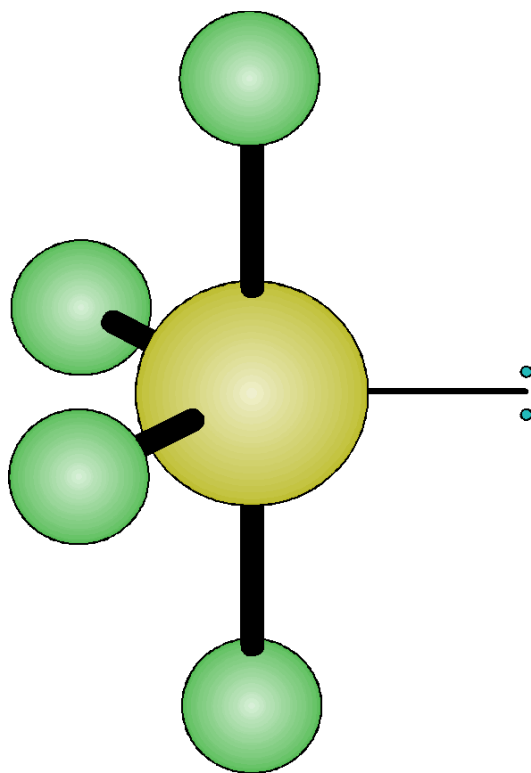


Grossmont College

Chemistry 141

Laboratory Manual



6th Edition

Grossmont College

Periodic Table of the Elements

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	1A	2A											3A	4A	5A	6A	7A	8A
1	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
3	11 Na 22.990	12 Mg 24.305	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.066	17 Cl 35.453	18 Ar 39.948
4	19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.880	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.410	31 Ga 69.723	32 Ge 72.640	33 As 74.922	34 Se 78.960	35 Br 79.904	36 Kr 83.800
5	37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.95	43 Tc (98)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.868	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 I 126.905	54 Xe 131.29
6	55 Cs 132.905	56 Ba 137.327	57 La 138.906	72 Hf 178.49	73 Ta 180.948	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.967	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.980	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (269)	109 Mt (268)	110 Ds (281)	111 Rg (272)	112 Cn (285)	113 Uut (284)	114 Fl (289)	115 Uup (288)	116 Lv (293)	117 Uus (294)	118 Uuo (294)

6	58 Ce 140.115	59 Pr 140.908	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.965	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.967
7	90 Th 232.038	91 Pa 231.036	92 U 238.029	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

Chemistry 141 Laboratory Manual

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Prepared for printing on December 12, 2012

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Measuring Density with Different Types of Glassware

Objective

In Part A of this experiment, you will measure the volume that is delivered from three pieces of laboratory glassware: a beaker, a graduated cylinder, and a volumetric pipet. In Part B, you will use the appropriate glassware to measure the density of Coke and Diet Coke. The goal is to determine the accuracy and precision for each type of glassware. The accuracy and precision for a device is determined by a method of calibration. Calibration means that the user understands the limitations inherent in a particular piece of equipment and gives a good estimate of the actual values that can be relied upon when using that equipment for measuring.

Introduction

Chemistry is an experimental science and therefore chemistry will always involve the taking of measurements. These measurements may be multiple measurements of the same object, measurements of a single object by multiple observers, or one observer's measurements of many different objects. What is the interpretation of each set of measurements? Are the measurements giving the correct answer (i.e. are they accurate)? Are they consistent (i.e. precise)? One thing scientist must keep in mind is that no matter how much care is taken when measuring; uncertainty in measurement is always present.

The rules that apply to significant figures are basically an elementary form of error analysis. For the most part, following the rules that govern significant figures are sufficient when there is a single measurement, or at most a duplicate trial. However, there may be times when we have the opportunity to carry out more exacting experiments where uncertainties in measurements can be estimated quite accurately.

Errors in Observational Data

There exists a degree of uncertainty with nearly every type of measurement. A balance that measures to the nearest gram will obviously introduce some uncertainty in the mass of objects that

weigh approximately 1.5 grams. If you try to measure the length of a board and the end of the board falls between two of the marks on your measuring tape; you would have to estimate the last fractional length. The only measurement that can be determined with certainty is counting a small set of objects, for example, the number of students in your class. However, counting large sets of objects is not an exact measurement. To determine the population of the US for example, actually counting every person is impractical and difficult to the point that estimates must be made to complete the task.

When we say that a measurement is uncertain, we mean that the measurement includes error. An **error** is the difference between a measured value and the true value. Errors are typically expressed as the uncertainty in the measurement using statistical quantities. There are two types of errors, systematic errors and random errors.

Random errors are the uncertainties associated with a measuring device; for example, an object measured for length may fall between the smallest divisions on a ruler and its value would have to be estimated. The reality is, no matter how carefully measurements are taken there is always a certain amount of “scatter” in the data. This scatter is due to the inability of an instrument or an observer of that instrument to discriminate between readings differing by less than some small amount. Random errors do not follow any regular pattern. Since random errors occur in an unpredictable manner, it is impossible to eliminate them. Fortunately, random errors can be dealt with statistically. Sometimes mistakes are made during a procedure (e.g. spilling part of a solution, dropping a piece of equipment, overfilling or underfilling a graduated cylinder, or when performing a titration you titrate each sample to a slightly different endpoint, etc.). These will all be good data points, but they will differ slightly due to random or indeterminate errors. If you average the data points, this random error is represented by the deviation of each individual measurements from the mean. These are not errors; they are *mistakes* and cannot be dealt with in any fashion, except perhaps as a learning exercise. Random errors are impossible to eliminate, but because they randomly fluctuate around the measurement the average value should reflect a good value for the measurement in the absence of systematic error.

Systematic errors (sometimes referred to as determinate error) are errors of a definite size and sign that can often be traced to specific sources introduced during the lab. Generally, such errors can be avoided or corrected. For example, this type of error may be caused by improper calibration of an instrument, uncompensated instrumental drift, leakage of material (e.g. gas in a pressure system), incomplete fulfillment of assumed conditions for a measurement (e.g. incomplete reaction in a calorimeter or incomplete drying of a weighed precipitate), personal errors in reading an instrument or a measuring device (e.g. parallax error) or, biased methods implemented during the procedure (e.g. uncompensated human reaction times). Systematic errors often announce their presence in some sort of pattern. Systematic errors must be eliminated (corrected) since there is no statistical method to handle these errors, while random errors can produce a result which is either too high or too low. When systematic errors are made, accuracy rarely matches precision. Therