. Larger polarizability should lead to longer retention time. In the case of acetic acid there is evidence that indicates acetic acid will primarily exist as a dimer under our experimental conditions (see

Figure 12-9 in reference 2). Since primarily dimers of acetic acid interact with the column coating, multiply the polarizability that you calculated for acetic acid by two to approximate the polarizability of the dimer. Use your polarizability values to predict the order for retention times of your molecules, as you did when you considered only their Lewis dot structures and physical properties. After gathering experimental values for the retention times in the laboratory, you will discuss how good your predictions were.

In-Laboratory Exercise

It is important that you carefully read and fully understand the directions for the care and use of the GC syringes and the Mini-GC itself before coming to the laboratory. You will find these at http://www.vernier.com/files/manuals/gc-mini.pdf; *Appendix C: Syringe Usage Instructions* contains some particularly useful information. The syringes are particularly delicate and so are easily damaged. Familiarizing oneself with the standard operating procedures for the GC syringe will minimize the chances that you will cause damage to a GC syringe, which will result in you being charged the full approximately $100 replacement cost.

Keep all chemicals used in this exercise away from open flames or sparks since they are flammable. **CAUTION**! Handle the glacial acetic acid with care. It can cause painful burns if it comes in contact with the skin, nasal tissue, or eyes. Wash off immediately!

Obtain a glass syringe from the Stockroom. A set of vials containing the known substances and one unknown mixture containing three to five substances to be identified should be already at your bench. If this is not the case, your instructor will inform you of how to obtain the samples for analysis. Note that you will not only test acetone but use it to clean the syringe needle.

Preparing the Mini-GC for Data Collection

You may use either a LabQuest 2 or your personal laptop to collect the data for this exercise (your instructor will tell you his/her preference), but you should be aware, however, that the Chemistry Department will bear no responsibility for any damage to your personal electronic equipment used in this way in the laboratory. See the *Operation of the Vernier LabQuest 2* and *Basic Data Collection Using Logger Pro* sections for more information.

Connect the Mini GC to the USB port on the LabQuest, or your computer, using a USB cable. Turn on the instrument using the power switch on the side. If you are using a LabQuest, it should automatically recognize the GC as soon as it is plugged in, set the mode to Gas Chromatograph, and display USB: Signal on the screen. With a laptop, you should wait a bit before starting Logger Pro to ensure that the GC device drivers have loaded. If the GC is not listed as the current device, or if there is no device listed, the device driver did not load, and you will need to shut everything down and try again (but wait a longer time before starting Logger Pro). Your instructor will assist you, if needed.

On a LabQuest, tap on *Mode* or simply tap the *Collect* button (either on the screen or on the body of the LabQuest itself). In Logger Pro, you can click on the *Data Collection* icon, or select *Experiment, Data Collection* from the menu bar or simply *Cntrl*-d. Any of these will cause the *Temperature-Pressure* profile set-up screen to appear. Set the temperature and pressure values to the following:

Start temperature	35°C
Hold time	1 min
Ramp rate	10°C/min
Final temperature	65°C
Hold time	6 min
Total length	10.0 min
Pressure	4.0 kPa

Select *Done* to initiate the Mini-GC warm up (note that if the profile screen was brought up by clicking the *Collect* icon in Logger Pro, it will immediately start the run). The computer/LabQuest will display "Do not inject until GC is ready," the LED on the GC will be red, and the GC display will read "GC Not Ready". The GC will take a few minutes to warm up and stabilize. When the GC is ready for injection, the message "Inject and click Collect simultaneously" will be displayed, the LED should turn green (on some of the Mini-GCs the red LED simply goes off), and the GC display will show "Ready to Inject."

Cleaning and Flushing the Syringe

The following steps must be done BOTH BEFORE AND AFTER a sample is injected on to the GC column. Note that you will be cleaning the syringe with acetone and acetone will also be analyzed as part of the exercise. **IMPORTANT!** The glass syringe is fragile. Be careful not to bend the needle or bend the plunger. Never pull the plunger back more than 50% of its total volume. Be careful not to bend the plunger as you press it down. Any damage to a syringe will mean that you will be charged its full replacement cost ($100).

Depress the plunger fully, and submerge the tip of the syringe needle into the vial of acetone. Pull back the plunger to fill the barrel about 1/3 full of acetone. Examine the barrel of the syringe and estimate the amount of acetone in the barrel. Carefully expel the liquid onto a Kimwipe or a paper towel. Repeat the uptake and expulsion of acetone at least two times to clean and flush the syringe. It may take more than three flushes to feel the syringe plunger move smoothly again, which is your indicator that the syringe and needle are both suitably clean. The first time you clean the syringe you may wish to do the cleaning/flushing cycle until you are comfortable pulling up a liquid into the syringe and measuring the volume in the syringe barrel. Use a Kimwipe to carefully pat around the tip of the syringe needle. The syringe is now ready for use.

Collecting a Sample for Injection

Helpful hint: do NOT collect the sample for injection until the Mini GC has reached the correct start temperature and pressure, this will prevent loss of sample by evaporation.

Submerge the tip of the syringe needle into the vial containing the sample. Draw up 0.15 μL of liquid. Record your actual volume, as you may need to decrease the volume in order to obtain the sharp peaks shown in Figure 1. You will also need to gradually decrease the volume that you use from 0.15 μL to about 0.10 μL as the molar mass of the compound being analyzes increases. Record the volumes that you inject for each compound. For at least <u>one</u> sample, see what happens when you use different volumes. After collecting your sample, gently wipe the needle, from barrel to tip, with a lint-free tissue such as a Kimwipe.

You are now ready for sample injection and data collection. **IMPORTANT!** You and your lab partner <u>must</u> divide the tasks in the injection/start data collection step: one person will operate the syringe and the other person will operate the computer controls.

To insert the needle of the syringe into the injection port of the Mini-GC, hold the syringe with one hand and steady the needle with your other hand, as shown in Fig. 2. Insert the needle into the injection port until the needle stop is fully seated. If the needle sticks, rotate it slightly while inserting. **Do not move the plunger yet!**

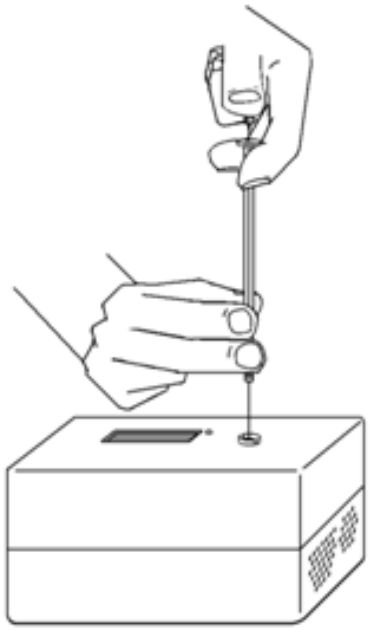


Figure 2. Proper method for injecting a sample into a Vernier Mini-GC.[1]

Simultaneously, depress the syringe plunger and tap/click on *Collect* to begin data collection. Pull the needle out of the injection port immediately.

While the data collection proceeds, thoroughly clean the syringe and needle with acetone so that the next chemical can be injected into the GC in a timely fashion.

The data collection will end after 10 minutes. You may stop the data collection early if you are certain that the entire injected sample has passed through the detector, although you may need to use a longer collection time for one of the compounds.

Save the chromatogram to a flash drive, your Y: drive or email it to yourself (if using a LabQuest). If you save as a CMBL file type and then open the file on a campus computer or other computer with a recent version of Logger Pro, you will see the chromatogram. Choose *Save* or *Save As* from the *File* menu; if you have already saved a file, clicking the *Save* button will save over the pre-existing file. See the *Data File Transfer* subsection of the *Operation of the Vernier LabQuest 2* section or the *Basic Data Collection Using Logger Pro* and the *Basic Data Analysis Using Logger Pro 3* sections for more information on saving data.

If you start the next run without saving, the message "this collection will overwrite the latest run. Do you wish to store, append or discard the latest run?" Be sure to click *Store*, otherwise your data will be lost. A new set of columns will be created under the heading *Latest Run* containing the time and instrument response values, while the previous data set will be under the heading *Run #*, where # is whatever number the last run was. If you choose to store your data in this way (i. e., all of the runs in one file) and you are using a *LabQuest*, you **MUST** save or transfer your data to somewhere else for storage, otherwise it will be lost. Note that if you click *Store*, the *Temperature-Pressure* profile will appear and it will be the same as for your previous run. Select *Done* to initiate the run. Note that if you choose to store that data in this fashion, each run will be displayed on the screen. To hide a run, you can, in Logger Pro, choose *Graph Options* from the *Options* menu, then choose *Axes Options*. Scroll down the list in the *y*-axis box and remove the check marks in each of the runs that you want to hide.

Repeat the process for the remaining pure substances and unknown mixture. Be sure to clean the syringe thoroughly between each sample, otherwise you will have spurious peaks in your chromatogram. For the unknown, you may need to inject up to 0.3 μL (record the volume that you actually use in your notebook).

After you have completed your final data collection, turn off the Mini GC.

If you wish to transfer the data into Excel, you can either copy and paste the data directly from Logger Pro to Excel, or select *Export As* in the *File* menu and then select CSV (comma separated value) to create a file that Excel can read.

Summarize your experimental results in a table, such as shown as Table 2, below.

Table 2. Example table to summarize the results from this exercise.

Compound	Formula	Retention Time (min)
Acetone	CH_3COCH_3	
2-Butanone	$CH_3COCH_2CH_3$	
2-Pentanone	$CH_3COCH_2CH_2CH_3$	
4-Methyl-2-pentanone	$CH_3COCH_2CH(CH_3)_2$	
2-Heptanone	$CH_3COCH_2CH_2CH_2CH_2CH_3$	
Methanol	CH_3OH	
Ethanol	CH_3CH_2OH	
Ethyl acetate	$CH_3COOCH_2CH_3$	
Acetic acid	CH_3COOH	

Results and Analysis

Determine retention times for each compound. This can the time when the signal is largest, or when the peak begins. Based on your experimental results, which way would you say is preferable, why might this be true? You may also wish to explore the chromatogram analysis tools described in section 10 (*Analyze your chromatogram*) of the Mini-GC manual (see http://www.vernier.com/files/manuals/gc-mini.pdf).

Discuss the retention times of the substances with regard to molar masses, boiling points, and polarizability. Describe any patterns that emerge and explain both the patterns and deviations. Report your unknown number and identify the substances that are present in your mixture. Are there more than one possible compound which might give a peak in your unknown? What compounds can you exclude from being in your unknown? Support your identification, which means that you include and refer to tables and graphs, in addition to having a well-reasoned, logical argument.

References

1. This exercise was adapted from Experiment #1 (*Using a Gas Chromatograph: Identifying Unknown Compounds*) available on the Vernier webpage at http://www.vernier.com/products/sensors/gc-mini/ (June 16, 2013). This is also available in hardcopy (Mlsna, D. and Randall, J. *Gas Chromatography Investigations with the Mini GC*, 1st Ed.; Vernier Software and Technology, Beaverton, OR, 2009).

2. See, for example, Petrucci, R. H.; Herring, F. G.; Madura, J. D. and Bissonnette, C. *General Chemistry: Principles and Modern Applications*, 10th Ed.; Pearson, Toronto, Ontario, Canada, 2011; §12-1, for more information.

3. Polik, W. F and Schmidt, J. R. *WebMO Enterprise 14.0.006e*; WebMO LLC: Holland, MI, 2011; http://www.webmo.net/ (accessed June 21, 2014).

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5. The point group of an object is a way to describe the symmetry that the object possess based on the ways in which the object may be manipulated in three-dimensional space which results in a configuration that is indistinguishable from its starting configuration. See the *Group H: Symmetry* section of the *Molecular Modeling 1: Classic Molecular Modeling* exercise.

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Inorganic Qualitative Analysis

B. K. Kramer* and J. M. McCormick

Introduction

Qualitative analysis is the identification a sample's component(s). Unlike a *quantitative* analysis, we are not concerned with the amount of a substance present in a sample but only with its identity. In this exercise we will focus on identifying the cations and anions that make up ionic compounds, both solid and in solution. Ideally there would be chemical tests that could be used to identify individual ions without interference by any other ions. Unfortunately, there are often complications. For example, the formation of a yellow precipitate upon addition of aqueous S^{2-} confirms the presence of Cd^{2+} in a solution. The color of this compound, however, will be hidden if any Pb^{2+} or Cu^{2+} are present in solution since they will form a black precipitate with added S^{2-}. In order to test for cadmium, then, any interfering ions must first be removed. This will be the case for most ions in a mixture: before their identities can be confirmed, they must be isolated from the remaining solution.

The separation of ions in solution can be accomplished by the addition of a precipitating agent that will selectively react with an ion in the solution and not with others that may be present. The solid that is produced can then be removed from the liquid by centrifugation and decanting. Because many ions may behave similarly, separation of individual ions from a complex mixture is not usually possible. Instead, a group of ions with similar reactivity may be separated by precipitation from a larger mixture. After they are isolated in a solid, they must be further separated and reacted to confirm each one's identity.

There are several types of reactions that can be used to confirm the presence of ions in solution. The most common are *precipitation* and *complexation*. In a precipitation reaction, an ion in solution reacts with an added reagent to form a solid. Whether a solid will form from a given reaction can be predicted by the solubility product constant (K_{sp}) of the solid under the given conditions. Solubility product constants are the equilibrium constants for the dissolution of an "insoluble" ionic solid in water. A low K_{sp} implies that the compound does not dissolve to an appreciable degree in water. If the two ions are mixed in solution, a precipitate will tend to form. If steps have been taken to remove ions that form competing precipitates, the presence of a properly colored solid can be used to confirm the presence of a given ion. If several different precipitates remain, the conditions of the solution can be manipulated to selectively re-dissolve one or more of the solids. When the equilibria involved are well understood, selective precipitation can be a powerful tool in the identification of unknown ions.

Complexation can also be used to determine the presence of an ion in solution. In a complexation reaction, a Lewis acid, typically a metal cation, forms a *coordinate covalent*, or *dative*, bond with one or more Lewis bases, called *ligands*. A ligand may be a neutral or a negatively charged species. These complexes may either be neutral or charged, depending on the charge on the metal and on the ligand. Complexes with as few as one ligand and with as many as twelve ligands are known, but complexes with four, five or six ligands are the most common, especially for the transition metals of the fourth period. The number and type of ligands that can surround a metal ion is determined by metal ion's size and how many electrons it has.

When a complex forms it may not precipitate (charged complexes are often quite soluble in water, for example), and the formation of a complex is one way in which an insoluble metal ion can be forced to dissolve. Similarly, complex formation can also be used to separate a mixture of ions by keeping one or more in solution while others precipitate. When the complex formed between a metal ion and a specific ligand has a distinct color, complex formation can be used to demonstrate the presence of a specific metal ion by simply adding the ligand to the solution. Thus, they are useful in confirming the presence of a single ion after separation has been achieved. The tendency to form a complex can be determined by the formation constant (K_f) of the reaction. Formation constants are defined as the equilibrium constant for the reaction of the metal ion with the ligand(s) to form a complex. A large K_f implies a strong tendency for complex formation.

Qualitative analysis schemes have been performed by introductory chemistry students for many years. They are used to help students understand reactivity and to develop problem solving skills. There are several different approaches to these experiments. In one case, students are given a step-by-step procedure, often in the form of a flow chart, which they can use to isolate and identify unknown ions in solution. In another, students first analyze known solutions to determine how different anions will behave when reacted with various reagents. They then compile these results into their own flow chart that they apply to their unknowns. The experiments can be carried out on solutions containing mixtures of cations (same anion), mixtures of anions (same cation) or on salt mixtures.

The creation of the flow chart from scratch is very valuable but is also a very time consuming process. Your experiment will involve a modification of the flow chart procedure. The reactivity of the different ions with precipitating agents can be predicted based on the K_{sp} of the salt formed if the two were to react. You will use the K_{sp}'s of several salts to determine the best way to cause their separation. You will then prepare a flowchart to separate and identify these components. You will test this flowchart in the lab. Ideally you would create a flowchart for the separation of the entire mixture. Because of time constraints, the flowcharts for the remaining species you need to separate will be given to you.

The overall experiment has three parts. In the first part you will analyze known mixtures of cations using your predetermined procedure and procedures that are given to you. This part is expected to take one to one and a half weeks. In the second part you will apply similar procedures to known mixtures of anions in solution. This part should take less than a full laboratory period. In the final week you will be given three unknown mixtures: a solution of three unknown cations, a solution of three unknown anions and a solid salt consisting of a single cation and a single anion. You will need to use the procedures you learned the previous weeks to identify the components of your unknowns.

Experimental[1,2]

Most compounds of lead, mercury and barium are toxic, and should be handled with care. The concentrated (greater than 1 M) acid and base solutions used in this exercise can cause a minimum of skin irritation and the more concentrated solutions can cause severe burns. Silver nitrate solutions can stain the skin black. So, exercise care when working with it. If any of these solutions are spilled on your skin, immediately wash the affected area with a copious amount of

water. Be sure to wash your hands thoroughly before leaving the lab. In addition to the chemical hazards, there are physical hazards associated with the use of hot plates, Bunsen burners and centrifuges. Be sure to review their safety protocols before coming to lab and remember to treat them with respect at all times.

The separation flow chart for the cations and anions encountered in this exercise are shown in Fig. 1a, Fig. 1b and Fig. 2, respectively. These flow charts show the steps required to separate

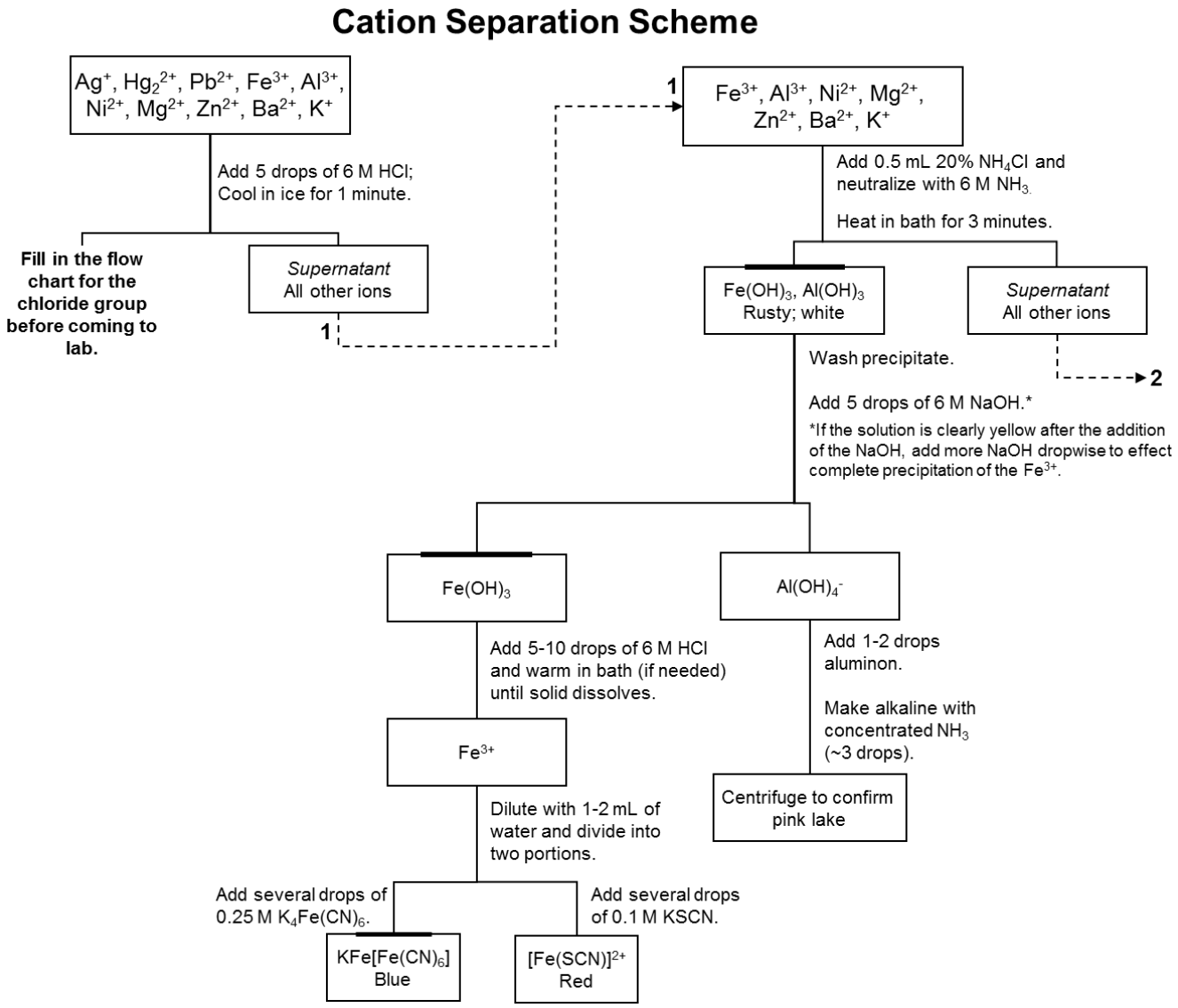

Figure 1a. A partial view of the cation separation scheme for this exercise. It is in continued in Fig. 1b (where the arrow labeled **2** on the scheme above), and you will prepare the portion of the flow chart for the chloride group (Ag^+, Hg_2^{2+}, Pb^{2+}) before starting this exercise. See Fig. 3 for an explanation of the symbols used.

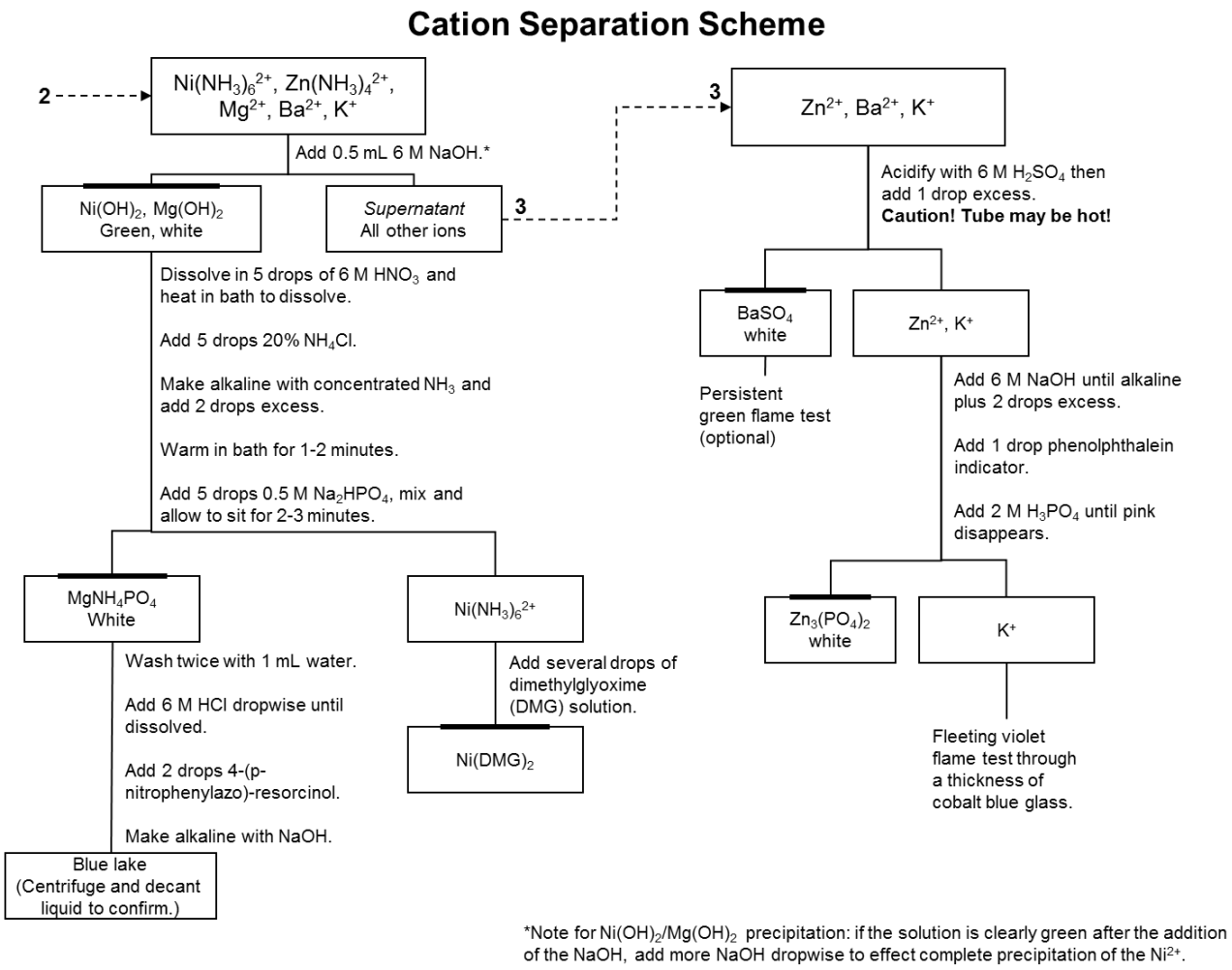

Figure 1b. The conclusion of the cation separation scheme for this exercise (the first part is in Fig. 1a). See Fig. 3 for an explanation of the symbols used.

and identify the cations and anions that you may find in your known and unknown mixtures. These charts have been prepared based on theoretical information about the ions and experimental observations. The flow charts can help you understand the order in which separations must take place in order to isolate ions that may behave similarly.

Throughout the flow charts, reagent additions and other procedures are indicated along the connecting lines; these are explained in more detail below. The formula for each species, along with any identifying physical characteristics (such as color), is given in the box. The symbols and formalism used in the flow charts are given in Fig. 3.

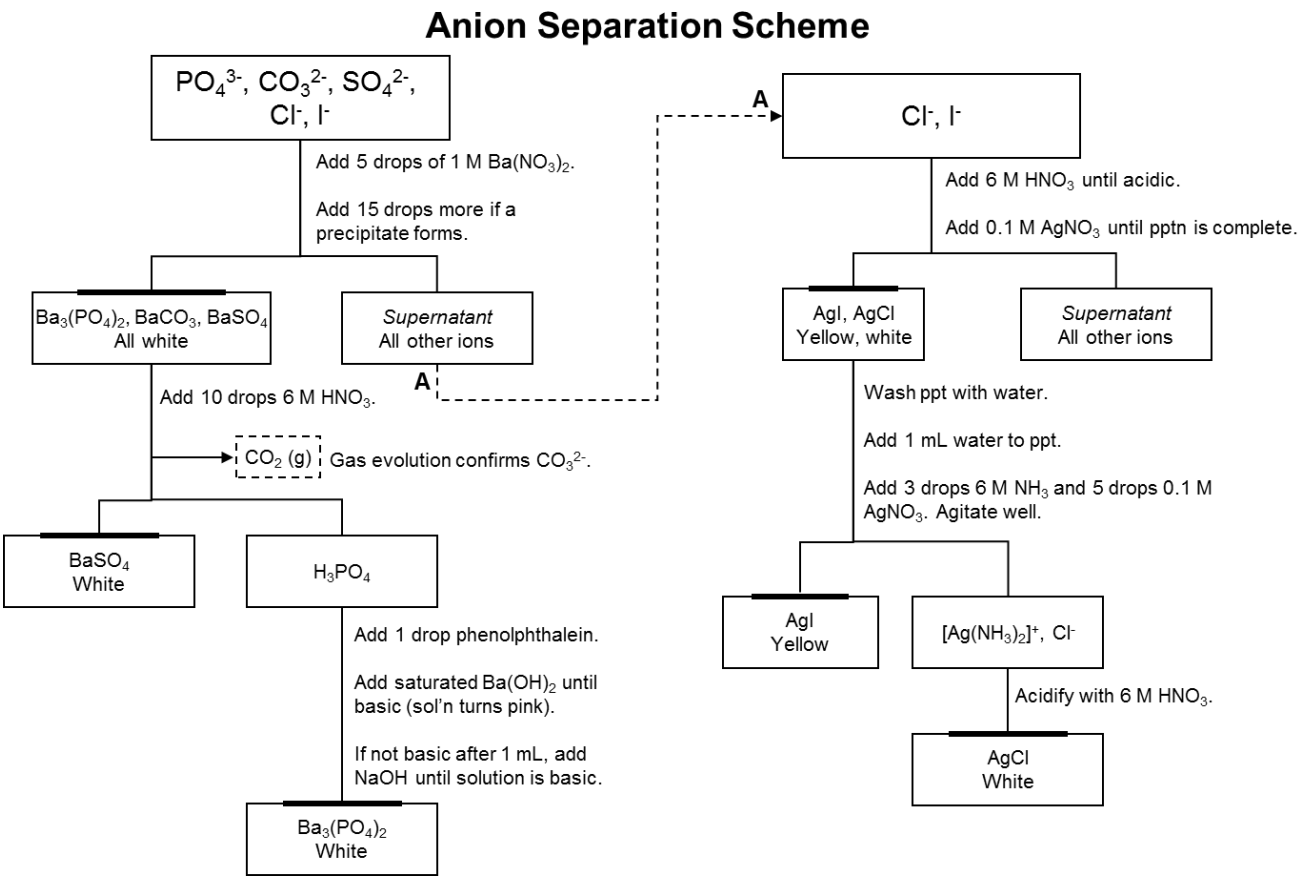

Figure 2. The anion separation scheme used in this exercise. See Fig. 3 for an explanation of the symbols used.

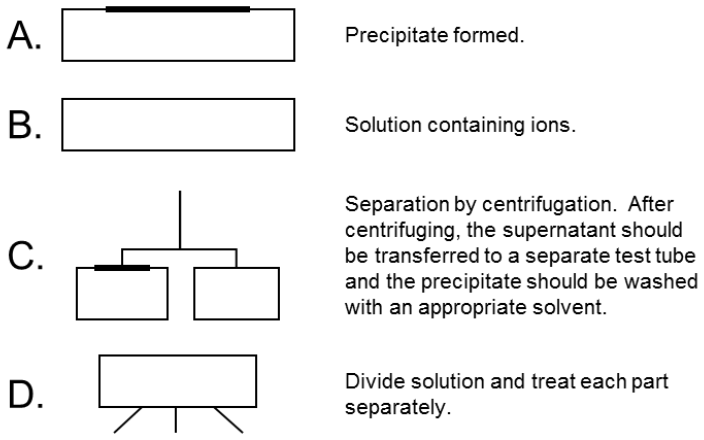

Figure 3. Key for the ion separation flow charts given in Fig. 1 and Fig. 2.

General Procedures

Since this analysis is qualitative and not quantitative, it is not necessary that exact amounts of reagent be added at each step, but it may be useful to know that there are approximately 20 drops in 1 mL. Each procedure should be performed on approximately 0.5 mL of a fresh sample of solution. **IMPORTANT!** Since some ions removed early in a given procedure may mask those determined later, it is essential that the entire chart is followed in order.

You will be using microcentrifuge tubes throughout this procedure. The tubes can hold either 1.5 or 2.0 mL (listed on the tube). If the volume of your solution exceeds that of the tube, separate the solution into two tubes and treat each one according to the flowchart.

Throughout this series of experiments, you will be expected to follow the directions that are presented in the flow charts included in this lab. The reactions shown in the charts are described in the accompanying text. There are several procedural steps that are indicated in the flow chart that are described here.

Precipitation After the addition of a precipitating agent, it is important to mix the solution thoroughly by shaking or by stirring with a clean glass stir rod. B e sure not to add more of a precipitating agent than indicated in the procedure as this may cause undesired side reactions.

Separation After the addition of a precipitating agent to a solution, a solid (precipitate) and liquid (supernatant) will result. These often must be isolated and treated separately. The most common method for separating a supernatant and precipitate is to centrifuge the mixture to cause the solid to compact at the bottom of the tube. The procedure for centrifuging will be demonstrated by your instructor. It is essential that the centrifuge is balanced with a tube containing the same volume of liquid as your sample to prevent it from "walking" off the table!! After centrifuging, the supernatant can be decanted by simply pouring from one test tube into another or by careful removal with a clean pipet.

Washing When a supernatant is removed from a solid, it is almost certain that some of the liquid has been left behind. This liquid can be removed by the addition of a clean solvent (usually cold water, but indicated in the procedure if not) which is thoroughly mixed with the precipitate. After centrifuging and decanting, the solid is now ready for further reaction as dictated in the procedure. **IMPORTANT!** Improper separation and washing of precipitates is the most common source of error in this exercise. So, be sure that you learn how to do this properly using the known solutions.

pH Adjustment Often it is necessary to adjust the pH of a solution until it is just alkaline or just acidic. This is usually accomplished by the dropwise addition of a strong acid or base. In order to make sure that the solution does not become too acidic or basic, the pH of the solution must be monitored. You will use universal indicator paper to determine the pH of your solutions. The proper method for finding the pH of a solution involves stirring the solution with a clean glass rod and then touching the tip of the rod to a piece of indicator paper. Do **NOT** place the indicator paper directly in your solution! You should check the pH of the solution after each addition of a drop of acid or base. If you are to acidify, stop the addition as soon as the paper registers a pH of just less than 7. If the solution is to be made basic, add base until the paper registers just more

than 7. If you are to neutralize the solution, add the appropriate acid or base until the paper reads very close to 7.

Heating Solutions There are two different heating methods that will be used in this exercise. If a solution needs to maintain a near boiling temperature for a few minutes, the tube should be placed in a boiling water bath. Microcentrifuge tubes can be heated by placing test tubes full of water in a water bath. After allowing the water to boil, place the microcentrifuge tube in the top of the test tube, making sure that the liquid contained is fully immersed in hot water. Make sure that the test tube is anchored so that it does not spill into the bath.

If the solution needs to be heated directly, the solution should be **transferred to a glass test tube** which should be held in a test tube clamp facing away from you and your fellow students and passed back and forth through the flame of a Bunsen burner. Be careful not to let the solution bump and jump out of the test tube by keeping the flame near the surface of the solution rather than at the bottom. Stirring the solution with a glass rod may also help. The procedures will indicate which heating method is necessary for each step. **DO NOT place a plastic microcentrifuge tube in or near a flame.**

Flame Tests In many cases, the color emitted when a cation is heated directly in a flame can help identify the element. If a procedure calls for a flame test, follow the directions below.

1) Clean a wire loop by first dipping it in 6 M HCl and then heating it long enough to drive off any contaminants from the surface.

2) Place the loop in the solution or solid to be tested, making sure a drop of liquid or crystal remains in the loop.

3) Place the wire in the flame and observe the color emitted. If instructed, view the flame through a piece of cobalt blue glass.

Pre-Laboratory Exercise

Throughout the experiment, you will use a flow chart (Fig. 1) to help you separate and identify the cations in your system. The first part of the chart has been left blank. Using the information in the paragraphs below, propose the steps to fill in the flow chart to isolate the chloride group (Ag^+, Hg_2^{2+} and Pb^{2+}) from a mixture, separate each ion from the others and confirm the presence of each ion. You will not be allowed to begin your experiment until your instructor has confirmed that your flow chart is prepared correctly. Your instructor will then give you a completed chart that includes the amounts of each solution to be added in each step.

Silver, mercury(I) and lead(II) are often called the "chloride" group because they form sparingly soluble to insoluble precipitates with chloride ions. All three solids are white. The first step in isolating these ions from a solution is to add HCl to form the chloride precipitates. Silver and mercury(I) chlorides are much less soluble (K_{sp} values of 1.8×10^{-10} and 1.3×10^{-18}, respectively) than lead(II) chloride (K_{sp} of 1.6×10^{-5}). If solid $PbCl_2$ is heated in water to 100 ^oC for a few minutes, it will dissolve. The other two chlorides will not. Lead(II) in solution will form an insoluble white precipitate when allowed to react with sulfuric acid ($K_{sp} = 6.3 \times 10^{-7}$). The addition of ammonia to solid silver chloride causes the formation of a colorless silver-ammonia

complex ($[Ag(NH_3)_2]^+$, $K_f = 1.7 \times 10^7$). The addition of nitric acid will cause the equilibrium to shift to free the silver which can then react with the chloride again. Mercury(I) chloride reacts with ammonia to form Hg (metallic liquid), $HgNH_2Cl$ (s, white), and Hg_2O (s, black). The solid mixture will have an overall grayish color.

Cation Determination

Before examining an unknown mixture it is helpful to observe the behavior of known ions in a mixture. You will *separately* analyze two known mixtures of cations using the procedures outlined in Fig. 1. Mixture **A** contains silver(I) (Ag^+), mercury(I) (Hg_2^{2+}), aluminum (Al^{3+}), barium (Ba^{2+}) and potassium (K^+) ions. Mixture **B** contains lead(II) (Pb^{2+}), iron(III) (Fe^{3+}), nickel(II) (Ni^{2+}), magnesium (Mg^{2+}) and zinc (Zn^{2+}) ions. There will also be solutions available that contain the individual ions that you will be analyzing. You can use these solutions to confirm the behavior of the ions in your mixture.

For each sample, you should record every step of the analysis and your observations as you proceed in a table similar to the one shown as Table 1. You should be as specific as possible when describing your observations of the known mixtures so that you can use those observations to identify your unknowns.

Step Number	Procedure	Observations

Table 1. Sample data table for recording the results of each experimental step.

The first steps in the cation procedure are to identify and remove the chloride group as described above. After these have been isolated, the remaining cations will be separated based on their reactions with hydroxide. The reactions of hydroxide ions with cations are very interesting. By carefully controlling the pH of the solution, only certain metal hydroxides can be caused to precipitate from solution or form soluble complexes. After the chloride group ions are precipitated with hydrochloric acid, the solution will be acidic. An ammonia/ammonium buffer is then created in order to make it just neutral, which will shift the hydroxide concentration of the solution causing the precipitation of only the most highly insoluble hydroxides, $Fe(OH)_3$ ($K_{sp} = 1.6 \times 10^{-39}$) and $Al(OH)_3$ ($K_{sp} = 3 \times 10^{-34}$). It is important that the solution is not made overly basic as the additional hydroxide will cause the $[Al(OH)_4]^-$ complex to form too soon. The remaining ions will either form soluble complex ions with the added ammonia or remain dissolved in solution. After separation from the supernatant, the aluminum hydroxide can be re-dissolved by increasing the concentration of hydroxide ions with the addition of sodium hydroxide. This addition will favor the formation of the complex, $[Al(OH)_4]^-$ ($K_f = 2.0 \times 10^{33}$). However, the iron(III) hydroxide will not re-dissolve. Aluminum can be confirmed by adding aluminon, a dye, and then making the solution alkaline with concentrated ammonia. The presence of a pink *lake* (dyed precipitate) suspended in solution confirms the presence of aluminum. Make sure that it is not the solution itself that is pink by centrifuging. The presence

of Fe^{3+} can be confirmed in two ways. Iron forms a red complex with SCN^- and a blue solid, $KFe[Fe(CN)_6]$, upon the addition of $K_4Fe(CN)_6$.

After the iron and aluminum are removed from the solution, the hydroxide concentration can be manipulated, again, to selectively precipitate two cations. An increase in the concentration of hydroxide ions with the direct addition of aqueous sodium hydroxide will cause the precipitation of nickel hydroxide ($K_{sp} = 6 \times 10^{-16}$) and magnesium hydroxide ($K_{sp} = 6 \times 10^{-10}$). The other cations will remain in solution; zinc as the hydroxide complex $[Zn(OH)_4]^-$ and Ba^{2+} and K^+ as the solvated ions. Like most hydroxides, magnesium and nickel hydroxide can be dissolved in a solution that is acidified and warmed. After re-establishing the ammonia buffer, the addition of Na_2HPO_4 will cause the magnesium to slowly precipitate as $MgNH_4PO_4$. Nickel will remain in solution in the form of a nickel ammonia complex. The magnesium can be re-dissolved in hydrochloric acid. The magnesium will form a blue lake in an alkaline solution containing the organic compound 4-(p-nitrophenylazo)-resorcinol. Dissolved nickel ions will form a deep pink precipitate upon the addition of another organic compound, dimethylglyoxime.

The only ions remaining in solution after the hydroxide concentration is raised are zinc, barium and potassium. Barium forms an insoluble precipitate with sulfate ions ($K_{sp} = 1.1 \times 10^{-10}$). The barium can be further confirmed by the presence of a persistent green flame test. Zinc can be precipitated by the addition of phosphoric acid, H_3PO_4 (K_{sp} for $Zn_3(PO_4)_2$ is 5×10^{-36}).

At this point, the only unknown ion remaining in solution will be potassium. Potassium forms very few insoluble precipitates. The simplest way to identify it is by a flame test after other ions are removed. The flame will turn a fleeting violet color when exposed to potassium ions. Because this color may be masked by the orange flame of sodium ions, the flame should be viewed through a thickness of cobalt blue glass.

Anion Determination

The strategy for the analysis of anions is similar to that for cations; known reagents are added to a solution to selectively precipitate dissolved anions. In this case, the precipitating reagents will be cations that form insoluble salts with the dissolved anions. You will perform an analysis to identify chloride (Cl^-), iodide (I^-), carbonate (CO_3^{2-}), sulfate (SO_4^{2-}) and phosphate (PO_4^{3-}). The flow chart for the separation and identification of these anions is shown in Fig. 2. You will be given only one known solution to analyze in this section. This mixture will contain all five anions.

The first step in this procedure is the addition of barium nitrate to cause the precipitation of $BaCO_3$ ($K_{sp} = 5.0 \times 10^{-9}$), $BaSO_4$ ($K_{sp} = 1.1 \times 10^{-10}$) and $Ba_3(PO_4)_2$ ($K_{sp} = 6 \times 10^{-39}$). The addition of a strong acid (nitric, HNO_3) to these precipitates will adjust the solubility of the ions by taking advantage of their basic nature. The reaction of CO_3^{2-} and the acid will cause the evolution of carbon dioxide gas. Because of the limited number of anions possible in your procedure, the presence of this gas is a confirmation for the carbonate ion. The nitric acid will also cause the dissolution of barium phosphate. When the supernatant containing only barium phosphate is decanted and made basic with $Ba(OH)_2$the precipitate will reappear. Unlike the other two precipitates, barium sulfate will not re-dissolve when nitric acid is added. The presence of a white solid after the acidification of the barium precipitates is a confirmation of the sulfate ion.

The supernatant found after the addition of barium in the previous step will contain the other anions in this procedure, I^- and Cl^-, neither of which form insoluble salts with barium. (This procedure could be performed on a fresh sample of the analyte, as well.) They do, however, form insoluble salts with silver ions (K_{sp}(AgCl) = 1.6 x 10^{-10}, K_{sp}(AgI) = 1.5 x 10^{-16}). The solubility of these ions can be further decreased by acidifying the solution with nitric acid. The precipitate should be washed to remove any other ions and then stirred in clean distilled water. When aqueous ammonia and additional silver nitrate are added to the mixture, the silver chloride will re-dissolve to form the silver ammonia complex used in the detection of silver ions. The yellow silver iodide will not re-dissolve. If the supernatant containing the complex is acidified with nitric acid, the silver chloride will re-precipitate, confirming the presence of chloride ions.

Unknown Determination

You will be given three unknowns to analyze. The first will be a solution containing three cations. The second will be a solution containing three anions. The third will be a solid binary salt. As soon as you receive your unknowns, record your unknown numbers. You must include your unknown numbers in your reports to receive credit. Use the procedures you learned in the first two weeks to determine the compositions of your three unknowns.

When analyzing unknown mixtures, you should keep a few things in mind. Remember that you must have a confirmatory test for each cation you believe is present. Even if you are told the number of ions present in your mixture, you should not stop after finding that number of ions. It is possible that you have made a mistake or have a false positive. Complete the entire flow chart to make sure that no other species appear. If another is identified, you should repeat the procedure on a fresh sample of analyte. You should have plenty of your solution to repeat the entire analysis several times. There may be penalties if you ask for extra, however, so be careful when using your unknown.

If you are ever uncertain as to whether a test is positive for a given ion, you can repeat the test on the standard solutions provided to confirm the behavior of that ion. After you have identified your unknown mixtures, you may want to create a mixture containing the ions you believe are present in your solution. If you have time, you can test this solution and compare the results to your unknown mixture.

When you are analyzing for both cations and anions in a single unknown, it is important to recognize that the analyses must be performed separately. For example, the first step for a cation analysis is the addition of hydrochloric acid. A test on a solution after HCl is added would, obviously, be positive for chloride ions!

The various analytical procedures you will do must be performed on ions dissolved in a solution. The first step in your solid unknown analysis will be to dissolve the sample. Your sample may be insoluble or sparingly soluble in distilled water! The fact that your unknown is insoluble in water may give you an idea as to its identity. Try dissolving a small sample of the solid first in water, then nitric acid or another aqueous solvent until you find a solvent in which your unknown is completely soluble. You should then use this solvent to prepare a mixture that is 1-3% of your unknown by weight. Try to avoid using a solvent that contains any of the possible unknown ions!

Waste Collection
All waste is to be collected in the designate receptacle. **IMPORTANT!** You only need to empty the microcentrifuge tubes into the waste and then use the **MINIMUM** amount of water to dislodge any solids present. It should be possible to do this using NO MORE THAN ONE MILLILITER of water (use several, small rinses to accomplish the task)! You may be penalized for excessive waste generation, at your instructor's discretion.

Results and Analysis
Report to your instructor the identity of the ions in each of your unknowns. Your instructor may allow you to repeat the identification of an incorrect result, so you should submit your decision as soon as possible after you have confirmed your unknowns' identities. In the *Results* section of your lab notebook you should include the balanced net ionic equations of each reaction in the flow charts. You should attempt to determine these reactions and may be able to find some of them in your textbook or a reference text. Use equilibrium constants for the reactions to explain why one ion precipitated or formed a complex while others remained solvated. Some of the equilibrium constants you need are included in the procedures.

Conclusions
For this experiment you do not need to write any conclusions until you have finished the analysis of your unknowns. Use the outline for reporting on physical phenomena in the *The Laboratory Notebook* section as a starting point for your discussion.

Summary of Results
Use Table 2 to report the analysis of your unknowns.

Unknown Number	Ions found

Table 2. Summary table for reporting the identity of the unknowns.

References
1. Wismer, Robert K. *Qualitative Analysis with Ionic Equilibrium*; Macmillan Publishing Company: New York, 1991.

2. Zumdahl, S. S. *Chemical Principles, 4th Ed.*; Houghton-Mifflin: New York, 2002, chapter 8.

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Electrochemical Investigations

A. Fuller and J. M. McCormick

Introduction[1]

In the 1800s, Alessandro Volta built the first galvanic cell out of non-biological components. He found that when two metal rods (electrodes) were each placed in a solution of their respective salts and connected by a wire in the presence of a salt bridge between the two compartments that a potential (a voltage difference) developed between the two rods. This experimental set up is known as an electrochemical cell. Figure 1 shows a schematic of a typical electrochemical cell.

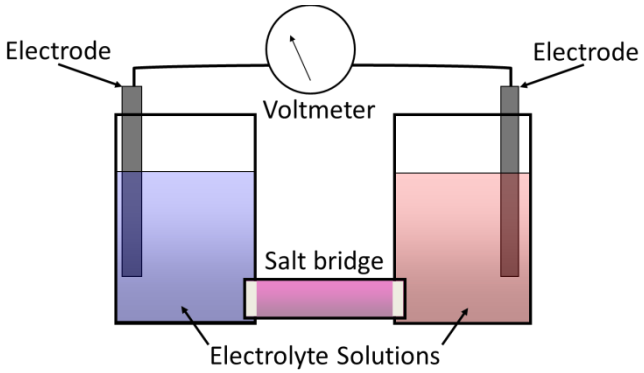

Figure 1. Schematic representation of an electrochemical cell.

It was found that the potential between the electrodes varied widely depending on the metals used and the salt concentrations in the solutions. In this exercise you will reproduce some of the critical experiments that were done using a more modern experimental apparatus to determine what role the metal and the salt solution's concentration have on the observed potential.

We would hope you realize that changing both the electrode and concentration simultaneously will not allow us to determine the effect that either one has on the potential. Therefore, we will approach the problem in two separate ways. First, we will use two electrodes made of the same metal and investigate the effect of changing the concentration of the metal salt solution on the potential. The metals and ions to be investigated are Al/Al^{3+}, Cu/Cu^{2+}, Ni/Ni^{2+}, Pb/Pb^{2+}, Fe/Fe^{3+} and Zn/Zn^{2+}. From your results in this section, you will, in conjunction with the other lab groups, develop a single mathematical equation to describe the effect that a concentration change has on the voltage that will work no matter the identity of the metal.

In the second part of the exercise, you will test the general applicability of your equation by investigating the effect of concentration when the two electrodes are made of different metals immersed in solutions of their respective salts. Based on these results, you will either revise your model or discard it and try to develop another, better model.

Experimental

For this exercise, you will be working with your bench mates in a group of four.

When you arrive in lab, you will find the electrochemical module (see Fig. 2), which will be filled with 1.00 M KNO_3 (the KNO_3 is the supporting electrolyte, which does not participate in

the cell's chemical reaction but is necessary to stabilize the cell's potential). The module's eight outer wells are connected to the central well via a porous barrier (the salt bridge in Fig. 1). The outer wells will contain the different solutions to be tested, while the central well will contain only the KNO_3 solution. Thus, when we place an electrode in any two of the solutions and connect the electrodes with a wire, we have constructed an electrochemical cell.

Figure 2. The electrochemical module used in this exercise.

Also on the bench will be a pair of metal strips or wires of the same metal and a third metal strip of a different metal (see Table 1). You will also find small bottles containing 0.500 M solutions of the two metals, which are also 1.00 M in KNO_3, and a bottle of 1.00 M KNO_3.

Table 1. Assigned primary electrode (two metal strips or wires provided) and secondary electrode (single metal strip or wire) combinations.

Bench	Primary Electrode	Secondary Electrode
A	Cu	Zn
B	Zn	Cu
C	Pb	Zn
D	Al	Zn
E	Fe	Zn
F	Ni	Zn

CAUTION! All of the metals used in this exercise and their salts are toxic (especially Pb) and care must be taken when handling them. You are advised to wear gloves when handling the electrodes, the solutions and the porcelain cups. Remove your gloves **before** handling the digital voltmeter or before using a computer to prevent cross contamination. All waste is to be properly disposed of in a waste container. You will be shown where this waste container is by your instructor.

IMPORTANT! These bottles will contain more than enough solution for you to complete the exercise. Be frugal in your use of the metal ion solutions; they are expensive both in terms of

their procurement cost, their disposal cost and their environmental impact. Therefore, excessive use of reagents will be penalized.

A digital voltmeter (DVM), like that shown in Fig. 2, will also be on your bench. **IMPORTANT!** Be sure that the red and black leads of the DVM are attached as shown in the figure. A voltage measurement is made by turning the large rotary switch on the DVM to the right to reach the direct current voltage position (V⎓). When you have finished making a measurement, turn the DVM rotary switch back to OFF (turn left only).

Figure 2. The Fluke 75 digital voltmeter used in this exercise to measure the potential.

The final piece of equipment on your bench will be a variable-volume micropipette that can dispense any volume from 100. μL to 1000. μL (i. e., from 0.100 mL to 1.000 mL). The pipette is shown in Fig. 3. The micropipette is expensive – read the instructions below carefully before coming to the laboratory. The operation of the micropipette will also be demonstrated by the instructor before you begin work, so that its operation is clear. When used properly this type pipette will give very precise and reproducible volume measurements.

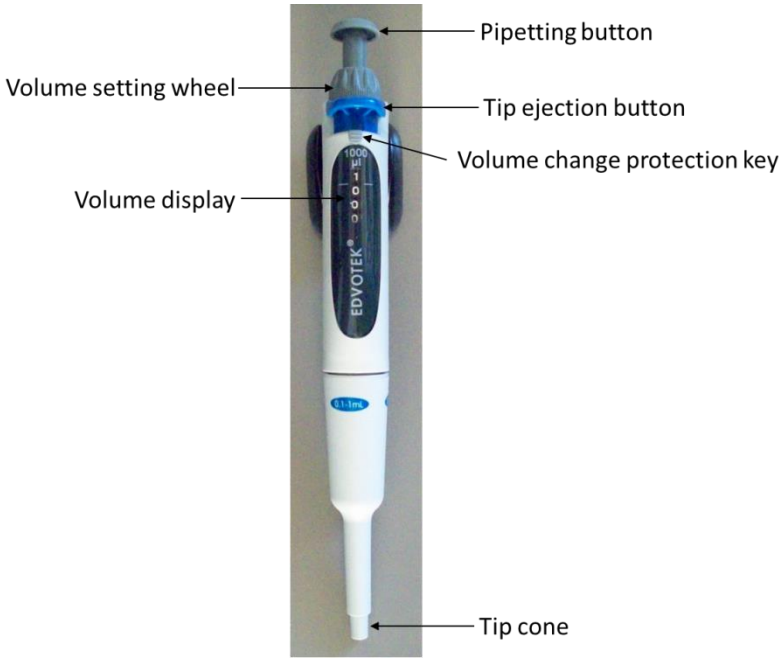

Figure 3. Variable-volume micropipette.

Micropipette Operation

To operate the micropipette, first securely put a tip on the pipette cone (be sure that this is not too tight). Next, set the volume by first sliding the volume-change protection key up. Select the desired volume by carefully rotating the volume-setting wheel at the top of the pipette until the volume is displayed. **IMPORTANT!** Do **NOT** set the pipette for volumes over 1000 mL or under 100 mL as this will damage the pipette. Slide the volume-change protection key down to lock in your volume.

Hold the pipette vertically and press the pipetting button down with your thumb to the first stop (right-handed people should hold the pipette in the right hand, and left-handed people should hold it in the left hand). Immerse the pipet tip 2 – 3 mm into the liquid. Let the pipetting button smoothly slide back; leave the tip immersed in the liquid for 1 – 2 sec after the button has stopped. If there are air bubbles in the tip or excessive splashing, follow the instructions below to expel the liquid and try again.

With the liquid successfully loaded, remove the pipette from the solution, and touch the tip against the container wall. To discharge the sample, place the tip into the receiving vessel (ideally this should be at against the vessel's wall at a 30 – 45° angle, but that won't be possible here), press the pipetting button down slowly to the first stop and hold it down. Expel the remaining solution by depressing the button to the second stop. Remove the pipette from the receiving vessel before letting the pipetting button slide back. To eject the tip, hold the pipette over a garbage can and press the tip ejection button to the stop.

Electrode Preparation

Remove the metal electrodes from their protective bags. Take care with the electrodes, some of the metals are very soft (Pb) and some of the electrodes may be very thin (Cu, Ni). Wearing

gloves, **lightly** buff the surface of the electrodes with the piece of fine steel wool that is on your bench. This will remove the outer layer of metal oxide that coats most metals and any contaminants on the surface, which can interfere with the potential measurements. Do **not** buff so hard that you remove large amounts of metal. Rinse the electrode with distilled water and pat the surface dry with a paper towel to remove any metal or metal oxide dust.

Cell Set-Up

With a disposable Pasteur pipette, remove the 1.00 M KNO_3 solution in all of the numbered wells, except the central well. Do **not** turn the module upside down to remove the liquid.

Solution Preparation

Prepare the test solutions given in Table 2 directly in the electrochemical module's wells from the provided concentrated stock solution of your metal's salt (between 0.20 and 0.50 M, depending on the salt's solubility) and the provided 1.00 M KNO_3 solution. Before coming to lab, work out the dilutions necessary (using $C_1V_1 = C_2V_2$) to prepare 2500. μL of each of these solutions using the variable-volume micropipette described above.

Be sure to record the actual concentration of the salt in the stock solution in your notebook and adjust your dilutions accordingly. Both of these solutions also contain KNO_3 so that the total concentration of the ions in the solution is at least 1.0 M, because it is important to maintain a high salt concentration when performing electrochemistry. Therefore, you **must** use the provided 1.0 M KNO_3 solution, **not** plain distilled water, when preparing these diluted solutions. Do **not** use a disposable Pasteur pipette to make your dilutions.

Helpful hint: pipet either the metal solution or the KNO_3 solution into all of the wells, changing the dispensed volume as needed. Place a new tip on the pipette, and then pipet the other solution into all of the wells. You should only need TWO pipette tips to make all of these solutions! Also note that you may need to transfer multiple volumes to give the desired total volume. For example, if you wish to add 2300. μL of the KNO_3 solution to a well, you would have to deliver 1000. μL twice and then 300. μL. By carefully planning your dilutions, the actual cell set-up can go very quickly.

Table 2. Test solutions for this exercise.

Well Number	Concentration (M)
1	0.100
2	0.500
3	0.400
4	0.200
5	0.100
6	0.0600
7	0.0400
8	0.0200

Investigation of Concentration's Effect on Potential

For this part of the exercise, well 1 (containing a 0.100 M solution of your primary electrode's salt) will be the reference compartment. Place one of the paired metal electrodes in well 1 and attach the DVM's red lead to this electrode. It is critical that the red lead always be attached to the electrode in the reference compartment in this part of the exercise.

Attach the black lead to the other electrode of the pair and place it in the solution in well 2 (take care that the electrodes or the leads do not touch), and measure the potential. Record the potential and the two concentrations involved in your notebook (Table 3 is a useful guide). Note that it may take up to 30 sec for the voltage to stabilize, but if the system does not stabilize within this time, there is likely a problem.

Table 3. Suggested table to organize the data for concentration's effect on potential.

Compartment A (Red Lead)	Compartment B (Black Lead)	Potential (V)
0.100	0.500	
0.100	0.400	
0.100	0.200	
0.100	0.100	
0.100	0.0600	
0.100	0.0400	
0.100	0.0200	

Remove the electrode from well 2, rinse with a small of amount of distilled water into a waste beaker, pat dry with a Kim-Wipe and place it in well 3. Record the voltage as before. Repeat until the second electrode has been placed into all of the wells (and you have seven voltages).

Now try between three and five other combinations and record the potential in each case. For example, place the electrode with the red lead into the 0.500 M solution and the electrode with the black lead into the 0.400 M solution; record the potential. Be sure to rinse and pat dry the electrodes when you transfer them between solutions.

From the data collected in Table 3, find a mathematical equation that will relate the potential to the concentrations. This is most easily done by finding a method of graphing the potential (give potential the symbol *E*) as a function of concentration that gives a straight line (**helpful hint:** you might try graphing potential as a function of a power of the concentration, or as a function of an exponential of the concentration, or as a function of the logarithm of the concentration, or as a function of concentration divided by the concentration in the reference compartment); be sure to follow the guidelines described on the *Preparing Graphs* page on ChemLab.truman.edu when you prepare these graphs. Collaborate with the other groups to find the relationship.

Determine the slope, the intercept (give the intercept the symbol E^0) of your line and their uncertainties at 95% confidence. Compare them to those of the other groups. Are the slopes and intercepts the same for all of the groups (remember each group is working with a different metal)? Do your data taken when the electrode with the red lead is not in the well with a 0.100

M concentration lie on your graph? What, if anything, do you need to do to make them fall on the graph?

Investigation of the Metal's Effect on Potential

With a disposable plastic Pasteur pipette, remove the solutions from all of the wells, except well 1 and the central well. Place the removed solutions in a waste beaker for later proper disposal.

Prepare solutions of the same concentrations given in Table 2 with your secondary electrode's salt solution in wells 2–8. For most groups the secondary electrode is Zn, and you would make a 0.500 M Zn^{2+} solution in well 2, a 0.400 M Zn^{2+} solution in well 3, and so on.

We will again use the solution in well 1 as the reference, and so the DVM's red lead must be attached to the electrode in well 1 (which is your primary electrode). Place the metal electrodes in their respective solutions with the secondary electrode (with the black lead attached) in well 2. Record the potential, and then move the secondary electrode sequentially from well to well, as you did previously. Table 3 can be used as a guide to summarizing the potential data in this part of the exercise. **IMPORTANT!** Be sure to record the sign of the potential in each case. The way that we are recording the potentials does not necessarily follow the accepted protocol, but there is a reason for this.

Can the equation that you found when the two metals were the same be used to describe the effect of concentration on the potential when the metals are different? What modifications do you need to make so that it does fit these data? Share your slope and E^0 (intercept) with the other groups.

Clean-Up

Use a disposable plastic Pasteur pipette to remove the solutions from all of the module's wells. Place the metal-containing solutions in the appropriate waste bottle that your instructor will show you. Refill all of the module's wells with the 1.00 M KNO_3 solution.

Rinse the electrodes with distilled water and dry them thoroughly with a paper towel or Kimwipe before returning them to the storage package.

Waste Collection

All waste will be collected in the designated waste receptacle. It is critical to minimize the amount of waste generated in this exercise, because of the high cost to both procure and dispose of the metal waste. A good student should be able to complete this exercise and not generate more than 100 mL of waste, total.

Results and Analysis

Share your data with the class.

Verify that all of the data can be accounted for using the general equation that you derived. In particular, you should compare the results for the groups at lab benches A and B in the second part of the exercise (where we compared the effect that different metals had on the potential).

Do the results differ, and if so how? What does the difference (or lack thereof) between these groups imply about the nature of electrochemical cells?

Examine the differences in the slopes and E^0 values from the different combinations of electrodes. Do these change in a systematic way as the metal is varied? Note that in each case Zn was involved, which means that we can compare the potentials since they are all relative to Zn. Place the metals in order of increasing potential. Is there anything interesting here?

We could have made have made the determination of the E^0 values for the different combinations by making a single potential measurement. What is the advantage of the method that we used to determine E^0?

Conclusions

This experiment is a measurement exercise and your discussion should address the points contained in outline found in *The Laboratory Notebook* section, as well as the questions raised above.

References

1. See, for example, Petrucci, R. H.; Herring, F. G.; Madura, J. D. and Bissonnette, C. *General Chemistry: Principles and Modern Applications*, 10th Ed.; Pearson, Toronto, Ontario, Canada, 2011; chapter 20, for more information.

Environmental Chemistry

J. M. McCormick and D. M. McCurdy*

Introduction

The quality of water is of vital importance to the planet. The characteristics of water that allow it to be the universal solvent also make obtaining pure water almost impossible. As water moves through earth, air, rocks or pipes, material is dissolved in the water affecting its quality.

Nitrates and phosphates are common pollutants in water sources with runoff from lands where fertilizers have been used. Hard water results from the presence of iron, aluminum, manganese, strontium, zinc, magnesium, and calcium ions dissolved in water. Rain falling through an atmosphere rich in covalent oxides, such as nitrogen oxides, carbon oxides and sulfur oxides produces acid rain. Old pipes containing lead can result in lead ion concentrations great enough to cause lead poisoning. Aquatic life depends upon the concentration of dissolved oxygen in water. Drinking water often has additives to improve the health benefits of water. Chlorine, bromine or ozone may be added to kill bacteria in the water, while fluoride ions are added to strengthen tooth enamel.

Scenario

In this exercise you are a chemist employed by a private laboratory which has just been hired by a local city to monitor a stream that arises within the city limits and flows out of the city. Under Missouri state law, all streams are protected under the general criteria contained in the Missouri Water Quality Standards, 10 CSR 20-7.31(3). Of particular interest to the city as it relates to its compliance with the State law are the sections that state: waters shall be free from substances or conditions in sufficient amounts to result in toxicity to human, animal or aquatic life and waters shall be free from physical, chemical or hydrologic changes that would impair the natural biological community.

The object of your study is Bear Creek, a small stream that has its head waters just west of the Truman State campus within the city limits of the City of Kirksville, Adair County, Missouri. The creek flows in a general southeasterly direction across the campus. It is a tributary of the Salt River and ultimately empties into the Mississippi River north of Saint Louis. The Missouri Department of Natural Resources has identified Bear Creek[1] as an endangered urban stream and a total maximum daily load (TMDL)[2] was established for Bear Creek[3] by action of the Federal Environmental Protection Agency (EPA) on December 23, 2010.[4] The EPA identified three areas of concern: total nitrogen, total phosphorous and total suspended solids.

The area immediate area around Bear Creek and the sampling sites are shown in Fig. 1. The five sampling sites are: (1) north side of Patterson Street culvert, (2) north side of Randolph Street culvert, (3) bridge on walkway that runs between the Truman State Student Recreation Center and Centennial Hall, (4a) West Campus Suites Culvert, northwest side, (4b) West Campus Suites Culvert, northeast side, and (5) outflow on the west side of the Truman Student Recreation Center. These sites were chosen for their accessibility and their proximity to potential sources of pollution.

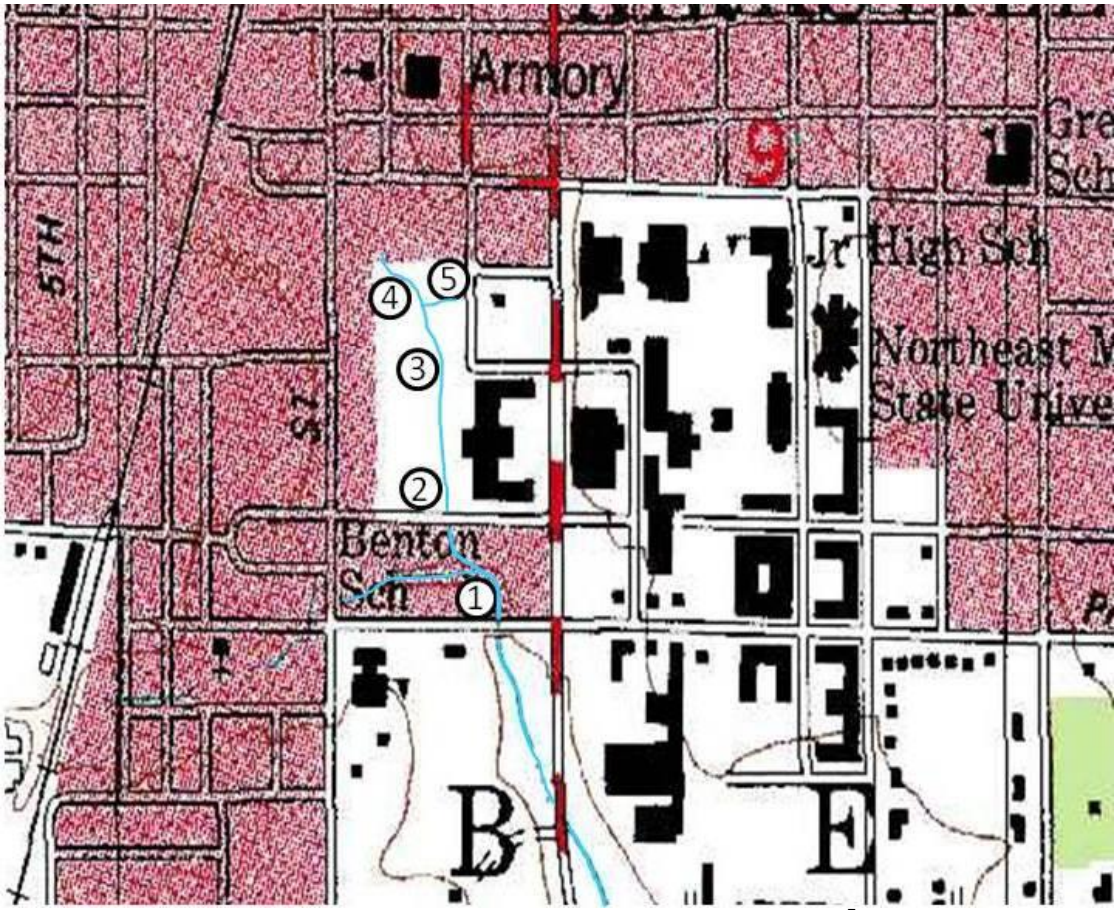

Figure 1. Map of the immediate area surrounding Bear Creek's source.[5] The approximate locations of the five sampling sites are shown.

The geology of the area is relevant to your analyses. The bedrock in the area is predominantly sedimentary in origin with limestone ($CaCO_3$), shale and sandstone being common. Low-grade coal seams are not uncommon in this area and until recently coal mining was a major industry in Adair county. The entire area was glaciated during a previous ice age, and glacial debris forms much of the soil above the bedrock.

Your section is responsible for performing a set of analyses which will be provided to you by your instructor. Groups of three or four will determine the best way to perform one of these analyses based on the written standard procedures and collect your samples during week 1, and then perform the analysis during week 2. The results will then be presented to the section in week 3.

Experimental

Your instructor will assign your group one of the analyses to perform during the first week of the exercise (see the ***Water Analyses*** section for the possible analyses). He/she may also provide you with additional background on your group's assignment. You should note any and all hazards associated with your procedure, be they written in the procedure or verbally communicated to you by your instructor. Be sure that you note the amount of sample that your method requires so that you collect enough water in the first week to complete your analysis in the second week.

IMPORTANT! During the first week you will be obtaining your samples. You should come to the laboratory prepared to both work in the laboratory and to be outside for a significant amount of time.

IMPORTANT! While the sampling locations have been chosen for their accessibility, there is always a risk of physical injury in sampling natural systems. It is expected that you will dress appropriately and will behave in such a manner to put your safety and the safety of your coworkers first. By your participation in this activity you are agreeing to abide by all the laboratory safety rules while out sampling, all general safety rules and any special instructions given to you directly by your instructor or indirectly through a teaching assistant.

Results and Analysis

Work up your data as described in the informational packet that your instructor provided. At the very least, you will need to perform a statistical analysis (e. g., determine the 95% confidence limits) on your results and compare them to established standards. Note that for some of the procedures you will need to consult other sources to obtain some information.

Conclusions

Use the outline for a measurement experiment in the *The Laboratory Notebook* section as the basis for your discussion of conclusions. Be sure to answer the questions posed in the Results and Analysis section above.

You will also be delivering a short group presentation on the results of your analysis. Your instructor will provide more details on what this will entail, but you should assume that you will need to give a short background on the problem you addressed, the method used and the theory behind the method, and present your results with a statistical analysis. The time limit for this presentation will be about 10 to 15 minutes. A basic outline and set of expectations for this presentation are available in the *Presentation of Water Analysis Laboratory Exercise Results*, but your instructor may modify these to fit the needs of your class.

References

1. http://dnr.mo.gov/env/wpp/tmdl/info/0115u-01-bear-ck-info.pdf (accessed April 2, 2011).

2. http://www.dnr.mo.gov/env/wpp/tmdl/ (accessed April 2, 2011).

3. http://dnr.mo.gov/env/wpp/tmdl/0115u-01-bear-ck-comments.pdf (accessed April 2, 2011).

4. http://www.dnr.mo.gov/env/wpp/tmdl/0115u-01-bear-ck-record.htm (accessed April 2, 2011).

5. Map taken from United States Geological Survey Kirksville Quadrangle 7.5 minute map, produced from photographs taken 1974 and lasted edited 1979. Available at http://store.usgs.gov/b2c_usgs/usgs/maplocator/(xcm=r3standardpitrex_prd&layout=6_1_61_48&uiarea=2&ctype=areaDetails&carea=%24ROOT)/.do (accessed April 2, 2011).

Water Analyses

Determination of Nitrate (NO_3^-)

Background

The nitrate ion absorbs ultraviolet radiation at 220 nm but not at 275 nm. The nitrate absorption at 220 nm follows Beer's law with linear behavior to 11 mg nitrogen/L solution. Because dissolved organic matter may also absorb at 220nm, one must be able to distinguish between the absorbance of nitrate and the other organic matter in water. This is accomplished by making a measurement of the water sample's absorbance at 275 nm, a wavelength that the organic matter can absorb electromagnetic radiation but in which the nitrate cannot. Once known, an empirical correction factor can be applied to the 220 nm measurement to distinguish the nitrate from the organic matter. Because this is an empirical correction, this method is not recommended for waters requiring a significant correction for organic matter. It is main use is as a screening tool for water samples in which the organic matter is relatively constant. If it is desired to create a more accurate method, another approach to the calibration process can be performed. This approach, known as the method of standard additions, is beyond the scope of the intent of this lab, though your instructor can steer you to reading information to more fully describe this approach.

Sample preparation consists of two steps. First, the sample will be filtered, to prevent scattering of UV light by suspended particles in the water sample, which will change the measured absorbance. The samples will next be acidified using 1 N HCl to prevent interferences due to the absorption of either OH^- or CO_3^{2-}, both of which can absorb at 220 nm. The acidification should prevent interferences from these ions up to 1000 mg $CaCO_3$/L. Hydrochloric acid is used because Cl^- does not absorb light in 250 – 290 nm region of the spectrum. Some other ions, such as Cr^{6+} (as either chromate or dichromate ion), nitrite, chlorate and chlorite, may also interfere, but these are expected to be low or nearly non-existent in the water samples used in our analysis.

Procedure

All solution must be prepared using the nitrate-free water available in the laboratory. Do <u>not</u> use tap water or regular distilled water. Exercise care when using the nitrate-free water and do not waste it.

In a volumetric flask prepare 1.00 L of a 100 μg N/mL stock solution from solid KNO_3 which has been dried in an oven at 105 ºC for 24 hours. Note that the dried KNO_3 will be provided to you. You will need to determine the mass of KNO_3 that you actually used to the nearest milligram and calculate your exact concentration from this.

From the nitrate stock solution prepare 500.0 mL of a nitrate solution that contains 10 μg N/mL. Note that your actual value may be slightly different depending on the actual amount of KNO_3 you used to prepare the first solution.

Prepare NO_3^- calibration standards in the range of 0 to 7 μg N/mL (this corresponds to the addition of between 0 and 350 μg N per 50 mL of solution). Use 50.0 mL volumetric flasks and pipets to create these solutions. Volumes of diluted standard nitrate solution ranging between 0 and 35 mL will be sufficient to cover this range of concentrations. To be useful, the calibration curve should be created at least five different standard solutions (plus a "blank") that "bracket"

the expected concentration of nitrate. Be sure to dilute carefully and mix thoroughly before using.

The water sample is prepared by first gravity filtering through acid-washed, ashless hard finish, filter paper to filter fine precipitates to remove large particles and debris. The filtered solution will then be filtered through a 0.45 μm pore diameter membrane filter using a syringe to force the water through the filter. Filter at least 75 mL of sample through the filter paper and then filter only as much sample as needed through the membrane filter. To each 50 mL of clear sample, add 1 mL of the 1 M HCl solution and mix thoroughly.

Use the Ocean Optics spectrometer and cells provided to measure the absorbance of each solution (the blank, the calibration standards and the water sample) at 220 nm and at 275 nm. You will be using a special sample cell for this experiment (either quartz or a special plastic), because ordinary glass and plastic do not transmit light in the ultraviolet region of the spectrum. Handle these cells very carefully, as they are extremely expensive and fragile. Also, be sure to keep fingerprints off of the surfaces that light passes through, as the acids in your fingerprints can be permanently etched into the surface of the expensive cuvette when exposed to UV light. If this happens, the cuvettes are ruined. Please see ChemLab.truman.edu to review proper spectrophotometer operation. Note if your absorbance readings are much larger than 1, or if your water sample's absorbance is much higher than your highest standard solution, you will need to dilute your samples accordingly.

Results and Analysis

Subtract 2 times the absorbance reading of the water sample at 275 nm from the value of absorbance for that sample at 220 nm. This operation will give a value for the experimental absorbance due to NO_3^-.

From the corrected absorbances of the standard solutions create a calibration curve of absorbance as a function of the concentration of NO_3^- (in mg N/L) that includes best fit line though the data. Include the correlation coefficient for this fit.

Using the measured absorbances of your water samples, determine the concentration of nitrogen in each your water samples in μg N/mL solution. Convert this value to the concentration of NO_3^- in μg/mL solution. Don't forget that in the determination of any real samples, you should also report the standard deviation and confidence limits for your results.

What are the predominant sources of nitrate in natural waters? How do your results compare with what is expected of natural water sources in the Midwest? If elevated, what ways might the nitrate be remediated?

Determination of Dissolved Oxygen in Water

Background

Oxygen is poorly soluble in water. Where creatures that live in the atmosphere have about 19% oxygen available for consumption, organisms living in water have a maximum of about 0.15 % oxygen. Moreover, as temperature or as salt content in the water increases, the dissolved oxygen (DO) concentration decreases. DO in pure water (no salt content) ranges from 7.6 mg/L at 30°C to 14.6 mg/L at 0°C. Many organisms, such as the mountain trout, have specific oxygen needs, so that they can only live in a small range of these variable O_2 concentrations. The mountain trout is only found in icy cold water with the highest concentration of DO.

DO concentrations can be determined by the Winkler, or iodometric, method. This method involves a series of oxidation-reduction reactions starting with the oxidation of Mn^{2+} (added to the sample in the form of $MnSO_4$) by O_2 in basic solution (by addition of an alkaline potassium iodide solution, KI in NaOH) to give solid MnO_2, as shown in following reaction.

$$2Mn^{2+}\,(aq) + 4\,OH^{-}\,(aq) + O_2\,(aq) \rightarrow 2MnO_2(s) + 2\,H_2O\,(l)$$

The formation of MnO_2 stabilizes essentially locks up the dissolved O_2 in a form that allows for short term storage of the sample before it is analyzed.

To start the actual analysis of oxygen, H_2SO_4 and more KI are added to the solution containing the MnO_2 precipitate. At low pH, the MnO_2 oxidizes I^- completely into I_2, according to the reaction

$$MnO_2\,(s) + 2\,I^{-}\,(aq) + 4\,H^{+}\,(aq) \rightarrow Mn^{2+}\,(aq) + I_2\,(aq) + 2\,H_2O\,(l)$$

Because both of these reactions go to completion, the I_2 formed is directly related to the amount of DO in the sample.

The I_2 produced by the second reaction is determined by titration with standardized sodium thiosulfate ($Na_2S_2O_3$), via another oxidation-reduction reaction in which thiosulfate reduces the I_2 back into I^-. The balanced chemical equation for this reaction is illustrated is

$$2\,S_2O_3^{2-}\,(aq) + I_2\,(aq) \rightarrow S_4O_6^{2-}\,(aq) + 2\,I^{-}\,(aq)$$

The endpoint of the reaction is detected using a starch indicator. When I_2 is present, the indicator has a deep blue color (due to a complexation of iodine by the starch), but when no I_2 is present in solution, the solution is colorless. So, once the equivalence point is reached, there will be no I_2 remaining in solution and the dark blue color that was initially present in the solution will disappear.

From the known $S_2O_3^{2-}$ concentration and the volume of the $S_2O_3^{2-}$ solution used to reach the equivalence point, we can ultimately determine the number of moles of O_2 that were originally present in your sample of water. Since the volume of the original sample is known, we can

calculate the concentration of O_2 in mg/L, which is what will be reported along with the temperature of the water when it was sampled.

To prevent nitrite interference (a real possibility in fresh water samples) sodium azide (NaN_3) is added with the alkali-KI reagent to the water sample as it is taken from the source. The addition of sulfuric acid then results in the removal of NO_2^- through the following series of reactions.

$$NaN_3\ (aq) + H^+\ (aq) \rightarrow HN_3\ (aq) + Na^+\ (aq)$$

$$HN_3\ (aq) + NO_2^-\ (aq) + H^+\ (aq) \rightarrow N_2\ (g) + N_2O\ (g) + H_2O\ (l)$$

Sample Collection
The following steps are for collecting the samples. As you will not be collecting the samples yourself, these are included here for your information only.

Prepare a manganese(II) sulfate solution by dissolving 480 g of $MnSO_4 \cdot 4H_2O$ (or 400 g of $MnSO_4 \cdot 2H_2O$, or 364 g of $MnSO_4 \cdot H_2O$) in about 800 mL of deionized water. Filter the solution and dilute to 1.0 L. Prepare the alkali-iodide-azide reagent by dissolve 500 g of NaOH (or 700 g KOH) and 135 g of NaI (or 150 g KI) in deionized water and dilute to 1.0 L. Add 10 g of NaN_3 dissolved in 40 mL of deionized water.

Samples should be collected as close to analysis as possible. Collected samples should be stored with little or no head space, on ice and in the dark and care should be taken to avoid shaking samples.

To a 250-300 mL plastic sample bottle almost filled with the water sample, add 1 mL of $MnSO_4$ solution, followed by 1 mL of alkali-iodide-azide reagent (this is best done with graduated two graduated cylinders). If the solution turns white, no DO is present.

Gently squeeze the sample bottle to raise the sample's level in the bottle to its lip. Seal the sample bottle so that no air bubbles are present and mix by inverting the bottle rapidly a few times. When the precipitate has settled to half the bottle volume, repeat the mixing and allow the precipitate to resettle.

Procedure
All solutions can be disposed of down the drain.

Prepare the sodium thiosulfate titrant by dissolving 6.205 g of $Na_2S_2O_3 \cdot 5H_2O$ in deionized water. To this solution add 0.4 g of solid NaOH. Once the NaOH has dissolved dilute to 1.0 L. This solution is approximately 0.0250 M, but because the solid can be oxidized by oxygen in air during storage, we will need to standardize it with biiodate.

Dissolve 0.81 g of $KH(IO_3)_2$ in deionized water (measured to the nearest milligram) and dilute to 1.000 L. This solution should be 0.00210 M in $KH(IO_3)_2$ and will be our standard biiodate solution.

Approximately 2 g of KI (measure to the nearest 0.001 g) is dissolved in 100 – 150 mL deionized water in an Erlenmeyer flask and 1 mL of 6 M H_2SO_4 is added to the resulting solution. Pipet 20.00 mL of the standard biiodate solution into the flask; I_2 will be formed from the reaction.

Titrate the liberated I_2 with the thiosulfate titrant until a pale straw (yellow) color is reached. Add a few drops of starch indicator (already prepared for you by dissolving 2 g of lab-grade soluble starch and 0.2 g of salicylic acid as a preservative in 100 mL of hot distilled water and cooled before use). The solution should turn blue. Continue the adding titrant until the blue color is gone, which is the endpoint. If the solutions were made correctly with pure reagents, 2 g of KI and 20.00 mL of $KH(IO_3)_2$ should require 20.00 mL of the $Na_2S_2O_3$ titrant to reach the endpoint. Determine the concentration of thiosulfate and repeat the titration until three concentrations agree within about 3% of each other.

Once the $Na_2S_2O_3$ has been standardized, open the sealed sample bottle and add 1 mL of concentrated H_2SO_4. Reseal the bottle and mix by inverting the bottle rapidly and dissolve the precipitate. You may open the bottle and pour the sample at this point since the DO and reagents have been "fixed" and will not react further.

Titrate 200 mL of the water sample with your standard thiosulfate solution as in the standardization (first titrate to a pale straw color, add starch indicator, and titrate to the clear endpoint). Take care with these titrations! Only enough samples will be collected for each group to do four titrations. Once your allotment of samples is gone, there will be no more available!

Determine the DO concentration in the water samples and repeat the titrations at least twice more or until three concentrations agree within about 3%.

Results and Analysis

Calculate the mean, standard deviation and confidence limit of the results of your titration. The concentration of O_2 should be reported in mg O_2 per L solution. Compare your results with that expected for standard fresh water at the temperature in which your sample was taken (this can be calculated from Henry's Law or looked up in reference books).

Determination of Ions Using an Ion Selective Electrode

Introduction

An ion-selective electrode (ISE) incorporates a special, ion-sensitive membrane, which may be glass, a crystalline inorganic material or an organic ion-exchanger. The membrane interacts specifically with the ion of choice, allowing the electrical potential of the half-cell to be controlled predominantly by the ion's concentration. ISEs are available for measuring more than 20 different cations (e.g., Ag^+, Na^+, K^+, Ca^{2+}, Cu^{2+}) and anions (e.g., F^-, Cl^-, S^{2-}, CN^-).

The potential of the ISE is measured against a suitable reference electrode (another half-cell which gives a complete electrochemical cell) using an electrometer or pH meter. The electrode potential is related to the logarithm of the concentration of the measured ion by the form of the Nernst equation given as Eqn. 1. In Eqn. 1 *n* is the ion charge (negative for anions), [*X*] is the concentration of the species of interest, and the factor 2.303 RT/F has a theoretical value of 59 mV at 25 °C.

$$E = E^0 + 2.303\frac{RT}{nF}log[X] \qquad (1)$$

The Nernst equation is only valid for very dilute solutions or for solutions where the ionic strength, *I*, is constant. Ionic strength is defined by Eqn. 2, where Z_i is the charge on an ion and C_i is its concentration. In this analysis the ionic strength will be maintained by adding another salt to the solution in excess. This supporting electrolyte will be NaCl for a fluoride analysis and $NaNO_3$ for a chloride analysis.

$$I = \frac{1}{2}\sum Z_i C_i \qquad (2)$$

Procedure

The following procedure assumes that you are doing a fluoride analysis. If you are performing a chloride analysis, substitute NaCl for NaF and use $NaNO_3$, instead of NaCl, as the supporting electrolyte.

Dry the NaF solid for 1 hour at 100 °C (already done for you) to remove any water that has adhered to the solid's surface.

Accurately prepare 100 mL of a 0.1 NaF solution by weighing out about 0.42 g of NaF into a 100-mL volumetric flask. Dissolve the salt in deionized water, dilute to the mark and mix well. This is your fluoride stock solution.

Prepare 100 mL of a 0.01 M NaF solution by dilution of the fluoride stock solution using volumetric glassware.

Weigh out 7.55 g of KCl on a top-loading balance and dissolve in 100 mL of deionized water. This solution is 1 M in KCl.
Prepare standard solutions in four 100-mL volumetric flasks as follows:

Flask Number	Volume of 0.01 M NaF (mL)	Volume of 1 M KCl (mL)
I	1.00	10.00
II	2.00	10.00
III	5.00	10.00
IV	10.00	10.00

Dilute each flask to volume with deionized water and mix well.

Add 1.00 mL of your unknown, then 10.00 mL of KCl to a 100 mL volumetric flask. Dilute to the
100 mL mark with deionized water.

Pour about 30 mL of either a standard or unknown solution into a clean, dry 100 mL beaker and immerse the electrodes in the solution to a depth of not more than 2 cm. Measure the electrode potential (in mV) with the voltmeter. **CAUTION!** Do not touch the ISE membrane. Rinse it with deionized water between measurements and then with a small volume of the new solution. Do not wipe it dry.

When you finish, rinse the electrodes with deionized water. Leave the reference electrode in the appropriate storage solution. The F^- ISE should be stored dry and loosely capped. DO NOT force the cap onto the electrode tip!

Results and Analysis
Prepare a calibration curve in Excel relating log[NaF] in the standard solutions to the measured potential of each solution in mV. Determine the best line through the four standard solution experimental points. The slope of the calibration curve should be close to -59 mV.

Utilizing the calibration curve, determine the concentration of NaF in your original unknown solution.

Presentation of Water Analysis Laboratory Exercise Results

Presentation Format

The presentation will occur in lab next week and should address the points listed below. Each presentation should require no more than 10 to 15 minutes, although shorter presentations are acceptable (and expected). You may present your results in the form of a "chalk-talk" (writing on the white board in lab), or you may create overheads (handwritten are fine). The presentations should be both informal and informational. All group members are expected to participate in the presentation (although your group may elect one person to make the presentation).

Points to Address in the Presentation

1) A statement of the importance of the analyte that you measured in the natural water sample.

2) A **brief** explanation of the theory behind the measurements that you made. Include how the measurement results were used to determine the concentration of the analyte.

3) A presentation of the results that includes the average, standard deviation and confidence limits at the 95% confidence level. Also include information relevant to any calibration curve or standardization.

4) A judgment on your results' quality. Include a comparison of the results that might be expected for a natural water sample.

5) Any errors that might have been made.

6) Conclusions that you can make about the water sample based on your results.

Assessment

Your grade will be determined largely by whether you address these points given above. Less emphasis will be made on how the results are presented, but a sloppy and poorly constructed presentation will receive fewer points. The accuracy of statements made during the presentation will also be an important component of the final grade. Other assessment criteria will include: was a meaningful result obtained, were there flaws in the experimental design or how the analysis was carried out.

One grade will be assigned per group.

Equipment and Techniques

Operation of the Vernier LabQuest 2

B. D. Lamp* and J. M. McCormick

Before using the LabQuest 2, familiarize yourself with the interface by viewing these links: http://www.vernier.com/products/interfaces/labq2/hardware/ (hardware overview) and http://www.vernier.com/products/interfaces/labq2/software/ (software overview).

As you use the LabQuest app, you will spend most of your time in one of three screens (or "modes"): *Meter*, *Graph*, or *Data Table*. You can switch between *Meter*, *Graph*, or *Data Table* modes by tapping on the appropriate icon on the top of the screen with the stylus attached to the LabQuest.

Mode	Icon	Available Menus in this Mode
Meter		File, Sensors
Graph		File, Graph, Analyze
Data Table		File, Table

Common Operations of the LabQuest

Powering Up and Configuring the LabQuest

Power the LabQuest on by pressing the power button located on the top of the device.

Plug a sensor, or multiple senors, into the appropriate port (this can be done before or after powering on). Most sensors used in our chemistry labs are analog sensors that plug into the ports on the left side of the device. If the sensor does not seem to fit in the port; you are using the wrong port. The LabQuest should recognize the sensor automatically and display the sensor's current reading on the screen in *Meter* mode. The sampling mode, sampling rate and duration will also be displayed. Note that switching probes on the fly by unplugging one and plugging in another (especially if one is a spectrometer) may result in neither being recognized by the LabQuest, or one of them living on as a zombie. In this case, you will need to power cycle the LabQuest (turn it off, then on) or reboot the LabQuest by tapping on the *Reboot* button in the *System* folder of the LabQuest *Home Page* (push the house button on the right side of the LabQuest or tap on the house button on the LabQuest).

To configure the sensor, tap **Sensors** to open a drop-down menu that allows the user to adjust a variety of parameters. The most common adjustments will occur in the **Data Collection** section, where the collection mode and acquisition parameters (sampling rate, sample duration, etc.) can be adjusted as needed for the experiment. This can also be done by tapping on **Mode** on the upper right of the *Meter* screen or on the rectangle that shows what sensor is attached, to which port the sensor is attached and its current reading. Tapping on the rectangle will cause a pop-up to appear with the various options, depending on the sensor.

A sensor will display and store a factory-set number of significant figures, even though it records many more. The number of digits to the right of the decimal place displayed and stored can be set by switching to the *Data Table* mode and then tapping on the column corresponding to the measured value whose significant figures or number of digits to the right of the decimal that you want to change. Set the *Displayed Precision* to whatever number that you want and select either

Decimal Places or *Significant Figures*. Note that these often give similar results, but they are not the same! This should set the number of displayed (and stored) digits until the sensor is unplugged.

Data Acquisition and Manipulation

To initiate data collection, tap the green arrow (think "play button") on the bottom left of the screen or press the collect button. During data collection, the green arrow becomes a red square (think "stop button") and data is plotted graphically in *Graph* mode. Data collection will continue until the experiment duration has elapsed or until the red square icon is pressed.

Once a run is completed, it is wise to save the data. Students may save runs to the device itself and later transfer the data files via e-mail or USB drive. See the section entitled *Data File Transfer* for more details.

Multiple runs may be saved in a single data file. After collection, runs can be stored when in the *Graph* mode by tapping the **Graph** menu and selecting **Store Run**. As a shortcut, a run can be stored by tapping the file cabinet icon () on the right side of the screen. Individual runs (or all runs) can be displayed by tapping the *Run #* button to the left of the file cabinet icon. (Storing a run only keeps the run in memory; you must eventually **Save** the file that contains the run to avoid losing the data).

Curve fitting can be accomplished through the **Analyze** menu in the *Graph* mode. Entire runs or selected portions of runs can be fit to a variety of relationships. Note that it may be more convenient to export the data file and use Logger Pro for such an analysis (see *Basic Data Analysis Using Logger Pro 3*).

To fit only a portion of a run, select the portion (**Graph**, **Graph Options** from the menu bar at the top of the screen in *Graph* mode) of the run before tapping on the *Analyze* menu. A portion of the data may be selected by first tapping on the graph. Then touch the small circle that appears where you tapped with the stylus, and leaving the stylus on the screen, drag it across to the other end of the data that you wish to select. Tap **Graph**, Zoom In to enlarge it. **Graph**, **Zoom Out** will return you to the previous view (**Graph**, **Autoscale once** will return the original view).

Individual runs may be renamed or deleted using the *Data Table* mode. In this mode, tapping on the name of a run will allow you to edit the name. To delete a run, tap on **Table**, select **Delete Run** and choose the run to be deleted. Column calculations can also be done in *Data Table* mode.

Shut Down

For the introductory laboratories at Truman, you will usually not need to shut down the LabQuest at the end of your laboratory period. However, you should check that you have logged off the wireless network before you leave.

You only need to press the power button to shut down the LabQuest (shut-down can also be accomplished by tapping on the Shut Down icon in the *System* folder of the LabQuest's home

screen). You will receive a warning if you have any unsaved data, and you should choose the appropriate option. After power-down is complete, the sensors may be unplugged and they and the LabQuest can be returned to their storage location, as directed by your instructor.

Data File Transfer
Students may use the LabQuest File menu to save your data on the LabQuest. For further data analysis and permanent storage, you will need to either transfer the file to a USB thumb drive or e-mail the file to yourself (or both if you are a little paranoid!). Files will be periodically removed from the LabQuest devices so be sure to transfer your data!

USB Drive Instructions
You can transfer the data file to a USB flash drive by inserting the drive into the USB port on the LabQuest and tapping "File" and "Save". The screen that appears should have a USB drive icon on the top left of the screen, if it does not, be sure the USB drive has been inserted completely. Tap on the USB icon to select the drive and tap "Save" to save the file to the drive.

E-Mail Instructions
To e-mail the file to yourself, you must first log in to the wireless network. Tap on the Wi-Fi icon next to the battery icon on the bottom right of the screen to enter the *Connections* screen. Tap on the "gear" icon on the top right side of the screen that appears to open the Network Settings screen. On the *Network Settings* screen, select the *TrumanSecureWireless* network and use your Truman credentials to log in. Once you are logged in, tap "OK" and tap the "X" in the connections window to return to the data screen. From the data screen, tap "File" and select "Email" and "Data File". In the screen that appears, enter your e-mail address in the "To" field, tap "Done" and "Send". In your inbox you should receive a message from trumalabquest@gmail.com that has the LoggerPro data file attached. To log out of the wireless network, tap on the Wi-Fi icon again to enter the *Connections* screen and tap on the gear icon in the top right of the screen to open the *Network Settings* screen. Click on the gear icon on at the top right corner of the screen to open the *Network Details* and tap "Forget Network". Tap *Ok* to exit the screen and then tap on the "X" in the upper right corner to return to the data screen.

Using a Temperature Probe with the LabQuest
Plug the temperature probe into a port on the left side of the LabQuest, as described above.

The LabQuest2 will display a large red rectangle showing what channel the probe is in and the temperature it is reading (note if more than one sensor is attached, there will be other boxes of different colors, one for each of the other probes). The acquisition mode will be set to *Time Based* by default when the LabQuest is powered up, but it will be set for whatever the last acquisition mode was if the LabQuest is already on.

The acquisition parameters can be set as described above. The temperature probes do not require calibration.

See the online user's manual at http://www.vernier.com/files/manuals/tmp-bta/tmp-bta.pdf for more information on the Vernier temperature probe.

Using a Spectrometer with the LabQuest

Set-Up

Plug a Vernier spectrometer, shown in Fig. 1 into the USB port on the left side of the LabQuest (note that Ocean Optics and other mini-spectrometers will not work with the LabQuest). The LabQuest will automatically recognize the spectrometer and display a box labeled USB: Abs.

Calibration

First set the acquisition mode to *Full Spectrum* (although there are many modes available, but the only ones of relevance for a spectrometer are *Full Spectrum* and *Time Based*).

Figure 1. The Vernier SpectroVis Plus spectrometer. The wavelength range of this spectrometer is from ~380 nm – ~900 nm.

From the **Sensors** menu in the *Meter* display on the LabQuest, select **Calibrate** and choose the USB: Spectrometer. This can also be done by clicking on the box labeled USB: Abs and selecting **Calibrate** in the pop-up. With either method, it may take a few seconds for the calibration routine to start; don't get impatient.

Once the calibration routine has started, the LabQuest will wait 90 seconds for the spectrometer to warm up. If the spectrometer has been in use, this step may be skipped by tapping *Skip Warmup*. You will then be asked to place a blank cuvette in the device; tap *Finish Calibration*. When the calibration is finished the LabQuest will display "Calibration completed," at which point you can click *Ok* to return to the data screen.

Obtaining Data

If you are interested in obtaining a spectrum on the full wavelength range you ready to acquire data once the spectrometer is calibrated. Note in the *Full Spectrum* mode you will need to stop acquisition manually by tapping the *Stop* button.

For a time-based measurement, change the acquisition mode to *Time Based*, as described above and enter the rate of acquisition or the interval between data points, the duration of the experiment and the time units, as needed. Click *Ok*. If you are switching between *Full Spectrum* and *Time Based* modes you may receive a warning message about saving your data, if you acquired in the first mode. Choose whichever option you want. The LabQuest will now display the absorbance reading at some wavelength (the format will be USB: Abs @ xxx nm and then below that the absorbance at that wavelength will be given). This wavelength can be changed by

tapping on the absorbance reading and selecting **Change Wavelength** in the pop-up. Enter the wavelength and tap *Ok*. Data acquisition (absorbance at the selected wavelength as a function of time) can be initiated by tapping the green *Go* icon.

For more information on the Vernier SpectroVis spectrometer see the online user's manual at http://www.vernier.com/files/manuals/svis-pl/svis-pl.pdf.

Using a pH Sensor on the LabQuest

A pH sensor attaches to the LabQuest in the same way as a temperature probe and the information given in that section applies equally to the pH sensor. Normally, we are only interested in the pH value at the time of measurement, and so it is not necessary to change the acquisition mode or to take data over a set time period (although you could do so, if you wished). However, like the spectrometer, the pH sensor must be calibrated before use.

Calibration a pH Sensor

Once the pH sensor is attached to the LabQuest, it will need to be calibrated before it can be used. Calibrate the pH sensor using two pH buffers (7 and 4 if working in acidic solutions or 7 and 10 if working with basic solutions)

From the **Sensors** menu in the *Meter* display on the LabQuest, select **Calibrate** and choose the pH Sensor.

Immerse the pH Sensor in the pH 7 buffer. Tap *Calibrate Now*. Observe the value under *Live voltage*, once it has stabilized, enter 7.00 for "Value 1" and tap *Keep*.

Remove the pH sensor from the pH 7 buffer, rinse it with distilled water, and immerse it into the second buffer. Again observe the value under *Live voltage*, once it has stabilized, enter the corresponding pH for "Value 2" and tap *Keep*.

Tap *Ok* to exit the calibration routine. The pH sensor is now ready for use. It should be removed from the buffer solution and placed into your unknown solution.

This calibration process may be repeated as needed to assure accurate results.

See the online user's manual at http://www.vernier.com/files/manuals/ph-bta/ph-bta.pdf for more information on the Vernier pH probe.

Using a Mini-Gas Chromatograph on the LabQuest

The mini-gas chromatograph (mini-GC) has an external power supply that must be plugged into both the mini-GC and a wall outlet. It is interfaced to the LabQuest via a USB cable in the same way the spectrometer is. Make the necessary connections before powering anything up. Power up the mini-GC (power switch on the side near the power cable) and then the LabQuest.

For more information on the Vernier mini-GCs see the online user's manual at http://www.vernier.com/files/manuals/gc-mini.pdf.

Other Features of the LabQuest

By pressing the home button on the side of the LabQuest or tapping the home icon you can access other LabQuest functions. Most of the settings and apps here should not be modified, but you might find the **Periodic Table** app, the **Calculator** app (in the *Accessories* folder), and the **Quick-Start Guide** app in the *System* folder to be useful. To return to the *Home* screen, tap on the house icon and to return to the data acquisition and analysis modes described above, tap on the **LabQuest App** icon.

Basic Data Collection Using Logger Pro

B. D. Lamp* and J. M. McCormick

Vernier's Logger Pro is a software package that can be used to control a simple data acquisition system attached to a USB port of the computer. This LabPro interface is an analog to digital converter capable of being applied to several measurement scenarios, from temperature and pH measurement, to instrument interfacing. Once data is collected, the Logger Pro software provides several options for basic data analysis. This document provides the basics that you will need to set up the interface, connect a sensor (or sensors) and acquire data. More detailed instructions are available (http://www2.vernier.com/manuals/LP3QuickRefManual.pdf).

Hardware Setup

Verify that the LabPro interface is plugged into a USB port on the computer, and that the power supply for the LabPro is plugged in (green light is lit).

Connect the appropriate sensor(s) to one of the four channel inputs on the left side if the LabPro. Depending on the specific measurement being done, additional connections or preparation may be necessary.

Software Setup:

Start the Logger Pro software. The opening screen should appear as shown in Fig. 1. The left portion of the screen is a spreadsheet-like table which will hold data that is collected. Multiple

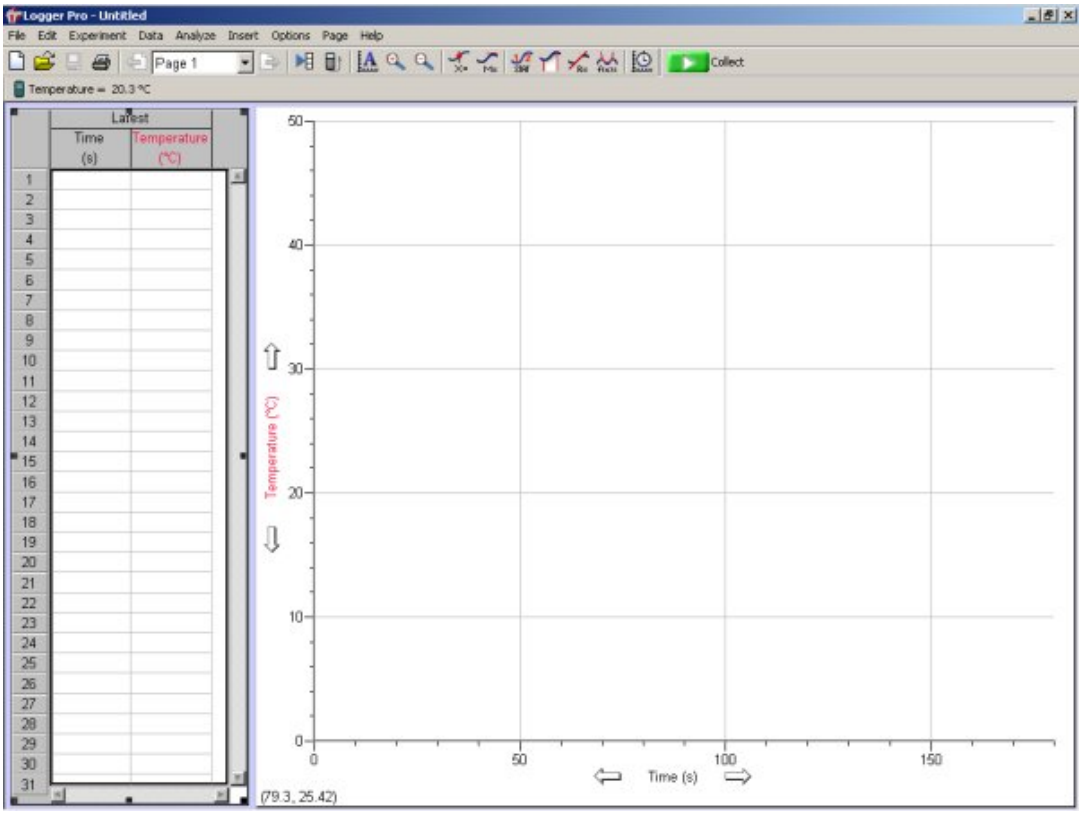

Figure 1. Opening screen for the LoggerPro software.

runs can be stored in a single table. Explore the *Data* menu to see how. Data can also be copied and pasted to and from Excel for plotting or manipulation. The right portion of the screen will present a graphical display of the data. The button and menu bars across the top of the window contain many useful data handling and analysis functions. It will likely be worth your time to explore these (don't forget the *Help* menu!)

Open a new file by selecting *File, New* from the menu bar.

It is very likely that the LabPro interface and Logger Pro software will have automatically recognized the sensor you have installed on the device. However, it is a wise idea to verify this by selecting *Experiment, Setup Sensors* and choosing the appropriate LabPro interface. Once selected, the window shown in Fig. 2 should appear:

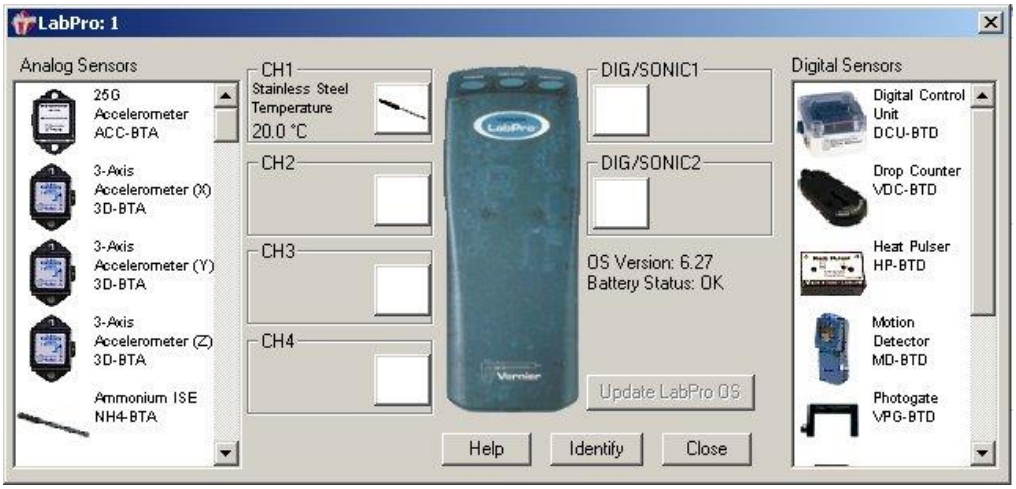

Figure 2. LoggerPro *Setup Sensors* window.

In the example above, a Stainless Steel Temperature probe has been connected to channel 1 (CH1). If your sensor is not automatically detected, simply find it in one of the scroll-down lists, click on the sensor icon and "drag and drop" it on the appropriate channel. Once all sensors are being recognized, select *Close*.

Select Experiment, Data Collection or click on the *Data Collection* icon ( ) to define your data collection parameters. The window shown in Fig. 3 will appear:

Select the appropriate sampling mode, duration, and sampling rate for your application. Once setup is complete, click Done.

You are now ready to collect data. Near the top of the screen (above the data table), you should see a live display of the signal(s) at the probe(s).

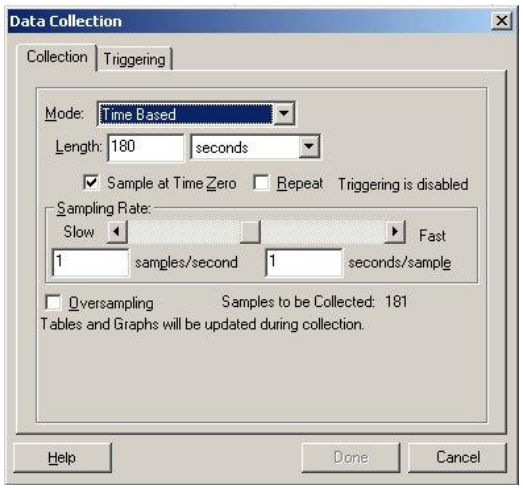

Figure 3. LoggerPro *Data Collection* window.

Data collection can be started and stopped by clicking on the 

and 

buttons, or by pressing *Enter* on the keyboard. As data is collected, it is recorded in the table on the left of the screen and plotted on the graph on the right. The table can be used to store several individual runs, the most recently collected data set is called "Latest". If you intend to save your data for later use, it is important to "store" this run before collecting a new dataset, because it will be overwritten by the new data. Selecting *Experiment, Store Latest Run* places the most recently acquired data into a new column in this spreadsheet (usually named "Run #"). Overwritten data is lost and cannot be recovered. Individual datasets can be renamed by selecting *Data, Data Set Options* and selecting the appropriate data set from the menu.

Basic Data Analysis Using Logger Pro 3

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Vernier's Logger Pro is a software package that can be used to control the LabPro data acquisition system via the USB port of the computer. The LabPro is what is called an analog to digital converter and is capable of being applied to several measurement scenarios, from temperature and pH measurement, to instrument interfacing. Once data is collected, the Logger Pro software provides several options for basic data analysis. Logger Pro can also be used as a stand-alone data analysis package. Because our introductory chemistry laboratories use LabQuests for data acquisition, only the basics of data analysis with Logger Pro will be described. More information is available at http://www2.vernier.com/manuals/LP3QuickRefManual.pdf.

Student Access to LoggerPro

Aside from being installed on the university image, students may install a copy of LoggerPro on their personal computers through our site license with Vernier. Instructions are located at: http://wp-internal.truman.edu/chemistry/installing-loggerpro/.

Data Management and Analysis

Multiple data sets can be open in Logger Pro and they will be displayed simultaneously on the screen, but this can be somewhat messy. Data files can be renamed, hidden, or displayed using the *Data Browser*, activated by clicking  , Once activated, a window such as the one shown in Fig. 1 will appear. Double-clicking on the name for a dataset will bring up a dialog box with a checkbox for hiding the data set, a place to change the data set's name, as well as a place to enter notes regarding the data. Data that has been hidden is not erased; it is simply not displayed on the graph or in the data table.

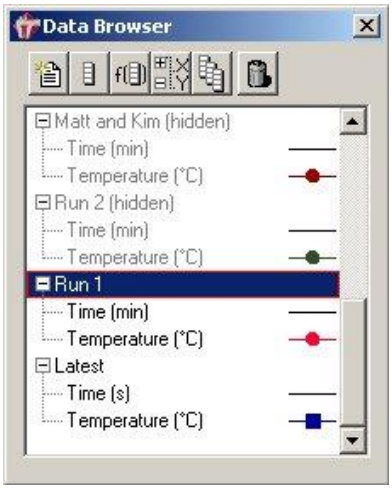


Figure 1. The LoggerPro *Data Browser* window.

Many of the data analysis functions, such as integration and linear fitting, require that a portion of the data set be selected prior to executing the function. To select a portion of the data, simply left-click on one end of the desired range and drag the mouse to the other end of the range. The

selected area will appear in grey. Only this selected area will be subject to a function such as integration or linear fitting. If no area is selected, the entire data set will be used. If multiple data sets are being displayed, you will be given the option of applying the function to any or all of the data.

The data files generated by a LabQuest or LoggerPro can only be read by a LabQuest or LoggerPro. To save your file in a format that Excel can read, select *File, Export As* from the menu bar In LoggerPro and then select the *Text* option. It is also possible to cut and paste from LoggerPro directly into Excel and vice versa. Record the file name in your notebook.

Adjusting the Graphical Display

Many of the features of the displayed graph can be adjusted by double-clicking on the appropriate part of the graph. For example, the *x* and *y* axes can be adjusted manually by clicking on one of the minima or maxima on the axes and typing in a new value. Double-clicking anywhere else on the graph brings up a *Graph Options* window which presents a wide variety of options for modifying the graph. The arrows on either side of an axis title can be used to "slide" the plot along the chosen axis. To quickly auto-scale the X and Y axes, click the  icon.

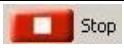
Helpful Hints

Right-clicking on an item will probably bring up a menu allowing you to change the properties of that item. If all else fails, try the *Help* menu!

You should save your file frequently to prevent accidental loss.

The data in the spreadsheet can be copied and pasted into Excel.

Below are some useful menu buttons. These buttons, as well as the others below the menu bar provide several useful features; you will find it worth your while to explore these buttons.

Button	Operation (left-click these buttons to)
	Initiate data collection.
	Stop data collection.
	Open the Data Collection setup window.
	Open the Data Browser.
	Turns on the "Examine" function which allows you to use a cursor to examine individual data points.
	Integrates the selected area.
	Calculates a linear fit over the selected data range. Outputs slope, intercept, and correlation coefficient for the linear fit.
	Auto scales the graph axes.
	Zooms graph to the selected area.
	Zooms graph out

Data Analysis, Recordkeeping and Reporting Results

What You need to do Before Coming to Laboratory

1. Before your first lab meeting, make sure that you have written your contact information in the front of your notebook, and have prepared a "Table of Contents". See *The Laboratory Notebook* section for more information on the laboratory notebook.

2. Be sure that the entries (calculations, graphs and conclusions) for any previous experiments that have been completed are ready to be presented to the instructor. If your class has post-lab questions with its laboratory exercises, don't forget to answer them and be prepared to turn them in, as your instructor directs you.

3. Answer any pre-laboratory questions for the current exercise. Your instructor will give your further information on how to complete these questions.

4. Begin the new exercise on the first blank page. Write the title of the lab, your lab partner's name, and the date on the top of the page. Write the lab's title and starting page number in the "Table of Contents".

Helpful Hints: read the "Background" and "Procedural Outline" sections of the *The Laboratory Notebook* section before proceeding. Use a highlighter to note important steps and materials (this is key to writing the "Background" and "Procedural Outline"). The first few times you may want to write out steps 5 through 7 on loose-leaf paper first (not in the notebook). In this way you can edit what you've written before you transfer the final version to your notebook. Do **not**, however, get in the habit of doing it this way; it is too time-consuming. You must quickly learn what you need to have in your notebook to perform effectively in the laboratory. As you are preparing your notebook, always remember that once something is written in the notebook, you must never recopy it (you may edit it).

5. Complete the "Statement of Purpose." Remember that this is a concise (two sentences maximum) description of what is to be done and how it is to be done.

6. Complete any required "Background" information. This section is usually omitted in CHEM 130 and CHEM 131 exercises, but check with your instructor to be sure. If you are required to have background information, check that all the necessary information is present before writing the next section.

7. Write the "Procedural Outline" (see *The Laboratory Notebook* section for formatting). The key here is to summarize the procedure in your own words so that you can do the exercise without the laboratory manual or handout.

8. Reserve space for your "Observations" and "Calculations". Unless you wish to do some of the calculations before lab, leave these spaces blank.

Your instructor may want to check your notebook, or may require you to turn in the duplicate pages from your notebook, before you begin the laboratory exercise. Be sure to read the course's syllabus and ask the instructor, if you are unclear on his or her requirements.

The Laboratory Notebook

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Introduction

The laboratory notebook is perhaps the single most important piece of laboratory equipment. A scientist's notebook may be directly entered as evidence in court, and as such may be worth millions to a company in patent litigation. While you may never be in a situation where your notebook is worth a million dollars, good record keeping is essential in all scientific research. In an academic laboratory, the consequences of poor record keeping are wasted time as you repeat the experiment, or simply failing the exercise. In an industrial laboratory, inadequate lab records ultimately cost the company money, either in the cost of time and materials or as the result of legal action. In either case, the cost to the responsible employee is their job and all possible future employment. Thus, adequate record keeping will be stressed in all chemistry laboratories at Truman.

There are many different sets of rules for keeping a laboratory notebook,[1,2] which range from the very elaborate rules followed by industrial chemists to the simplified rules listed below. Not all of the points given here will apply to all courses; your instructor will point out modifications to these procedures in his or her syllabus or in the laboratory. No matter what guidelines you use, the goal is to produce a record of a scientific endeavor that is understandable to a knowledgeable reader and which can be used to repeat the experiment and, presumably, get the same results.

Notebook Format and Rules

Laboratory records are to be kept in a bound notebook (i. e., secured with glue), not a spiral notebook or a loose-leaf binder. The pages are to be consecutively numbered. No pages are ever to be removed (except for the copies produced by duplicating notebooks).

All entries are to be made directly in the notebook in black or blue ink. Everything related to the laboratory work must be recorded in the notebook in an organized and neat manner (if it cannot be easily read, it is not adequately recorded). It is critical that the material is intelligible and understandable to the notebook author and any trained chemist who reads the records, attempts to reproduce these results, or endeavors to finish an incomplete analysis. This concept is often known as "traceable" in the industrial world.

It is **unacceptable** under all circumstances to rewrite (or "copy over") an experiment in the notebook outside of lab. It is also unacceptable to type up portions of the laboratory notebook in a word processor and then attach the printout to your notebook. Plan your activities in the laboratory so that all information is properly entered into the notebook while you are in the laboratory.

Include in the notebook a complete description of the work performed, all reference materials consulted, and ideas that you have related to the work. There should be no loose scraps of paper in the notebook. Graphs, charts, spectra, or spreadsheet analyses should be affixed to the pages of the notebook with tape or glue (to both the original and duplicate pages of duplicating notebooks). Label the space where this material is to go with a description of the item and the

results it contained. This way, if it is removed, there will be a record of it. Make no notes on the inserted material.

On the first page of your notebook are written the name of the class, your laboratory section and your name. It is also a good idea to put contact information (e. g., your phone number or email address) here, in case your notebook is lost. The next two pages are reserved for a table of contents (some notebooks come with a table of contents section on the inside front cover, or as a separate, removable sheet; these should not be used). The words "Table of Contents" are to be written at the top of these pages. The first entry is to be the table of contents itself. An entry is made in the *Table of Contents* for each experiment when it is begun. This entry includes the title of each experiment and the page number on which the experiment begins.

You may wish to dedicate one page to a "Preface" in which you describe yourself and the contents of the notebook. Another item that is sometimes included is a page titled "Abbreviations and Other Useful Information". These items must be completed before the first laboratory session.

If you are using a non-duplicating notebook, one usually uses only the right side pages. The left pages are reserved for minor calculations, notes of no consequence to the experiment and notes that refer to material found elsewhere in the notebook. In academic laboratories, especially in teaching laboratories, this rule is relaxed as a cost-saving measure for the student. Please check with your instructor on which protocol he/she wishes you to use.

If a page is skipped, a large "X" must be drawn across it. The page is then initialed and dated. While generally frowned upon, you may skip a line as needed to separate sections. There should be no unused empty space on a page, except for the printed margins. Treat large blocks of blank space like a blank page (this assures the reader that no information was added later).

At the top of each page write the title of the experiment that matches that in the table of contents. At the bottom of the page place the date that the last entry was made on that page, your printed name and signature (or initials).

If an error is made, draw a single bold horizontal line through the error so that it can still be read. Write the correct information to the right of the incorrect entry and have a short accompanying explanation of the reason for exclusion. Never use whiteout or completely obliterate the incorrect entry.

Do not copy any information from the notebooks of former or current students. The only exception is when working in a group, and only one member of the group recorded the data during the experiment. In this case, you must indicate in your notebook that the results were copied from the other person's notebook. Write the recorder's name and the page number from which the data were copied next to the copied data.

In general, the notebook should be arranged in chronological order, so that when one experiment ends the next one begins. In an undergraduate laboratory this is very easy to do, but as you progress in your study of chemistry, things are not always so well-ordered. If you must start a

new experiment before another is finished, you simply note on the last page of the unfinished experiment the page on which it will be continued.

Arrangement of an Experiment in the Notebook

Each experiment's record includes the following sections: *Title, Statement of Purpose, Background, Procedural Outline, Results, Calculations, Discussion of Conclusions and Error Analysis*, and *Summary of Results*. Each section should be clearly labeled with the underlined words indicated below. Sign and date each page as it is completed. The *Title, Statement of Purpose, Background* and *Procedural Outline* sections must be prepared prior to the laboratory period (click here for a checklist of what to do before lab).

Title: This should include the experiment's title, your name, the name(s) of your lab partner(s), and the date the experiment was begun.

Statement of Purpose: Clearly and concisely (two or three complete sentences) describe the purpose of the experiment, including the general method that will be used and anticipated results. Do not begin a *Statement of Purpose* with the phrase "The purpose of this lab is to. .". Don't resort to stock phrases; be somewhat creative. The pedagogical purpose of an exercise is not the same as the *Statement of Purpose*. For the "Determination of Density" exercise in CHEM 130, the pedagogical purpose is to learn about precision and accuracy, and the statistical treatment of data. But your statement of purpose might read "The density of a copper block will be determined by two methods: (1) from its dimensions and mass, and (2) from its mass and volume, as measured by water displacement."

Background: This section contains more information on the goals of the experiment, the methods used and the procedure followed. The content of the *Background* section varies with the type of experiment being performed and the requirements of each laboratory course. Check with your instructor about what to include, but in general the *Background* section must include:

1) reference(s) to the procedure that you are using following American Chemical Society guidelines. This reference should contain the full title of the article, or the title of the book and the name of the experiment.

2) balanced chemical equations for any chemical reactions that you will be performing. Mechanisms are to be included, when appropriate.

3) a table of important physical properties of all the materials (starting materials, solvents, and products) with which you will be working. Be sure that you have thoroughly read the experiment before preparing this table so that it includes all the chemicals that you will use. The following information must be in this table: the name of the compound, its molecular structure, and its molar mass. Other properties that may be important are melting points, boiling points, density, optical rotation, etc, depending on the particular laboratory exercise. Textbooks, laboratory manuals and library references (such as the *CRC Handbook of Chemistry and Physics*, the *Merck Index*, and the *Aldrich Catalog of Fine Chemicals*) are good sources of information on chemicals and their properties. There are some internet resources that also contain the same material. Care

should be taken in consulting internet sources because there is often no independent scrutiny of these sites.

4) record any hazardous properties (flammability, toxicity, etc.) of the substances that you will encounter in the exercise. The *Merck Index* and the *Safety Data Sheet* (SDS) for a chemical are excellent sources of this information. Both are available from the library or the stockroom.

Procedural Outline: This section is a brief (this section should not be more than one or two pages long, at most), but complete, description of the steps taken to carry out the experiment. It is not a rewrite of the source material (e. g., laboratory manual, textbook or journal article); use your own words. You may use a bulleted list for the steps. At your instructor's discretion, you may not be allowed to bring the source material to the laboratory. So, be sure that your procedure is complete.

Before beginning the *Procedural Outline*, divide the pages that will contain the procedure into two parts by drawing a vertical line on the page, approximately 3/5 of the way across the page from the left-hand margin (many notebooks already have this line drawn for you). Record the procedure on the left-hand side, and any modifications or procedural notes on the right-hand side. You do not record your results on the right-hand side! Results are recorded in the Results section.

Read the experimental section for the exercise before recording any part of the procedural outline in your notebook. This will make writing the outline much easier and minimize errors. As you read, think through the manipulations that are required and re-read sections that indicate particularly hazardous or important steps (usually denoted by "**CAUTION!**"). Once you are sure of what you are going to do, go back and write out a step-by-step procedure in your notebook.

Results: This section does not need to be completed before you come to the lab, but you may want to prepare blank tables for recording data. Include in this section a listing of the reduced data (e. g., tables), all graphs, spreadsheet results, and spectra. Unlike the *Procedural Outline*, this and all following sections may use the entire right-hand page. A common error is to forget to leave space for the graphs (a hand-drawn graph should take up most, if not all, of the page so as to maximize the results' precision) and other items (e. g., spreadsheet output) that will be prepared as part of the exercise.

All data should be recorded in this section in chronological order. Include all measurements made (with proper units and correct number of significant figures) and any important observations noted when performing the work. When observations are recorded in the laboratory notebook, they are always written in the passive past tense. So instead of "I saw the solution turn green," one writes, "The solution turned green." In general, personal pronouns (e. g., "I," "we") are not used in scientific writing (the overuse of personal pronouns is taken as a sign of arrogance and the passive is thought to sound more objective). The observations are always written in complete sentences.

When possible, set up tables for repetitive data before coming to the lab. Thinking carefully about the data that will be taken should allow you to prepare a data table, which, although difficult to accomplish for the first few experiments, will save time and space in your lab notebook. The use of tables will make it much easier for the reader to assess your methods and results.

Information on the chemicals and instruments used in the experiment are also included in the Results. For a chemical, the name of its manufacturer, its purity, and the lot number of the chemical are recorded, if this information is available (look the bottle's label). It is easiest to record this information when a chemical is first mentioned. For example, "A saline solution was prepared by dissolving 5.00 g NaCl (99.999%, Aldrich, Lot # 56390-BX) in 500 mL of distilled water." The identity of all instruments used must be recorded, preferably including serial number, model, manufacturer, and any information on the calibration or settings used. Remember that you want to have enough information in your notebook so that you can easily repeat this measurement, if and when necessary (e. g., you find a mistake). If the instrumental data were saved on disk, include the filename(s) with the data (More Info).

Calculations: An example of each calculation performed to reach the final reported answers should be shown with the units clearly shown at each step. For most exercises in a teaching laboratory, only one example of each different calculation needs to be included. Be sure to label each calculation and parallel the order in which the calculations appear in the procedure. You may want to set up the calculations before coming to lab to maximize your laboratory efficiency.

It is sometimes acceptable to include calculations in the Results section as needed. This is usually done in research situations where you need to make a calculation that you did not anticipate at the start of the experiment, but is sometimes allowed in upper-level courses where the laboratory exercises are not "cookbook." Check your instructor's syllabus, or ask him/her, for the format that you are to follow in your course.

If you made more than one measurement on the same phenomenon, calculate the average and standard deviation. Perform other statistical analyses as instructed. When an accepted or theoretical value is available, calculate a percent error. Include the output from any programs used to perform these calculations, and the filename under which the data were saved.

Discussion of Conclusions and Error Analysis: Summarize your results paralleling what you set forth in the Statement of Purpose, compare them to the expected results and try to place them in context (either in the larger field of chemistry or what you have done in class). This is not a long section; it may only be two or three pages long in the notebook. The key to a good discussion section is to concisely cover the important points.

Do not write things like "I liked this lab," "This lab went well" or "This lab was successfully completed," and do not use personal pronouns. Take your time and put some thought into your conclusions.

The discussion should try to pinpoint various specific sources of error encountered from the standpoint of the most likely determinate and indeterminate errors in the procedure. Once you

have identified a source of error in your measurement, evaluate how it affected the result, and then suggest how this error could be minimized or eliminated. Simply attributing everything to "human error" is insufficient, and will be graded accordingly. Some labs won't have numerical results to discuss, but you can still indicate sources of uncertainty and how they could be, or were, minimized. To help you learn how to organize your discussion, brief outlines for the three types of exercises usually encountered in undergraduate chemistry laboratory exercises are given below. The types are: 1) exercises with a primary focus on measurement, 2) those which are focused on the synthesis of a compound, and 3) those exercises which require you to observe and report on physical phenomena.

Many aspects of the discussion section are the same in all three, but there are subtle differences that you should appreciate. These outlines are meant only as guides; you will need to adapt them to each particular experiment. Some experiments may incorporate components of each of these three broad categories. In that case, you will need to write a conclusion that combines the three types of discussions.

Outline for Measurement Experiments

A. State the results and associated statistics.

-If an accepted value is known, assess whether the result is accurate (use a calculated percent error).
-Identify what factors lead to a decrease or increase in accuracy.
-Discuss how the accuracy could have been improved.
-Is there evidence for systematic or gross error? What is the source of that error?
-Is the result precise? (use the standard deviation and/or confidence limits)
-State what factors limited the precision (use propagation of error results).
-State what experimental methods or practices maximized the precision.
-Suggest ways that the precision could be improved.
-In the absence of a true value, discuss whether the precision allows you to have any confidence in the accuracy of the result. You may be able to qualitatively assess the accuracy of your results (e. g., if wood floats, then its density must be less than water's, do your data support this conclusion?).

B. Evaluate the experimental procedure.

-Was the procedure sufficient to provide an accurate and precise result?
-If not, how could it be improved?

C. Discuss whether the result(s) is(are) reasonable in comparison to known values or in the context of similar measurements.

Outline for Synthesis Experiments

A. Report the properties of the prepared material and what methods were used in the characterization.

-Do your results match published properties?
-Compare the published and the experimental properties to assess purity.
-In the absence of published values, evaluate the purity based on the material's properties.

B. Report the percent yield.

-Is the yield reasonable? Compare to the literature or others in class.

-Evaluate the factors and experimental techniques that gave a less than, or better than, average yield.

C. Evaluate the utility of the synthetic procedure.

-Does the reaction give the product in high enough yield?

-Is the material sufficiently pure?

-Is it not too complicated or lengthy?

-Suggest improvements.

Outline for Reporting on Physical Phenomena

A. Describe the system that observed and how you probed its properties. Use sufficient detail so that reader can clearly picture the experiment, but avoid being overly verbose.

B. Describe what you saw.

-Did you see what you expected to see, or were there differences?

-Are the results reasonable, based on what you know about chemistry?

C. Try to explain any differences between what you observed and what you expected.

-Was the difference because of your experimental procedure? If so, how could you modify the procedure to change the result?

-Was the difference a result of reactions or other things that you didn't consider initially? If so, how will you need to change your assumptions to accommodate the new data?

Summary of Results: For measurement and synthetic exercises you will need to include a final table summarizing the results of your experiment. For a measurement exercise this table should include each individual value used in the establishment of the average (check with your instructor if you have more than three or four individual values), the standard deviation, and the confidence limit. For a synthetic exercise your summary table should include the percent yield and the measured physical properties of the new substance. Once the Summary of Results has been recorded, sign and date the experiment.

Labels for Products: If you prepared a substance in the exercise, you must place it in a properly labeled bottle and give it to your instructor. The bottle label must include:

Your Name, Instructor's Initials
CHEM xxx, Date Prepared
Name of Chemical
Formula of Compound (Structure is Optional)
Percent Yield
Physical Properties used in Characterization

The other physical properties used in characterization may include: experimental melting point, boiling point, melting point, NMR chemical shifts, IR peaks, etc. Only one or two physical

properties need to be listed (check with your instructor as to which one, or ones, to include). The corresponding literature value for each property should also be listed, if known.

References

1. Kanare, H. M. *Writing the Laboratory Notebook*; The American Chemical Society: Washington, D. C., 1985.

2. Eisenberg, A. *J. Chem. Educ.* **1982**, *59*, 1045-1046. This article is available as a PDF file at http://pubs.acs.org/doi/pdfplus/10.1021/ed059p1045 for Truman addresses and *J. Chem. Educ.* subscribers.

Introduction to Statistics in Chemistry

B. D. Lamp, D. L. McCurdy, V. M. Pultz and J. M. McCormick*

Introduction

"Figures often beguile me, particularly when I have the arranging of them myself; in which case the remark attributed to Disraeli would often apply with justice and force: 'There are three kinds of lies: lies, damned lies and statistics.'" -Mark Twain

Twain's dyspeptic view of figures and statistics notwithstanding, the predictive power of science derives from quantifying (placing numbers on) physical properties, and then writing mathematical equations to describe the Universe's behavior (laws and theories).[1] In this way, we can predict the outcomes of experiments that we have not yet done, and thereby test our models of the Universe. Once we have actually done the experiments we will also need a mathematical way of assessing the reliability of our results. It is in the latter application that scientists rely on statistics. The following is intended to provide you with a basic, working understanding of statistical analysis in chemistry. For a more complete treatment of statistics you will want to take STATS 190/2903 and CHEM 222.[2-4]

There are three terms that are used by scientists in relation to their data's reliability. They are *accuracy*, *precision* and *error*. Accuracy is how close a measured value is to the true, or accepted, value, while precision is how carefully a single measurement was made or how reproducible measurements in a series are. The terms accuracy and precision are not synonymous, but they are related, as we will see. Error is anything that lessens a measurement's accuracy or its precision.

To beginning science students the scientific meaning of "error" is very confusing, because it does not exactly match the common usage. In everyday usage "error" means a mistake, but in science an "error" is anything that contributes to a measured value being different than the "true" value. The term "error" in science is synonymous with "mistake" when we speak of *gross errors* (also known as *illegitimate errors*). Gross errors are easy to deal with, once they are found. Some gross errors are correctable (a mistake in a calculation, for example), while some are not (using the wrong amount of a reactant in a chemical reaction). When met with uncorrectable gross errors, it is usually best to discard that result and start again.

The other types of "errors" that are encountered in science might be better referred to as *uncertainties*. They are not necessarily mistakes, but they place limits on our ability to be perfectly quantitative in our measurements because they result from the extension of a measurement tool to its maximum limits. These uncertainties fall into two groups: *systematic errors* (or *determinate errors*) and *random errors* (or *indeterminate errors*).

A systematic error is a non-random bias in the data and its greatest impact is on a measurement's accuracy. A systematic error can be recognized from multiple measurements of the same quantity, if the true value is known. For example, if you made three measurements of copper's density and got values of 9.54, 9.55 and 9.56 g/cm^3, you would not be able to determine whether a systematic error was present, unless you knew that the accepted value of copper's density is 8.96 g/cm3. You might then suspect a systematic error because all of the measured values are

consistently too high (although the closeness of the data to each other implies some level of confidence). Often in science one needs to assess the accuracy of a measurement without prior knowledge of the true value. In this case the same experiment is performed with samples where the quantity to be measured is known. These *standards*, or *knowns*, can reveal systematic errors in a procedure before measurements are made on unknowns, and give the experimenter confidence that they are getting accurate results.

The last type of uncertainty is random error. As the name suggests, these uncertainties arise from random events that are not necessarily under the control of the experimentalist. Random errors can be thought of as background noise. The noise restricts our ability to make an exact measurement by limiting the precision of the measurement. Because indeterminate errors are random, they may be treated statistically.

Assessing Accuracy

Accuracy can be expressed as a percent error, defined by Eqn. 1, if the true value is known. Note that the percent error has a sign associated with it ('+' if the measured value is larger than the true value, and '-' if it is less than the true value). Using the copper density data from above

$$percent\ error = \frac{measured\ value - true\ value}{true\ value} \times 100 \qquad (1)$$

and Eqn. 1, we can calculate a percent error for each data point of approximately +6.5%. This suggests the presence of a systematic error because, if there were no systematic error, we would expect the percent error for each member of the data set to be very small and that there would be both positive and negative values. When the true value is not known, no conclusion about accuracy may be made using a percent error. In this case, standards must be run or other statistical methods based on the precision can be used. However, the latter can be used only to assess the accuracy of a group of measurements.

In the absence of systematic errors, the average, $\bar{x}$, of a set of measurements (Eqn. 2) should approximate the true value, as the number of measurements, *N*, becomes very large (i. e., there are many individual data points, x_i). But if a systematic error is present, then making more

$$\bar{x} = \frac{x_1 + x_2 + x_3 + \cdots + x_n}{N} = \frac{1}{N}(x_1 + x_2 + x_3 + \cdots + x_n) = \frac{1}{N}\sum_{i=1}^{N} x_i \qquad (2)$$

measurements will not make the average approach the true value (as is the case for the copper data we have been discussing). So to make the most accurate measurements (smallest percent error), all systematic errors must be eliminated. Note that the percent error for a set of measurements can be made using the average. The average value of copper's density, using the data that we have been discussing, is 9.55 g/cm^3, which has +6.6% error.

Assessing Precision

The range is the simplest, and crudest, measure of the precision for a set or measurements. The range is simply the highest value minus the lowest value, and can be used to get a rough idea of the spread in the data, but not much more. Sometimes you will see a range reported in the form

± (range/2), which should not be confused with the confidence limits discussed below. To avoid confusion, chemists almost never report the range in this way.

A better measurement of precision for a data set is the standard deviation (σ) which may be calculated using Eqn. 3 for data sets that have more than about 20 points.

$$\sigma = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(x_i - \mu)^2} \tag{3}$$

In Eqn. 3 μ is the true mean (what the average becomes when *N* is large). Since it is rare in chemistry to have more than three to five replicate experiments, the estimated standard deviation, *S*, is used instead (Eqn. 4). In either case, a smaller *S* or σ indicates higher precision.

$$S = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(x_i - \bar{x})^2} \tag{4}$$

Note the dependence of both *S* and σ on the number of data points. If the difference terms are all about the same, then the precision should increase (*S* and σ decrease) as *N* increases. So, it is statistically advantageous to make more measurements, although this must be balanced with practical considerations. No one wants to do a ten-day experiment 30 times just to get better statistics!

The standard deviation is related to another estimate of precision known as the confidence limit or the confidence interval. The confidence interval is a range of values, based on the mean and the standard deviation of the data set, where there is a known probability of finding the "true" value. A confidence limit is written as $\bar{x} \pm \Delta$ at the given confidence level. For example, a volume expressed as 2.16 ± 0.05 cm^3 at the 95% confidence level means that there is at least a 95% probability of finding the "true" value in the range 2.11 cm^3 to 2.21 cm^3 (in other words, within ± 0.05 cm^3 of the average, 2.16 cm^3). It does <u>not</u> mean that only 95% percent of the time we are confident of the result! To some extent precision is separate from accuracy. However, if enough precise measurements are made in the absence of systematic error, we have increased confidence that our average is a good approximation to the true value, even though we do not know the true value. So, a confidence limit also expresses a level of certainty that the true value lies within ±Δ of the average, in the absence of systematic error.

To determine a confidence limit, the uncertainty, Δ, must first be calculated from the estimated standard deviation using Eqn. 5. The value of *t* (called Student's *t*) in Eqn. 5 may be calculated

$$\Delta = t\frac{S}{\sqrt{N}} \tag{5}$$

in Excel using the TINV function, or may be taken from a table such as Table 1, which gives the value of *t* for various degrees of freedom (usually the number of data points minus one, i.e.,

$N - 1$) at the 95% confidence level. Note that as the precision of a set of measurements increases, Δ will decrease at a set confidence level. Higher confidence levels also reflect higher precision in the data set.

Degrees of Freedom	*t*
1	12.7
2	4.30
3	3.18
4	2.78
5	2.57
6	2.45
7	2.36
8	2.31
9	2.26
10	2.23
15	2.13
∞	1.96

Table 1. Values of *t* at the 95% confidence level for various degrees of freedom.

Precision and Significant Figures

In lecture and on exams and quizzes when we write a number, we assume that the precision is ±1 in the last number written (for example, the number 31.778 would be assumed to have a precision of ±0.001). We do this for simplicity. Because when we make this assumption we only need to concern ourselves with significant figures and we can ignore statistics and the propagation of error (see the *Propagation of Uncertainty* section for a more thorough discussion of error propagation). In real life we are not so lucky and we must worry about significant figures, statistics and the propagation of error. However, significant figures are always our first step in analyzing our data.

The uncertainty in a number tells us directly how many significant figures our result has. This is because the uncertainty tells us in what place the first uncertain digit is (or you could say it is the first digit where certainty ends). For example, if you had a result 15.678±0.035 kJ/mole at the 95% confidence level, then you could tell from the uncertainty that the first digit that has any uncertainty in it is the tenths place. We know the 1, the 5 and the 6 (and are confident that we know them), but the 7 we have some doubt about. We only really know this digit to ±3 at 95% confidence and the hundredths place is not known with any certainty. How we show this is discussed below.

Reporting Results

There are three ways in which the statistical information that accompanies a measurement (average, standard deviation, and confidence limit) can be stated. If, for example, five replicate measurements of a solid's density were made, and the average was 1.015 g/cm^3 with an estimated standard deviation of 0.006, then the results of this experiment could be reported in any of the following ways:

•The average density is 1.015 g/cm^3 with an estimated standard deviation of 0.006 g/cm^3.

•The density is 1.015(6) g/cm^3.

•The density is 1.015 ± 0.007 g/cm3 at the 95% confidence limit.

In this example the density has four significant figures, and the uncertainty is in the last decimal place. Sometimes the uncertainty and the number of significant figures in the measurement do not match. This means that each individual measurement was measured more exactly than the reproducibility within the group. If the standard deviation in the density experiment had instead been 0.010 g/cm^3, then the results might be reported as:

•The average density is 1.02 g/cm^3 with an estimated standard deviation of 0.01.

•The density is 1.02(1) g/cm^3.

•The density is 1.02 ± 0.01 g/cm^3 at the 95% confidence limit.

The results have been rounded off because the number of significant figures does not reflect the precision of the data set. In other words, the statistical analysis shows us that the first digit where uncertainty begins is the 1/100^{ths} place, even though each measurement was made to the 1/1000^{ths} place. The last significant figure is in the 1/100^{ths} place, so this is where rounding occurs. Sometimes the average and the uncertainties are quoted to the maximum number of significant figures (i. e., 1.015(10) g/cm^3). In this way the precision of each individual measurement and the precision of the set of measurements are shown.

Using Statistics to Identify Hidden Gross Error

Another way in which statistics can be used is in the evaluation of suspect data by the *Q*-test. The *Q*-test is used to identify outlying ("bad") data points in a data set for which there is no obvious gross error. The *Q*-test involves applying statistics to examine the overall scatter of the data. This is accomplished by comparing the gap between the suspect point (outlier) and its nearest neighbor with the range, as shown in Eqn. 6. The calculated *Q* is then compared to the critical *Q* values, Q_c, at given confidence level, like those in Table 2. If the measured *Q* is greater than Q_c, then that data point can be excluded on the basis of the *Q*-test.

$$Q = \frac{|suspect\ value - closest\ value|}{highest\ value - lowest\ value} \qquad (6)$$

N	3	4	5	6	7	8	9	10
Q_c	0.94	0.76	0.64	0.56	0.51	0.47	0.44	0.41

Table 2. Critical *Q* (Q_c) values at the 90% confidence limit for a small number of data points, *N*.

For large data sets ($N > 10$) a data point that lies more than 2.6 times *S* (or σ) from the average may be excluded. Although for medium-sized data sets (between 11 and 15 data points), there is an alternative treatment that is usually sufficient. In these cases, we can use Q_c for $N = 10$, but in

doing so, a higher criterion is placed on the data for exclusion of a point than is required by statistics. So, an outlying point that could have been discarded is retained and the precision is quoted as being less than it actually is. But again, it is better to err on the side of caution in our data treatment.

In any case, only one data point per data set may be excluded on the basis of the *Q*-test. More than one point may be tested, but only one may be discarded. For example, you have measured the density of copper as 9.43, 8.95, 8.97, 8.96 and 8.93 g/cm^3; can any of these points be excluded?

First, we must remember that the *Q*-test is only valid at the extremes, not in the middle of the data set. So before performing a *Q*-test, it is best to sort the data (as already been done with the data that we are considering). Now look at the extremes and see whether either of the points look odd. In this case, the low value (8.93 g/cm^3) is not that much different than the values in the middle of the set, while the high value (9.43 g/cm^3) looks to be suspect.

Having decided that the 9.43 g/cm^3 value is suspect, we can calculate *Q* using Eqn. 6, (suspect value = 9.43, closest value = 8.97, highest value = 9.43 and lowest value = 8.93). This gives $Q = 0.92$ for this point. Since this exceeds Q_c for five data points (for $N = 5$, $Q_c = 0.64$ in Table 2), this point may be excluded on the basis of the *Q*-test. The *Q*-test may **not** be repeated on the remaining data to exclude more points.

One last important thing about the *Q*-test is that it cannot be performed on identical data points. For example, if our data set had been 9.43, 9.43, 8.95, 8.97, 8.96 and 8.93 g/cm^3, we would not have been able to use the *Q*-test on the 9.43 g/cm^3 values.

Propagation of Uncertainty

So, now we have an average and an associated uncertainty at given confidence level for a data set. What happens if we use this result in a calculation? The simple answer is that the uncertainty carries through the calculation and affects the uncertainty of the final answer. This carrying over of uncertainty is called propagation of error, or propagation of uncertainty, and it represents the minimum uncertainty in the calculated value due entirely to the uncertainty in the original measurement(s). The equations that describe how the uncertainty is propagated depend on the calculation being done, and can be derived using calculus.[5] If you would like to learn more about how Eqn. 7 was derived, please see the *Propagation of Uncertainty* section. The following example demonstrates how a propagation of uncertainty analysis is done.

The dimensions of a regular rectangular wood block are 15.12 cm, 3.14 cm and 1.01 cm, all measured to the nearest 0.01 cm. What is the volume and the confidence limits on the volume based on this single measurement? The equation for the uncertainty in the volume is given in Eqn. 7, where ΔV, Δx, Δy and Δz are the uncertainties in the *volume* and the *x*, *y* and *z*

$$\Delta V = \pm V \sqrt{\left(\frac{\Delta x}{x}\right)^2 + \left(\frac{\Delta y}{y}\right)^2 + \left(\frac{\Delta z}{z}\right)^2} \qquad (7)$$

dimensions, respectively. Do not be confused by the notation! The Δ represents the uncertainty, not a change, in these parameters. Since each measurement was made to the nearest 0.01 cm, $\Delta x = \Delta y = \Delta z = \pm 0.01$ cm. First we calculate the volume, being careful with our significant figures (note the extra "insignificant" figures from the calculator output, shown as subscripts, carried along in the calculation for rounding purposes).

Substituting the known values of V, x, y, z, Δx, Δy and Δz into Eqn. 7 gives

$$\Delta V = \pm 47.9_{52}\ cm^3 \sqrt{\left(\frac{\pm 0.01\ cm}{15.12\ cm}\right)^2 + \left(\frac{\pm 0.01\ cm}{3.14\ cm}\right)^2 + \left(\frac{\pm 0.01\ cm}{1.01\ cm}\right)^2}$$

$$\Delta V = \pm 47.9_{52}\ cm^3 \sqrt{(4._{374}\, x10^{-7}) + (1._{014}\, x10^{-5}) + (9._{803}\, x10^{-5})}$$

$$\Delta V = \pm 47.9_{52}\ cm^3 \sqrt{1._{086}\, x10^{-4}}$$

$$\Delta V = \pm 47.9_{52}\ cm^3 (1._{042}\, x10^{-2}) = \pm 0.5\ cm^3$$

So, the volume would be reported as 48.0 ± 0.5 cm^3 for the single measurement, and this represents a minimum uncertainty in the volume based on the uncertainties in the block's dimensions. Note that the propagated uncertainty usually has only one significant figure.

To see how the propagated uncertainty differs from an uncertainty for a population (data set), imagine that we did this measurement three times and got volumes of 48.1, 47.8 and 48.3 cm^3. Each individual measurement has an uncertainty of ±0.5 cm^3, from the propagation of uncertainty analysis, but the uncertainty for the set of measurements is ±0.7 cm^3. This was calculated with S = 0.3 cm^3 (determined using Eqn. 4) and the value of t taken from Table 1 (for $N - 1 = 2$) by substitution into Eqn. 5. Thus, the volume would be reported as 48.1 ± 0.7 cm^3 at the 95% confidence limit. Notice that the uncertainty in the population is not the same as the uncertainty in each individual measurement. They are not required to be the same, nor are they often the same. In this example, the propagated uncertainty is less than that for a series of volume measurements, indicating another source of uncertainty besides that arising from the uncertainty in the block's dimensions. This is often the case, and in your conclusions to an exercise or experiment you should try to identify its source and discuss its impact on your result.

Regression Analysis

Once we have data from an experiment, the challenge is to determine the mathematical expression that relates one measured quantity to another. The problems that confront us when we attempt to mathematically describe our data are 1) how to establish the mathematical formula that connects the measured quantities and 2) how to determine the other parameters in the equation. The process by which a mathematical formula is extracted from a data set is called fitting, or regressing, the data.

A linear relationship is the simplest, and most useful, mathematical formula relating two measured quantities, x (the independent variable) and y (the dependent variable). This means that the equation takes the form $y = m \cdot x + b$, where m is the slope of the line and b is the

intercept. It is possible to relate two quantities with other equations, but unless there is a good theoretical basis for using another function, a line is always your best initial choice. For a linear relationship the values of *m* and *b* must be found from the data (*x* and *y* values), which is done through a linear least squares regression (or fit). The mathematics behind the fitting algorithm is not relevant at this time, but it is important to know that the least-squares procedure assumes that the uncertainty in the *x* values is less than the uncertainty in the *y* values. This means that, if we want to get a meaningful slope and intercept from our fit, we must make the measured quantity with the smallest uncertainty be the independent variable.

Some of pitfalls that you may encounter when performing a regression analysis (and why it is always a good idea to graph your data) have been discussed by Anscombe.[6]

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6. Anscombe, F. J. *The American Statistician* **1973**, *27*, 17-21. This article is available as a PDF file on JSTOR (http://www.jstor.org/stable/2682899?seq=1#page_scan_tab_contents). The Wikipedia entry for Anscombe's quartet summarizes the results nicely (available online at https://en.wikipedia.org/wiki/Anscombe%27s_quartet).

Preparing Graphs

J. M. McCormick

General Considerations[1]

When we prepare a graph the independent variable is always on the x-axis, and the dependent variable is always on the y-axis. We indicate which variable is which by saying "as a function of" or "versus", with the dependent variable coming first, and the independent variable coming second. So if someone says, "volume was plotted as a function of mass" or "the volume is plotted versus mass," it means that mass was on the x-axis and volume was on the y-axis. Watch what you say/write as there is only one correct usage!

All graphs must have axis labels. The axis labels have two parts: the first is the name of the parameter, and the second is the unit. The axis labels can have one of three formats: parameter name (unit); parameter name, unit; parameter name/unit. For example, if the parameter was temperature and it was measured in Kelvin, then the axis label could be Temperature (K), or Temperature, K or Temperature/K.

Devise a scale for each axis so that the tick mark labels end in a 0 or a 5. If this is not possible, use a scale so that the last digit in the tick mark labels is an even number. Tick mark labels with the last digit being an odd number, other than 5, are almost never used. The axes do not need to start at zero. For example, if all the x values occur between 400 and 600 nm, a graph of these data could start at 400 nm. The key to preparing good graphs is selecting a scale that shows all of the data and minimizes large regions of blank space. The one exception is when you need to extrapolate back to a certain value, but the data are not necessarily close to that value. In this case, you would want to have the value to which you will extrapolate shown on the graph, even though there may be some blank space.

The number of significant figures in the tick marks is usually less than that in the original data. For example, if our temperature axis has values between 200 and 320 K with each individual point measured to the nearest 0.01 K, we would not write the tick marks as 200.00, 220.00, etc., but rather 200, 220, etc. (see Fig. 1 and Fig. 2).

Graphs that will appear in a notebook must also have a title. The title should concisely tell the reader what is in the graph. Avoid the obvious use of vs. or versus or the word "plotted" in the title. Graphs that will appear as a figure in a publication or in a formal laboratory report will not have a title (the information is given in the figure caption).

Hand-Drawn Graphs

For hand-drawn graphs in the notebook choose a scale so that the graph fills most, if not all of the page. Use a small, dark dot for each data point. Draw a circle around the point to help the reader locate the actual data point. The radius of the circle usually approximates the uncertainty in the point unless this gives a circle that is too large. With hand-drawn graphs, one usually does a linear regression "by eye", which means that a ruler is used to put a line through the data such that all points lie as close as possible to the line. The slope and intercept can then be determined from the line itself using points on the line at the extremes of the graph to maximize the precision.

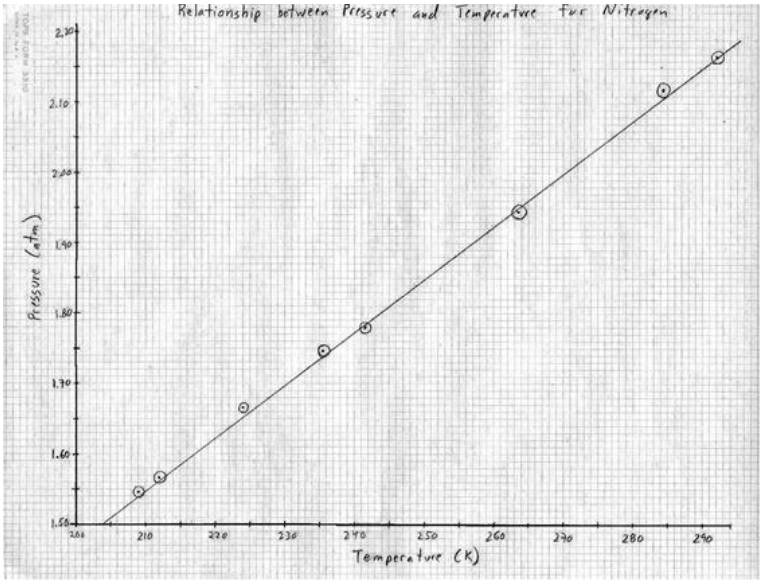

Figure 1. A properly executed hand-drawn graph.

Spreadsheet Graphs

With a spreadsheet it is much easier to prepare graphs, but it is also much easier to produce a poor quality graph. To assure that your graphs are correctly prepared (e. g., look good and are easy to understand by the reader), follow these standard procedures:

-Most of the graphs that you will prepare in a chemistry class are called *XY Scatter* plots in Excel. The other formats will be used sparingly because they are generally not useful in chemistry.

-When creating the graph, make the chart occupy a new sheet; do not create it in the worksheet containing the data.

-Make all lines (the axes, the tick marks, the box around the plot area and any data lines) black with medium intensity (third choice from the top under *Weight* in the format boxes).

-The plot area should have no fill color (not the default setting) and no box around it.

-Turn off all gridlines (not the default setting), unless told otherwise by your instructor.

-Legends showing what a given symbol means are useful, but not always needed (e. g., in a formal laboratory report this information is given in the caption that accompanies the figure). Be sure that your selection of lines and legend titles clearly distinguish between multiple data sets and fits.

-A title should be placed at the top of the graph if the graph is to be placed in the laboratory notebook. This helps the reader immediately know what the graph is. The title should be a concise description of what is being graphed (e. g., "Pressure as a Function of

Temperature for Nitrogen"). Usually you do not need to describe in the title the units used in the graph, but there are some instances where this is necessary. Avoid using the words "versus", "vs." and "plotted" in the title. The title is **omitted** when the graph will be used as a figure in a publication or formal laboratory report. This is because the information normally put in the title will be included in the figure caption.

-Watch your tick marks. The spreadsheet automatically selects the spacing, which may not be appropriate for your graph (see *General Considerations*).

- Be careful with the use of color to distinguish different data sets on the same graph. Yellow and light blue do not show up very well when printed either on color or black and white printers. Do not distinguish different data sets by color if you do not have a color printer. In general, it is best to dispense with color entirely and make all lines and symbols black (or at least a uniform dark color).

-Data are always shown as symbols and fits to the data are shown as lines or curves. Do not connect the data points with lines. This will confuse the reader as to whether these lines represent a fit, or not.

-For graphs that will be placed in a notebook, you can include the equation of a best-fit line and the R^2 value for the fit in a legend (but remember that this information should also be written in the notebook as part of the graph's description, in case the graph is removed). However, for graphs that will be submitted for publication or used in a formal laboratory report, this information is not shown on the graph itself. Rather, it is placed either in the figure caption or in the body of the text itself.

-Sometimes a fit is not required, or cannot be done, but you still want to show a trend in the data. In this case a smooth line that passes through the data as an "aid to the eye" is used, and is so indicated in the text accompanying the graph.

-A 16-point font for axis labels and graph titles and a 14-point font for the tick mark labels are better choices for general work than the default settings. The font used for the title should match that used for the axis labels.

-Depending on the final size of the graph, you might want to increase the size of the symbols to 9 point.

-Most spreadsheets automatically select the number of decimal places on the tick labels from the data, but not always correctly. For example, if your data were between 50 and 100, you would want tick labels of 50, 60, 70, 80, 90, and 100. But if the data in the spreadsheet are set to two decimal places, most spreadsheets would make the labels 50.00, 60.00, 70.00, 80.00, 90.00 and 100.00. Although this is not necessarily incorrect, the convention is to show the minimum number of decimal places on the tick labels.

Remember that the default settings in a spreadsheet may not fit your needs. Therefore, it is critical that you know how to change the settings (see the *Guide to Excel* section).

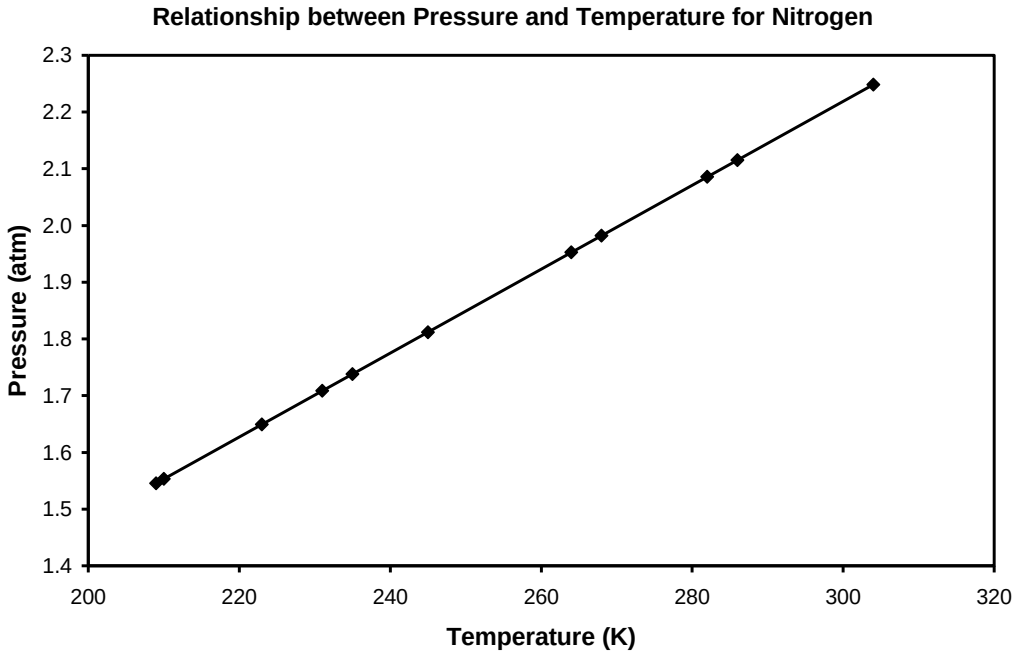

Figure 2. A graph that was properly prepared for a laboratory notebook using a spreadsheet.

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Guide to Excel

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Updates by S. Warner and V. Pultz

Introduction

The purpose of this section is to give the average student a brief introduction to Excel and provide a quick reference to those students who are more familiar with the program. It supplements, but does not replace, hands-on experience. This tutorial was written for Excel 2010, but other versions are similar, although where you find functions on the menu bar are different. If you encounter trouble, use the online help, or ask a more experienced user.

Cell References

All cells in a spreadsheet are referred to by their column (letter) and row (number). For example, cell A1 is the first cell in the upper left-hand corner of the worksheet. Many times it is easier to enter a formula once and then copy and paste it into other cells. When we do this, Excel will automatically change the row and column references. If we don't want the reference to a cell to change, we need to use an *absolute reference*. An absolute reference is denoted with the "$"symbol, and may proceed the column or row designation, or both. For example, if we wanted to subtract the value in cell B13 from that in cell A2, but keeping the reference to cell B13 constant, we might enter in cell C2 the formula "=A2-B13". If we then copy cell C2 and paste it into cell C3, cell C3 would contain the formula "=A3-B13". But if we pasted it into cell D2, cell D2 would contain the formula "=B2-B13".

Basic Mathematical Operations

Formulas may be entered with any combination of numbers and cell references using the standard symbols shown in Table 1. Note that all formulas begin with the equals sign. So, entering "=A1+B1" in cell C1 would add the contents of the two cells and place that result in C1, while entering "=A1+5" in C1 adds 5 to the value in A1 and places it in C1. The order of operation is important! Multiplication and division are performed before addition and subtraction. Use parentheses to ensure proper calculation. Convince yourself that the order of operations is important by entering "= (2+3)/4" in one cell and "=2+3/4" in another. These calculations do not give the same result!

=	Equals (starts all formulas entered in Excel)
+	Addition
–	Subtraction
/	Division
*	Multiplication
^	Power

Table 1. Symbols for basic mathematical operations in Excel.

Built in Functions

Pushing the "Insert Function" button in the "Formula" tab will give access to all of the built-in functions. These functions all require an *argument* (i. e., the *arg* in the parentheses), which can be either a list of numbers, cell references separated by commas, or two cell references separated

by a colon to denote a range of cells. Some useful functions are shown in Table 2, and examples of how they are used are given in Table 3.

AVERAGE(*arg*)	Calculates the average of a set of numbers.
COS(*arg*)	Calculates the cosine of the argument (in radians).
COUNT(*arg*)	Counts the number of cells that contain numbers in the specified range.
COUNTA(*arg*)	Counts the number of cells that are not empty in the specified range.
EXP(*arg*)	Raises *e* to the power of the argument.
LN(*arg*)	Returns the natural logarithm (ln) of argument.
LOG(*arg*)	Returns the logarithm of argument; defaults to base 10 if no base is specified
LOG10(*arg*)	Returns the base 10 logarithm (log) of argument.
PI()	Returns the number pi (this function has no argument).
SQRT(*arg*)	Takes the square root of the argument.
STDEV(*arg*)	Calculates the standard deviation of a set of numbers.
SIN(*arg*)	Calculates the sine of the argument (in radians).
SUM(*arg*)	Adds all the numbers in a range of cells.
TINV(α, N–1)	Calculates the value of t at a given confidence limit and degree of freedom ($N - 1$). Note that $(1 - \alpha)$ is the fractional confidence limit (*e. g.*, for the 95% confidence limit, $\alpha = 0.05$).

Table 2. Some useful built-in Excel functions.

Starting with Excel 2010 Microsoft introduced T.INV.2T to replace TINV. The new function may provide improved accuracy. The TINV function is available in Excel 2010 for backward compatibility, but it may not be available in future versions of Excel.

=AVERAGE (A2:A5)	Calculates the average of cells A2, A3, A4 and A5.
=AVERAGE (A2,A4,A5)	Calculates the average of cells A2, A4 and A5.
=SUM(A2:A5)	Adds all the numbers in cells A2, A3, A4, and A5.
=EXP(-1*A2)	Raises *e* to the -A2 power (note that writing -A2 instead of -1*A2 may not work in older versions of Excel).
=TINV(0.05,COUNT(A2:A10)-1)	Calculates the value of *t* at the 95% confidence limit for the data contained in cells A2 to A10, inclusive. Note the use of the COUNT function to determine the degrees of freedom.

Table 3. Examples of some Excel functions as they would appear in a spreadsheet cell.

Selecting Cells

To select a single cell, simply click (note that unless otherwise noted "click" means to momentarily depress the left mouse button) on it. To select more than one cell in the same row or column, click on the first cell, and while still holding the left mouse button down, drag the mouse to the last cell. The selected cells will be highlighted. You can also select a block of cells by clicking on a corner cell and dragging the mouse to the diagonal corner. An alternate way to select cells is to click on the first cell, hold the *Shift* key down and then select the last cell containing data. Once the cells are selected; let up the *Shift* key. If you want to select an entire column or row, click on the column or row header. To select multiple columns or row, simply

click on the header and drag. This last method of selecting cells is very useful if you have a large amount of data that needs to be formatted.

Non-adjacent cells can be selected by holding the *Ctrl* key while clicking on each cell. Highlighting non-adjacent rows or columns is a combination of the steps for selecting nonadjacent cells and rows/columns. Once the first column (or row) has been highlighted, the second column is selected by pressing and holding the *Ctrl* key while you click with the left mouse button in the first cell. While holding the *Ctrl* key and the left mouse button, drag to select the values in this column. The other way to select the second column is to press and hold the *Ctrl* key while clicking in the first cell, then let up the *Ctrl* key and press and hold the *Shift* key. Click on the last cell in the column that contains data and all the cells in between will be highlighted.

Formatting and Toolbar Functions

Many formatting functions are depicted as icons in the "Home" tab along the top of the spreadsheet. The formatting functions are grouped in a category (such as "Font" or "Alignment"). If the function you want is not displayed, there is an expansion button in the bottom right corner of the category which, when clicked, gives more formatting functions. For the "Font," "Alignment," and "Number" categories, this expansion button brings opens the "Format Cells" window. (see Fig. 1: *Format Cells* dialog box). For the "Clipboard" category, it opens the clipboard. If your Excel window is not maximized to full-screen, the function categories become buttons instead of displaying any of the functions. To access the functions, click the category's button. Some of the more commonly encountered formatting and toolbar functions are given in Table 4. You will note that some of these tools are the same as in word

Button	Function	Shortcut	Menu Bar Location
	Align left	*Ctrl*-l	*Home, Alignment*
	Align center	*Ctrl*-e	*Home, Alignment*
	Align right	*Ctrl*-r	*Home, Alignment*
	Bold	*Ctrl*-b	*Home, Font*
	Italic	*Ctrl*-i	*Home, Font*
	Underline	*Ctrl*-u	*Home, Font*
	Increase number of decimal places		*Home, Number*
	Decrease number of decimal places		*Home, Number*
	Undo last action(s)	*Ctrl*-z	*Window Title, Undo*
	Redo last action(s)	*Ctrl*-y	*Window Title, Redo*
	Sort cells in ascending order		*Data, Sort & Filter*
	Sort cells in descending order		*Data, Sort & Filter*

Table 4. Common tool bar function buttons.

processing programs and that some have menu bar buttons or shortcut keys (e. g., to make something bold you can either click the bold icon in the use the key sequence *Ctrl*-b). To perform any one of the various formatting options, select the object or cell that you wish to format, then use the appropriate shortcut or click the desired formatting button in the "Home" tab. Several formatting functions are also available in the menu displayed when a cell is right clicked. It is often more efficient to select multiple objects or cells to format before performing the actual formatting. To access the right-click menu with multiple cells selected, select the desired cells then right click one of the selected cells.

Clicking on any object, and selecting the appropriate format from the respective tab and category, allows you to change the formatting of the object. Right clicking on a selected object and choosing the format option will also bring up the format dialog box. To get the superscript (or a subscript), select the cell you wish to edit. The contents of the cell will appear in the formula bar. Use the mouse to highlight the text to be superscripted (or subscripted), right click, then select "Format Cells…" and click on the superscript (or subscript) check box. Another way to do this same formatting is to highlight the desired text and click the Format Font dialog box launcher (see Fig. 1) and click the superscript (or subscript) check box.

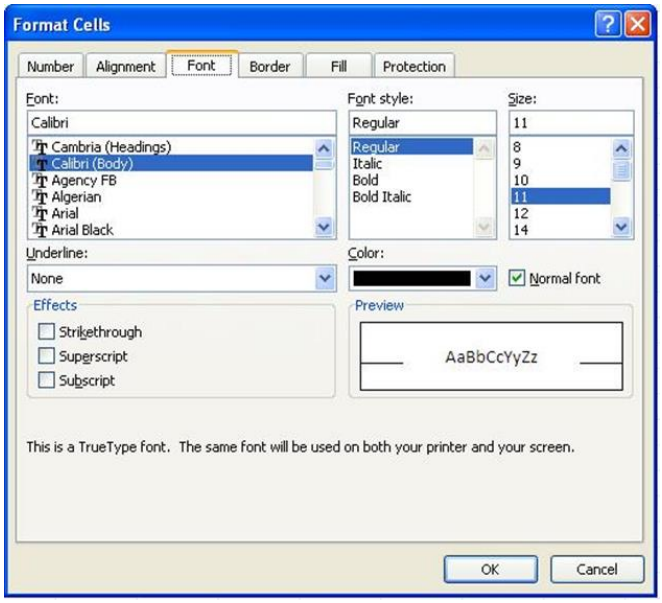

Figure 1. "Format Cells" dialog Box (font tab selected)

To put symbols in axis labels or titles, use the same procedure, except change the font to Symbol font. The correspondence between the Greek letters (Symbol font) and the Roman alphabet (Normal font) for selected symbols is given in Table 5. S ymbols that do not appear in Table 5 (such as ±, •, ≠, ≤, ≥, Å, Â, Ä, Ã, Ñ, …, etc.) can be added by selecting "Symbol" (Ω) from the Insert tab. Clicking on the appropriate symbol and then clicking the Insert button will complete the task. When finished inserting symbols, close the *Symbol* window.

Symbol	Roman
α	a
β	b
χ	c
δ	d
ε	e
ϕ	f
γ	g
η	h
ι	i
φ	j
κ	k
λ	l
μ	m

Symbol	Roman
ν	n
ο	o
π	p
θ	q
ρ	r
σ	s
τ	t
υ	u
ϖ	v
ω	w
ξ	x
ψ	y
ζ	z

Symbol	Roman
Α	A
Β	B
Χ	C
Δ	D
Ε	E
Φ	F
Γ	G
Η	H
Ι	I
ϑ	J
Κ	K
Λ	L
Μ	M

Symbol	Roman
Ν	N
Ο	O
Π	P
Θ	Q
Ρ	R
Σ	S
Τ	T
Υ	U
ς	V
Ω	W
Ξ	X
Ψ	Y
Ζ	Z

Table 5. The relationship between symbol and Roman fonts.

The number of significant figures displayed can be changed using the increase/decrease decimal place button (/) in the *Home* tab and *Number* category. One can also select the *Format Font* dialog box launcher (, see Fig. 1) and the *Number* tab to increase/decrease the number of decimal places displayed. The latter method also allows you to change all aspects of how the numbers are displayed. Note that Excel uses the format "0.00E+00" for scientific notation, not "0.00 x 10+00" or "0.00 x 1000". If you enter a number in the latter formats, Excel will treat it as text.

Sorting

To sort data you must first select the cells to sort. Go to the *Data* tab and click on the *Sort* button ( ) in the *Sort & Filter* category. If you have selected one column and there are data in adjacent cells Excel will give a warning message. If you *Continue* with the current selection, the selected cells will be sorted and the adjacent cells will **not** be sorted. Do **not** select this option if your data are (*x*, *y*) data pairs, because this will ruin the pairs. If you want to sort data pairs, select the cells containing both values and then sort. When several rows or columns have been selected, using the toolbar buttons such as causes the left-most column or top-most row to be sorted. If you use , you will be prompted for which row/column to sort by.

Graphing

To graph data in the spreadsheet, first select the data. Excel assumes that the *x*-values are in the first column/row selected and that the *y*-values are in the second and any subsequent column/row selected. Now select the *Insert* tab. In the *Charts* category, you will be able to select which type of chart is most appropriate. For most cases in chemistry, select the "Scatter"( ) drop-down menu and "Scatter with only Markers" as the graph type.1 The chart will be generated automatically and you will then be able to use the *Chart Tools* tabs. See the *Preparing Graphs* section for more information on graphing.[1]

The first *Chart Tools* tab is *Design* where you can revise your chart type, manipulate the data selected, and modify the layout of your chart. The *Layout* tab is where you can insert photos/shapes/text, add chart labels (chart title, axis titles, and legend labels), and turn gridlines on or off. The *Format* tab is where you can change colors of data selections and chart components and change the size of your chart. Your charts should be on separate Excel worksheets from your data. To do this, select your chart and go to the *Design* tab and *Location* category. There you will find a "Move Chart" option. With your chart selected, click on "Move Chart" (); a "Move Chart" dialog box will appear. Select *New Sheet* for the chart location.

Once a graph has been created it can be edited by simply right-clicking the chart object (axis, data series, etc.), and choosing *Format* from the drop-down menu.

A trendline can be added to a graph by selecting the *Layout* tab and in the *Analysis* category click the *Trendline* button. In chemistry we usually want a *Linear Trendline*. If there is more than one data set on the graph, you can choose which data set requires a trendline. If you click on *More Trendline Options…* you can check the boxes labeled "Display Equation on chart" and "Display *R*-squared value on chart". If you have a trendline but do not have its equation displayed, right-click the trendline and click "Format Trendline". From the "Format Trendline" dialog box, select the "Display Equation on chart" check box. Generally we will <u>not</u> force the line to go through a particular value on the *y*-axis, so leave the "Set Intercept" box unchecked. Once you close the dialog box, Excel will perform a linear least squares fit of the selected data. Note that while a trendline will give you the equation of the best-fit line through the data, it is usually insufficient for the data analysis that is often required in chemistry. Please see the *Regression Package* section below for a more powerful means of fitting data.

It is possible to copy a chart from Excel and paste it into another program. Make the chart that you wish to copy be the active chart, and while holding the shift key, click on *Copy* () in the *Home* tab and *Clipboard* category. When in the other program, paste the object by clicking the *Paste* button in the *Home* tab of Word, right clicking and selecting a *Paste* option, or use keyboard shortcut *Ctrl*+v. Once in Word, the image size can be modified to fit the page and further edited by selecting the *Format Picture* tab on the ribbon.

Regression Package

In addition to the trendline, Excel also has a more complete regression package, which gives much more information than the simple trendline treatment. This package is part of the *Analysis ToolPak* add-in that can be activated in Excel. Depending on your computer, you may need to install the *Analysis ToolPak* before using the regression tools described here. The installation varies depending on the version of Excel that you are using. Version-specific instructions are below. **NOTE:** The *Data Analysis* option will only appear if the active window is a worksheet; it will not appear if the active window is a chart.

- If you are using Excel 2010 or Excel 2007, select the *Data* tab. If *Data Analysis* appears as an option in the *Analysis* category, the *Analysis ToolPak* is already installed and the regression package can be accessed by clicking on *Data Analysis* and in the pop-up window selecting *Regression* and clicking *OK*. If *Data Analysis* is not an option on the *Data* tab, go to http://office.microsoft.com/en-us/excel-help/load-the-analysis-toolpak-

HP010342659.aspx?CTT=1 (last visited January 10, 2012) for Excel 2010 or to http://office.microsoft.com/en-us/excel/HP100215691033.aspx (last visited January 10, 2012) for Excel 2007 to install the *Analysis Toolpak*.

•If you are using Excel 2003, select the *Tools* menu. If *Data Analysis* appears as an option, the *Analysis ToolPak* is already installed. To use the regression package, select *Tools, Data Analysis* from the menu bar and in the pop-up window select *Regression* and click *OK*. If these statistical tools are not present, go http://office.microsoft.com/en-us/excel-help/load-the-analysis-toolpak-HP001127724.aspx?CTT=1 (last visited January 10, 2012) to install the *Analysis Toolpak*.

•Mac Users: The most recent version of Excel for the Mac does not have the *Analysis Toolpak* built in. Microsoft suggests the following alternative, which functions nearly identically to the *Analysis Toolpak*. You can use *StatPlus:mac LE* to perform many of the functions that were previously available in the *Analysis ToolPak*, such as regressions, histograms, analysis of variance (ANOVA), and *t*-tests. First, visit the *AnalystSoft* web site (http://www.analystsoft.com/en/products/statplusmacle/, last visited January 10, 2012), and then follow the instructions on the download page. After you have downloaded and installed *StatPlus:mac LE*, open the workbook that contains the data that you want to analyze. Then open *StatPlus:mac LE*. The functions are located on the StatPlus:mac LE menus.

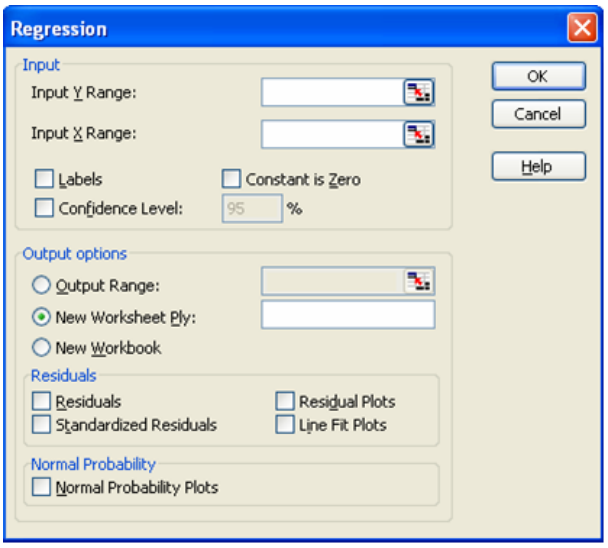

Figure 2. Pop-up window for configuring the regression routine in Excel.

When the regression package is selected, the window shown in Fig. 2 will appear. Input the *Y Range* and *X Range* (if you push the button in the regression window, the window will minimize and you can choose the desired range by clicking and dragging). Because we do not generally want to force a fit to go through zero, leave the check box for *Constant is Zero* unselected. By clicking on the check box next to *Confidence Level* and entering a new number in the input box, one can select a new confidence limit. For our purposes this is best left at 95%. Leave the "*Output Options*" set for a *New Worksheet Ply*. Press *OK*, and Excel will perform the

regression and output the results to a new worksheet, an example of which is shown as Fig. 3. The new worksheet contains a good deal of statistical information, but for a basic analysis we need be concerned with only a few items. The first is the value of R^2 (R Square), which is a measurement of how related the two measured quantities are ($R^2 = 1$ is a perfect linear relationship). For many of the fits that you will encounter in chemistry $R^2 > 0.999$ are common, and so the use of this parameter to determine how good the fit is or to compare two fits, is somewhat limited. In this case, the standard deviation about the regression, which is given as the *Standard Error* under the *Regression Statistics* heading, is more useful.

The values of the intercept and slope (*X Variable 1*) are under the heading of *Coefficients*, while the estimated standard deviation of each parameter is given under the heading *Standard Error*. The *Lower 95%* and *Upper 95%* entries give the confidence interval for a parameter at 95% confidence. If you selected a confidence level other than 95% the last two columns (the second set of columns in Fig. 3 labeled *Lower 95.0%* and *Upper 95.0%*) will contain the confidence interval at the level. You can calculate the uncertainty (at the xx% confidence level) by subtracting the entry under *Lower xx%* from the *Upper xx%* and dividing by 2. For the example given in Fig. 3, the uncertainty in the slope is (2.727447482 – 1.662430005)/2 which is rounded to one significant figure, giving ±0.5 as the answer.

Important! If you are performing a propagation of error analysis (see also the *Introduction to Statistics in Chemistry* and *Propagation of Uncertainty* sections of this document) on a value calculated from a regression analysis, you do not use the uncertainty! Instead, you must use the standard error (i. e., the standard deviation), not the confidence interval. For example, if we used the slope shown in Fig. 3 in a calculation and we wanted to see how its uncertainty affected the calculated value, we would use ±0.2 (the standard error in the slope rounded to one significant figure) not ±0.5! If an intercept of zero was specified in the regression window, or if an error occurred, the error "#N/A" will appear for some entries.

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.999509156
R Square	0.999018554
Adjusted R Square	0.998992726
Standard Error	0.005716936
Observations	40

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	1.264204688	1.264204688	38680.37433	9.01275E-59
Residual	38	0.001241968	3.26834E-05		
Total	39	1.265446655			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	-0.329484975	0.002183057	-150.9282695	2.08155E-54	-0.333904342	-0.325065608	-0.333904342	-0.325065608
X Variable 1	-0.00049891	2.53675E-06	-196.6732679	9.01275E-59	-0.000504045	-0.000493775	-0.000504045	-0.000493775

Figure 3. Typical output of the Excel regression package.

Excel's regression package also has a number of advanced features that you may read about, if you wish, in the *Advanced Regression with Microsoft Excel* section.

Printing

The appearance of hardcopy can be viewed by going to the File tab and selecting *Print*. On the right hand of the screen now is a preview of what your printed page would look like. To adjust page settings, such as margins, go to the *Page Layout* tab. You will need to experiment with combinations of page orientation (portrait or landscape), scaling, margins, etc., until you have the page that matches what you want. If possible, a table should fit completely on a single page. When satisfied with the page settings, return to the *Print* menu under the *File* tab, and push the large "Print" button.

Miscellaneous Features

Excel has a "fill" feature that is useful when one wants to construct a set of data where the *x* values are all equally spaced between some starting and ending value. For example, if we wanted a graph of the function e^{-x}, we could create the x values for the graph using the fill function. To fill a series first type the starting value in the first cell of the series and select it by clicking on that cell. Next, in the *Home* tab in the *Editing* category, select the *Fill* button (). Select whether you want the created series to occupy *Rows* or *Columns* under the "Series in" heading. Under the heading "Type", select *Linear*, which is the most commonly encountered way to fill a data series. Finally, select the *Step* value and the *Stop* value and hit *Okay*. Excel will fill in the column or row starting at the value initially by adding the step value to it until the stop value is reached.

Error bars, which show the uncertainty in a given point, may be added to a graph in Excel, by first going to the *Layout* tab, *Analysis* category, and selecting *Error Bars*. There are three default options. For more options, click "More Error Bar Options…" You will then be able to select among various options for how the error bars appear (on both sides, one side, or none) and how large to make them. The *Fixed* value option is good when all of the data have approximately the same uncertainty, while *Percentage* assigns the uncertainty as a certain percent of the *y* values. This author has never found the *Standard deviation* option to give any useful depiction of the uncertainty, but it may be useful in certain situations. The *Standard error* assigns the uncertainty based on the standard error, which seems to be very similar to the fixed value option. The final option of having *Custom* error bars is very useful when each point has a different uncertainty. You can always simply enter whatever value you want in the boxes, but by pushing the  button you can specify a range of cells in your spreadsheet that contains your uncertainties. For example, if you have a set of volumes in cells B3 through B10 and their estimated uncertainties from a propagation of error analysis in cells C3 through C10, you would only need to enter the cell references for the uncertainties in the boxes, and each point has its own error bar.

References

1. Dodd, J. S., Ed. *The ACS Style Guide: a Manual for Authors and Editors*; the American Chemical Society: Washington, DC, 1986.

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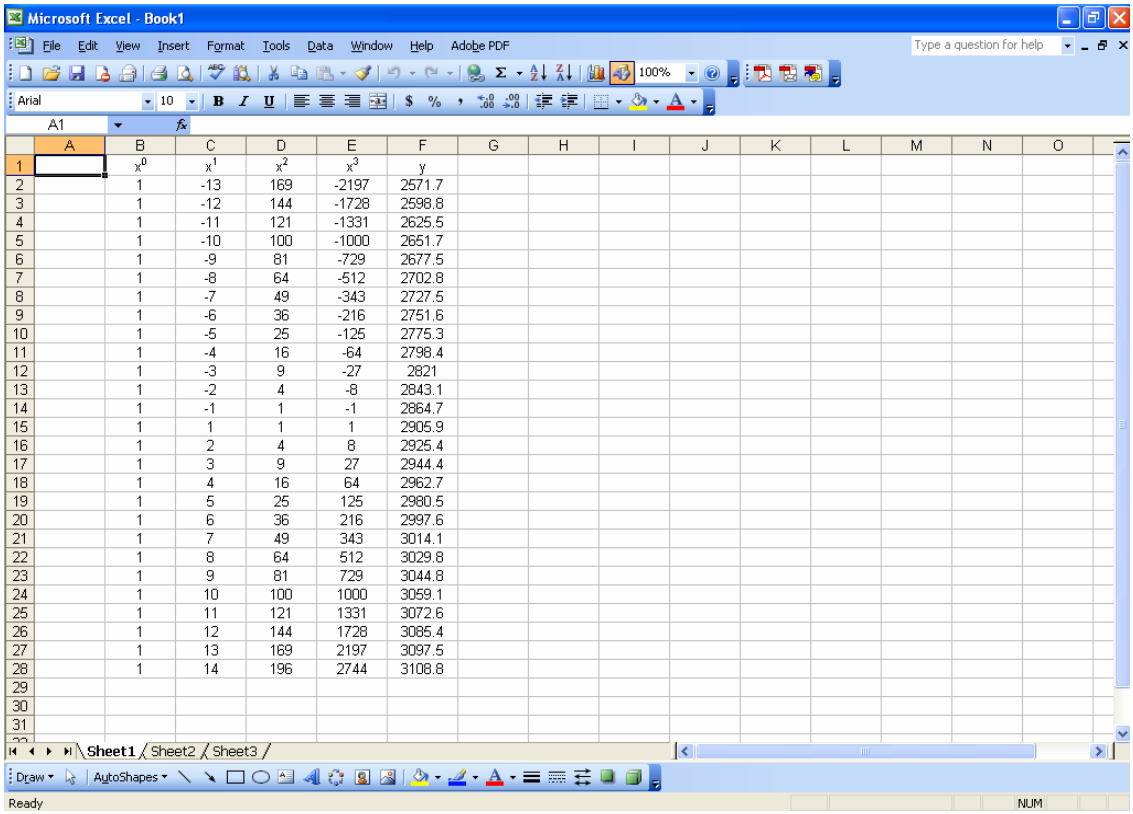
Advanced Regression with Microsoft Excel

J. M. McCormick

It is possible to have Excel perform a non-linear least square regression. One simple trick is to create columns each containing the variable of interest to the requisite power. For example, if we wanted to fit a set of data to a third order polynomial (i. e., $y = ax + bx^2 + cx^3 + d$, where a, b, c and d are constants that we need to find), then we would create columns containing the independent variable to the desired powers, as shown in Fig. 1. Note that in addition to x^1, x^2 and x^3 there must be a column containing x^0, which contains only ones. Once the spreadsheet is set up as shown below, select *Tools*, *Data Analysis* from the menu bar, and scroll down to *Regression*, select it and click OK.



	A	B	C	D	E	F
1		x^0	x^1	x^2	x^3	y
2		1	-13	169	-2197	2571.7
3		1	-12	144	-1728	2598.8
4		1	-11	121	-1331	2625.5
5		1	-10	100	-1000	2651.7
6		1	-9	81	-729	2677.5
7		1	-8	64	-512	2702.8
8		1	-7	49	-343	2727.5
9		1	-6	36	-216	2751.6
10		1	-5	25	-125	2775.3
11		1	-4	16	-64	2798.4
12		1	-3	9	-27	2821
13		1	-2	4	-8	2843.1
14		1	-1	1	-1	2864.7
15		1	1	1	1	2905.9
16		1	2	4	8	2925.4
17		1	3	9	27	2944.4
18		1	4	16	64	2962.7
19		1	5	25	125	2980.5
20		1	6	36	216	2997.6
21		1	7	49	343	3014.1
22		1	8	64	512	3029.8
23		1	9	81	729	3044.8
24		1	10	100	1000	3059.1
25		1	11	121	1331	3072.6
26		1	12	144	1728	3085.4
27		1	13	169	2197	3097.5
28		1	14	196	2744	3108.8
29						
30						
31						

Figure 1. Sample spreadsheet that is ready to be fit to the cubic expression $y = ax + bx^2 + cx^3 + d$ using Excel's regression package.

The regression pop up will appear (Fig. 2). In the *Input Y Range* box type in the cell addresses that contains your y values (or click and drag to select them from the worksheet). In Fig. 1 this would be the cells F2 to F28 (enter F2:F28 in the *Input Y Range* box). While entering the y values is no different than for a linear regression, inputting the x values is very different in that the *Input X Range* box must contain all of the columns containing a power of x. In Fig. 1 this would be columns B through E (cells B2 to E28). Once the x and y ranges are set, you can set any other parameters as desired, and click OK.

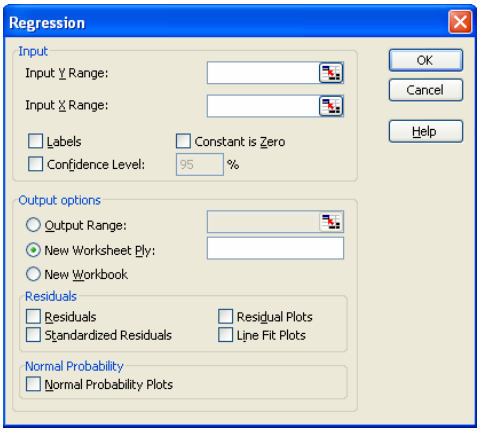


Figure 2. Excel's regression set-up window

If you have selected to have the results of the fit put in a new worksheet ply, then you will see something like what is shown in Fig. 3 (note that the columns in this spreadsheet have been modified to clearly show their contents). Each of the rows labeled *X Variable*, except *X Variable 1*, correspond to one of the constants in the polynomial. The row labeled *Intercept* will always be the constant in the polynomial that is not multiplied by x. In this case where the polynomial is $y = ax + bx^2 + cx^3 + d$, the *Intercept* is d, *X Variable 2* is a, *X Variable 3* is b and *X Variable 3* is c. *X Variable 1* will always be meaningless. The values under the *Standard Error* and *Upper* and *Lower 95%* for each variable have the same meaning as they do in a simple regression.

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	A	B	C	D	E	F	G	H	I	J	K
1	SUMMARY OUTPUT										
2											
3	*Regression Statistics*										
4	Multiple R	0.99999992									
5	R Square	0.99999984									
6	Adjusted R Square	0.956521558									
7	Standard Error	0.071913988									
8	Observations	27									
9											
10	ANOVA										
11		*df*	*SS*	*MS*	*F*	*Significance F*					
12	Regression	4	741557.0877	185389.2719	47796553.98	5.62092E-76					
13	Residual	23	0.118947299	0.005171622							
14	Total	27	741557.2067								
15											
16		*Coefficients*	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*		
17	Intercept	2885.475246	0.021356602	135109.2833	7.4211E-104	2885.431066	2885.519425	2885.431066	2885.519425		
18	X Variable 1	0	0	65535	#NUM!	0	0	0	0		
19	X Variable 2	20.57469078	0.004209556	4887.615914	1.06412E-70	20.56598265	20.58339891	20.56598265	20.58339891		
20	X Variable 3	-0.300961361	0.000244281	-1232.028513	6.19266E-57	-0.301466696	-0.300456027	-0.301466696	-0.300456027		
21	X Variable 4	-0.002082423	3.30678E-05	-62.97437398	2.93583E-27	-0.002150829	-0.002014017	-0.002150829	-0.002014017		
22											
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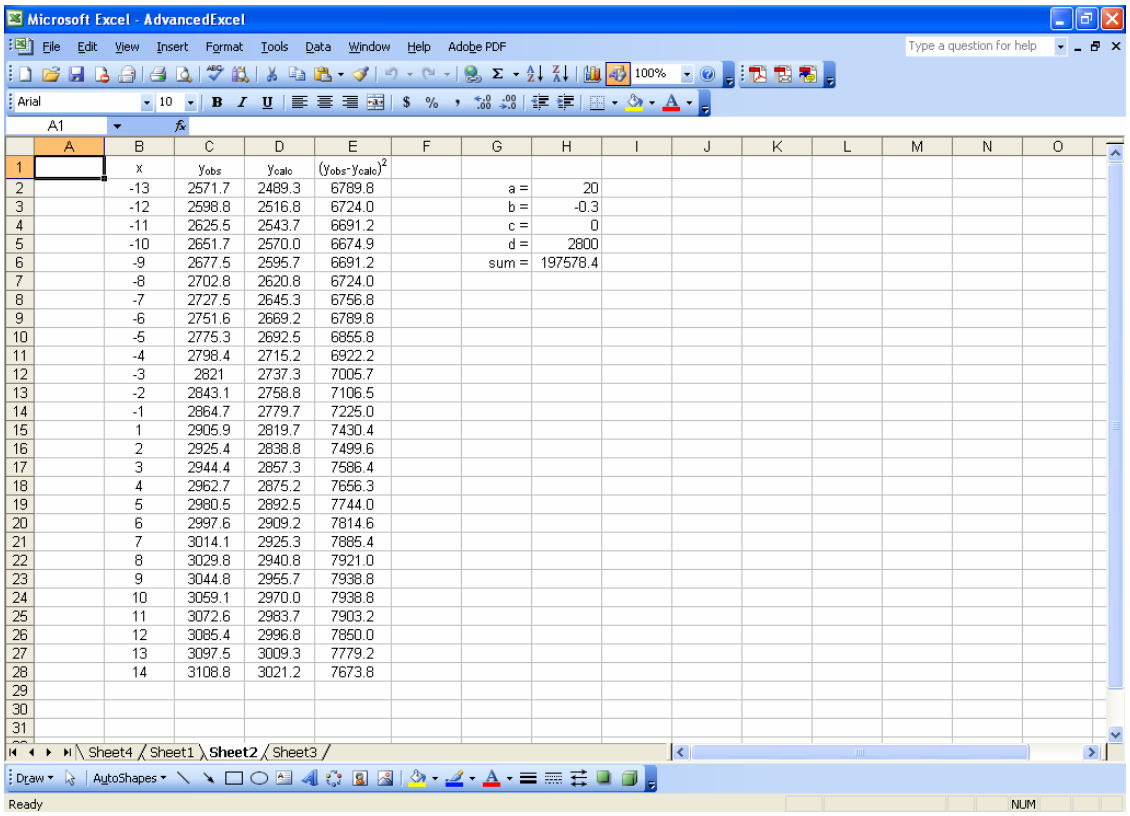
Sheet4 Sheet1 Sheet2 Sheet3

Ready NUM

Figure 3. Excel worksheet showing the results for the fit of the data in Fig. 1 to a cubic function.

Note that the values of R and R^2 are not going to be particularly useful in defining how well this expression fit the data, or in comparing this fit to a fit using another expression. For this one must use the standard error about the regression (listed as the *Standard Error* under the *Regression Statistics* heading). Also note that we could set up a column of calculated y values based on this fit (for example, in column G of the spreadsheet shown in Fig. 1) by entering the function in the appropriate column and using absolute references to the values in the output spreadsheet (Fig. 3).



	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
1		x	y_{obs}	y_{calc}	$(y_{obs}-y_{calc})^2$										
2		-13	2571.7	2489.3	6789.8		a =	20							
3		-12	2598.8	2516.8	6724.0		b =	-0.3							
4		-11	2625.5	2543.7	6691.2		c =	0							
5		-10	2651.7	2570.0	6674.9		d =	2800							
6		-9	2677.5	2595.7	6691.2		sum =	197578.4							
7		-8	2702.8	2620.8	6724.0										
8		-7	2727.5	2645.3	6756.8										
9		-6	2751.6	2669.2	6789.8										
10		-5	2775.3	2692.5	6855.8										
11		-4	2798.4	2715.2	6922.2										
12		-3	2821	2737.3	7005.7										
13		-2	2843.1	2758.8	7106.5										
14		-1	2864.7	2779.7	7225.0										
15		1	2905.9	2819.7	7430.4										
16		2	2925.4	2838.8	7499.6										
17		3	2944.4	2857.3	7586.4										
18		4	2962.7	2875.2	7656.3										
19		5	2980.5	2892.5	7744.0										
20		6	2997.6	2909.2	7814.6										
21		7	3014.1	2925.3	7885.4										
22		8	3029.8	2940.8	7921.0										
23		9	3044.8	2955.7	7938.8										
24		10	3059.1	2970.0	7938.8										
25		11	3072.6	2983.7	7903.2										
26		12	3085.4	2996.8	7850.0										
27		13	3097.5	3009.3	7779.2										
28		14	3108.8	3021.2	7673.8										
29															
30															
31															

Figure 4. Excel spreadsheet set up to fit a data set to any expression in the variable *x*using the *Solver* tool.

Another way to have Excel perform a non-linear least squares fit is to use the *Solver* tool. Before getting started, you will need to set up the spreadsheet, but in a different way than for the *Regression* package. Again let us assume that we want to fit a set of y values to a cubic expression in x (i. e., $y = ax + bx^2 + cx^3 + d$). We only need a single column for the x values, but we will need to have two columns for the y values (see Fig. 4). The first column of y values (column C in Fig. 4) will contain the y values that we actually measured. It is labeled y_{obs} (for observed values) to avoid confusion with the calculated y values (column D in Fig. 4), which we label y_{calc} (for calculated values). The y_{calc} are determined using the values of a, b, c and d. Thus, to find the values of y_{calc} we will have to have cells containing trial values of a, b, c and d (these trial values are sometimes referred to as seed values). These can be placed in any convenient place in the spreadsheet. In Fig. 4 they are in cells J2 through J5 (note that to minimize confusion the cells I2 through I5 contain labels for the adjacent cells). We could type in any number that we want as trial values, but to maximize the chance of quickly obtaining a successful fit, the trial

values should be reasonable guesses. The last column that we will need is one that contains the square of each y_{obs} minus the corresponding y_{calc} (hence the name least squares). In the current example, this is column E in Fig. 4. The final step is to create a cell containing the sum of the values in column E, which is cell H6 in Fig. 4.

Once the spreadsheet is ready, select *Tools*, *Solver* from the menu bar. The *Solver* window will pop up (Fig. 5). Under *Set Target Cell*, enter the cell containing the value of $S(y_{obs} - y_{calc})^2$, which in our example is cell H6. Select the *Min* (minimum) radio button under the *Equal To* heading (note that if you select *Value Of* and enter zero, you may not get a reasonable answer). In the *By Changing Cells* box, enter the cell(s) containing the trial values that you want to change. Since we want to fit the data by adjusting all of the values in cells H2 to H5, we would enter H2:H5 in this box (or by highlighting all of the cells in the spreadsheet). Note that you can choose to vary all or only some of the trial values by which cells you select at this point. Sometimes it is useful to vary only a subset of all the parameters, while holding others constant, but this is highly dependent on the situation. You may also apply additional constraints to the fit in the *Subject to Constraints* box by clicking the *Add* button. For example, to constrain the value in cell H2 to be positive, one would click *Add* and then in the new pop-up enter H2 in the *Cell Reference* box, select the "> =" in the middle pull-down box, and then enter "0" in the *Constraint* box.

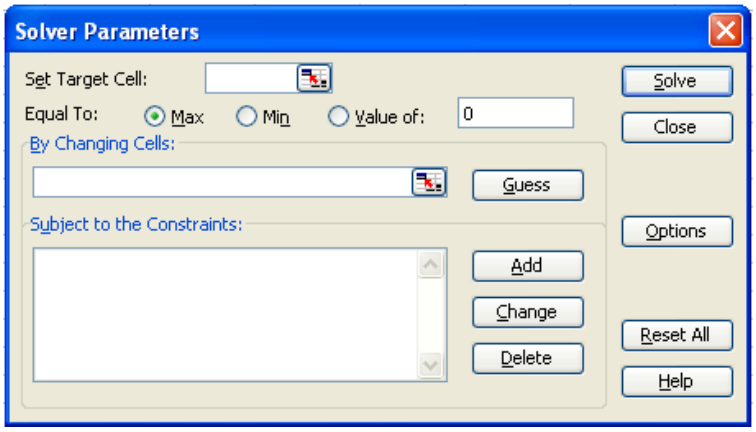


Figure 5. Solver set-up window

Once everything is set, click *Solve*. *Solver* will then attempt change the cells that you told it to change, subject to any constraints that you specified, to minimize the difference between the observed and calculated *y* values. If it is successful it will display a window stating that it found a solution and asking whether you want to keep it (note that the best fit values of your variables and the function that you were minimizing will be displayed in the spreadsheet behind the pop-up). If you want to keep the fit, click *OK*, if not click *CANCEL*. If a satisfactory fit was not found, a similar message will be displayed and you can either keep or discard the result.

Sometimes you will need to restart the *Solver* tool (that is reinitiate the procedure with the values from a previous fit) before a satisfactory fit is obtained. In any case, it is good practice to perform the fit with different values of the initial parameters to be sure that the procedure converges to a unique solution. It may also be necessary to adjust the fitting procedure itself

(done by clicking the *Options* button in the main *Solver* window) to get a good result. However, if this occurs it may be advisable to find a more robust fitting algorithm or to find a simpler model.

Unlike the *Regression* package, *Solver* does not give uncertainties in the fit parameters. However, there is a way to estimate the uncertainties,[1] but it is somewhat time consuming.

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Propagation of Uncertainty

J. M. McCormick

Introduction

Every measurement that we make in the laboratory has some degree of uncertainty associated with it simply because no measuring device is perfect. If a desired quantity can be found directly from a single measurement, then the uncertainty in the quantity is completely determined by the precision of the measurement. It is not so simple, however, when a quantity must be calculated from two or more measurements, each with their own uncertainty. In this case the precision of the final result depends on the uncertainties in each of the measurements that went into calculating it. In other words, uncertainty is always present and a measurement's uncertainty is always carried through all calculations that use it.

Fundamental Equations

One might think that all we need to do is perform the calculation at the extreme of each variable's confidence interval, and the result reflecting the uncertainty in the calculated quantity. Although this works in some instances, it usually fails, because we need to account for the distribution of possible values in all of the measured variables and how that affects the distribution of values in the calculated quantity. Although this seems like a daunting task, the problem is solvable, and it has been solved, but the proof will not be given here. The result is a general equation for the propagation of uncertainty that is given as Eqn. 1.[1] In Eqn. 1 f is a function in several variables, x_i, each with their own uncertainty, Δx_i.

$$\Delta f = \pm \sqrt{\sum_{i=1}^{n} \left(\frac{\partial f}{\partial x_i}\right)^2 (\Delta x_i)^2} \qquad (1)$$

From Eqn. 1, it is possible to calculate the uncertainty in the function, Δf, if we know the uncertainties in each variable and the functional form of f (so we can calculate the partial derivatives with respect to each variable). It is easier to understand how this all works by doing several examples.

Example 1: $f = x + y$ (the result is the same for $f = x - y$).

Let the uncertainty in x and y be Δx and Δy, respectively. Taking the partial derivatives with respect to each variable gives: $\frac{\partial f}{\partial x} = 1$ and $\frac{\partial f}{\partial y} = 1$. The uncertainty in f is then

$$\Delta f = \pm\sqrt{(1)^2(\Delta x)^2 + (1)^2(\Delta y)^2} = \pm\sqrt{(\Delta x)^2 + (\Delta y)^2} \qquad (2)$$

Example 2: $f = x \cdot y$ (also works for $f = x/y$)

Again let the uncertainty in x and y again be Δx and Δy, respectively. Taking the partial derivatives with respect to each variable gives: $\frac{\partial f}{\partial x} = y$ and $\frac{\partial f}{\partial y} = x$. The uncertainty in f is then $\Delta f = \pm\sqrt{(y)^2(\Delta x)^2 + (x)^2(\Delta y)^2}$.
This result is more commonly written by dividing both sides by $f = x \cdot y$ to give

$$\frac{\Delta f}{f} = \pm\sqrt{\left(\frac{\Delta x}{x}\right)^2 + \left(\frac{\Delta y}{y}\right)^2} \qquad (3)$$

Although the idea of error propagation may seem intimidating, you have already been using it since your first chemistry class when you applied the rules for significant figures in calculations. These rules are simplified versions of Eqn. 2 and Eqn. 3, assuming that Δx and Δy are both 1 in the last decimal place quoted. The formal mathematical proof of this is well beyond this short introduction, but two examples may convince you.

If we add 15.11 and 0.021, the answer is 15.13 according to the rules of significant figures. This assumed that $\Delta x = 0.01$ ($x = 15.11$) and $\Delta y = 0.001$ ($y = 0.021$), substituting these values into Eqn. 2, we get $\Delta f = \pm\sqrt{(0.01)^2 + (0.001)^2} = \pm 0.010050$. Remembering our basic statistics (see *Introduction to Statistics in Chemistry*), we know that the uncertainty begins in the first non-zero decimal place, which in this case this means that the last significant figure in the sum is the 1/100$^{\text{ths}}$ place. According to the rules for propagation of error the result of our calculation is 15.13 ± 0.01, exactly what the significant figure rules gave us.

If we had multiplied the numbers together, instead of adding them, our result would have been 0.32 according to the rules of significant figures. Again assuming $\Delta x = 0.01$ and $\Delta y = 0.001$, and using Eqn. 3, we can determine Δf as follows.

$$\Delta f = \pm f\sqrt{\left(\frac{\Delta x}{x}\right)^2 + \left(\frac{\Delta y}{y}\right)^2} = \pm(0.31731)\sqrt{\left(\frac{0.01}{15.11}\right)^2 + \left(\frac{0.001}{0.021}\right)^2} = \pm 0.015111$$

Once again we see that the uncertainty begins in the second decimal place, which gives the same result as the significant figures result gave.

The significant figure rules are important to know and use in all chemistry calculations, but they are limited in that they assume an uncertainty in the measured quantities. So while the significant figure rules are always to be used in any calculation, when precision matters a propagation of error analysis must also be performed to obtain an accurate prediction of the uncertainty arising from the precision of the measured quantities.

Worked Examples

Problem 1

In CHEM 130, you have measured the dimensions of a copper block (assumed to be a regular rectangular box) and calculated the box's volume from the dimensions. In that exercise you were given an equation that allowed you to calculate the minimum uncertainty that could be expected in the box's volume based solely on the uncertainties in the measured dimensions, now derive that equation using the procedure given above.

Solution

Let x, y and z be the box's length, width and height, respectively, and the uncertainties be Δx, Δy, Δz. Since $V = x \cdot y \cdot z$, we can use Eqn. 1 to determine the uncertainty in the volume (ΔV), which results in Eqn. 4. We know that $\frac{\partial V}{\partial x} = yz$, $\frac{\partial f}{\partial y} = xz$ and $\frac{\partial f}{\partial z} = xy$, and can then make these substitutions in Eqn. 4 to give Eqn. 5.

$$\Delta V = \pm\sqrt{\left(\frac{\partial V}{\partial x}\right)^2 (\Delta x)^2 + \left(\frac{\partial V}{\partial y}\right)^2 (\Delta y)^2 + \left(\frac{\partial V}{\partial z}\right)^2 (\Delta z)^2} \tag{4}$$

$$\Delta V = \pm\sqrt{(yz)^2(\Delta x)^2 + (xz)^2(\Delta y)^2 + (xy)^2(\Delta z)^2} \tag{5}$$

Dividing both sides by V gives Eqn. 6 and simplifying gives Eqn. 7 (which you probably could have guessed from the form of Eqn. 1 and Eqn. 3). Multiplying both sides by V then gives the equation used in the CHEM 130 *Determination of Density* exercise.

$$\frac{\Delta V}{V} = \pm\sqrt{\frac{(yz)^2(\Delta x)^2 + (xz)^2(\Delta y)^2 + (xy)^2(\Delta z)^2}{(xyz)^2}} \tag{6}$$

$$\frac{\Delta V}{V} = \pm\sqrt{\left(\frac{\Delta x}{x}\right)^2 + \left(\frac{\Delta y}{y}\right)^2 + \left(\frac{\Delta z}{z}\right)^2} \tag{7}$$

Note that there are several implications of Eqn. 7. First, if one side has a large uncertainty relative to the length of that side (such as when one side is very short), then this side will dominate the uncertainty. Second, when the volume is large and the uncertainty in measuring a dimension is small compared to the uncertainty in the measurement, then the uncertainty in the volume will be small. The experimental implication of this is that, if you want the smallest uncertainty in a box's volume, make sure it is a big box, with no unusually short side and use the most precise measurement tool possible.

Problem 2

You have measured the volume and mass of a set of regular wooden blocks and have fit a graph of their volume as a function of their mass to a straight line using the regression package in Excel. What is the predicted uncertainty in the density of the wood (Δd) given the uncertainty in

the slope, s, of the best fit line is Δs and the uncertainty in the intercept is Δb? Note that you have also seen this equation before in the *CHEM 130 Determination of Density* exercise, but now you can derive it.

Solution

The relationship between volume and mass is $V = \frac{1}{d}m$. This is a linear equation ($y = s{\cdot}x + b$) where $= \frac{1}{s}$. Note that b does not affect the value of d and so Δb has no effect on Δd. The relationship between Δs and Δd can be calculated by simply substituting d in place of f and s in place of x in Eqn. 3 to give $\Delta d = \pm d\sqrt{\left(\frac{\Delta s}{s}\right)^2} = \pm d\left(\frac{\Delta s}{s}\right)$.

We could have also have used Eqn. 1. First we need to find the first derivative of the density with respect to the slope, which is $\left(\frac{\partial d}{\partial s}\right) = -\frac{1}{s^2}$. Substituting this into Eqn. 1 gives $\Delta d = \pm\sqrt{\left(-\frac{1}{s^2}\right)^2 (\Delta s)^2}$, which rearranges to $\Delta d = \pm\sqrt{\left(\frac{\Delta s}{s}\right)^2 \left(\frac{1}{s^2}\right)}$. Recognizing the relationship between s and d, this simplifies to $\Delta d = \pm d\left(\frac{\Delta s}{s}\right)$.

This problem is the simplest example of how one determines the uncertainty in a quantity extracted from a best-fit line. In general you will have the uncertainty in the slope and intercept and the relationship between each of these to the desired quantities. It is then a simple process to apply Eqn. 1, where f is either the slope or intercept.

Propagation of Uncertainty through a Calibration Curve

A situation that is often encountered in chemistry is the use of a calibration curve to determine a value of some quantity from another, measured quantity, for example, in the *Preparation and Analysis of Alum* exercise in CHEM 130 you used a calibration curve in the determination of the percent by mass of aluminum in alum. In that exercise, we did not propagate the uncertainty associated with the absorbance measurement through the calibration curve to the percent by mass. However, in most quantitative measurements, it is necessary to propagate the uncertainty in a measured value through a calibration curve to the final value being sought. The general procedure is quite straight-forward, and is covered in detail in CHEM 222. Therefore, only a very basic review of the fundamental equations and how to implement them in Excel will be presented here. You are referred to any analytical chemistry textbook for more details.[2]

For a linear least squares analysis we need to define several parameters. We will assume that the equation of a straight line takes the form $y = mx + b$ (where m is the slope and b the intercept) and that the x values are known precisely. Let there be N individual data points (so there are N ordered pairs x_i, y_i) in the calibration curve. Further, let y_{meas} be the average response of our unknown sample based on M replicate measurements, and let S_{meas} be the standard deviation of the result from the calibration curve. Note that S_{meas} is the standard deviation associated with the x value (x_{meas}) corresponding to y_{meas}, and should not be confused with S_r, the standard deviation about the regression. We can then draw up the following table to summarize the equations that we need to calculate the parameters that we are most interested in (x_{meas} and S_{meas}).

Table 1. Relationships between standard equations encountered in a linear least squares analysis and the Excel regression package output and Excel commands. Note that *arg* in the Excel command refers to a range of cells over which the command is to be calculated (e. g., E5:E10).

Equation	Location on Regression Output Worksheet	Excel Command
$S_{xx} = \sum (x_i - x_{avg})$	----------	DEVSQ(*arg*)
$S_{yy} = \sum (y_i - y_{avg})$	Under the *ANOVA* heading it is the entry in the row labeled *Total* in the *SS* column.	DEVSQ(*arg*)
$S_{xy} = \sum (x_i - x_{avg})(y_i - y_{avg})$	----------	----------
$x_{avg} = \frac{\sum x_i}{N}$	----------	AVERAGE(*arg*)
$y_{avg} = \frac{\sum y_i}{N}$	----------	AVERAGE(*arg*)
$m = \frac{S_{xy}}{S_{xx}}$	Coefficient listed under *X Variable 1*.	SLOPE(known *y*'s, known *x*'s)
$b = y_{avg} - m x_{avg}$	Coefficient listed under *Intercept*.	INTERCEPT(known *y*'s, known *x*'s)
$S_r = \sqrt{\frac{S_{yy} - m^2 S_{xx}}{N-2}}$	*Standard Error* under the *Regression Statistics* heading.	STEYX(known *y*'s, known *x*'s)
$x_{meas} = \frac{y_{meas} - b}{m}$	----------	----------
$S_{meas} = \left(\frac{S_r}{m}\right)\sqrt{\frac{1}{M} + \frac{1}{N} + \frac{(y_{meas} - y_{avg})^2}{m^2}}$	----------	See below.

Although one could enter formulas in various cells to calculate all of the intermediate parameters needed to determine S_{meas}, it is not necessary. One only needs to have a cell in which to enter the number of replicate measurements on the unknown (*M*) and then it is possible to calculate S_{meas} using only the STEYX, SLOPE, INTERCEPT, COUNT, DEVSQ and SQRT Excel functions. For example, in the spreadsheet shown in Fig. 1, cell D16 contains the formula

"=(STEYX(D3:D13,C3:C13)/SLOPE(D3:D13,C3:C13))*SQRT((1/D15)+(1/COUNT(D3:D13))
+((D18-AVERAGE(D2:D13))^2/(SLOPE(D3:D13,C3:C13)^2*DEVSQ(C2:C13))))"

which calculates S_{meas} directly from the potential as a function of temperature data. Adding a cell that will contain y_{meas} (cell D17 in Fig. 1), allows calculation of x_{meas} value (cell D18) and its

uncertainty at 95% confidence (cell D19). To review how this is done using S_{meas} and Student's *t*, please see the *Introduction to Statistics in Chemistry* section). Note that instead of using *N* in the calculation of the uncertainty from S_{meas}, one must use $N - 2$ because two degrees of freedom have been used to find the slope and the intercept.

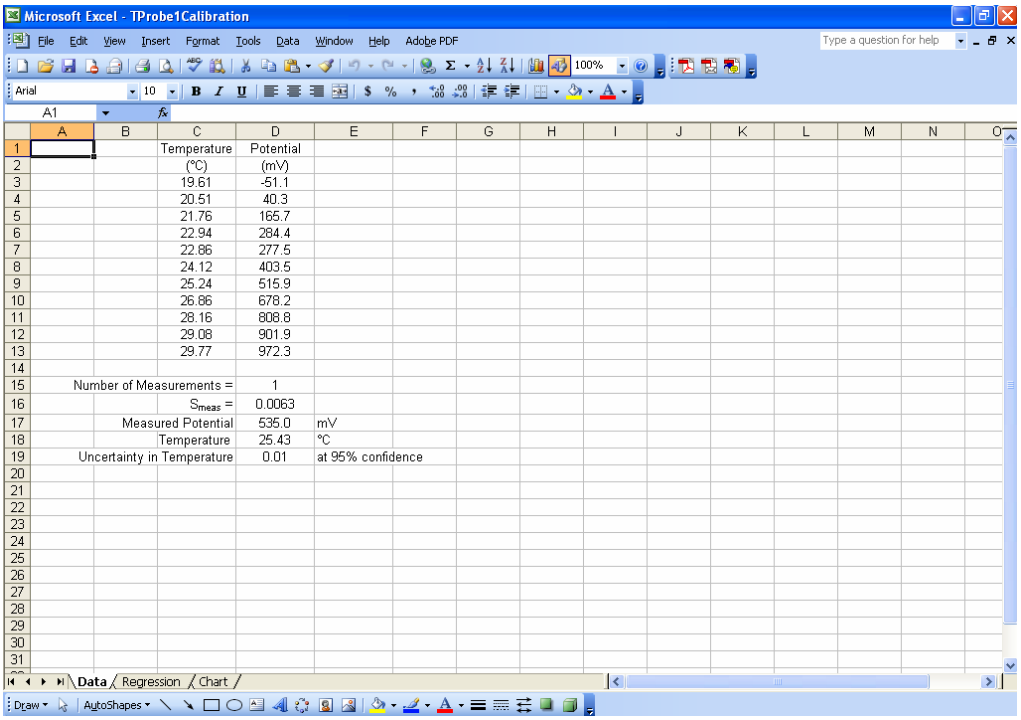

Figure 1. An example of an Excel spreadsheet that may be used to calculate an *x* value (temperature, in this case) from a measured *y* value (potential) along with the uncertainty in the measured *x* value at 95% confidence.

Propagation of Uncertainty of Two Lines to their Intersection

Sometimes it is necessary to determine the uncertainty in the intersection of two lines. This problem is not trivial and the reader is referred to the literature for more details.[3]

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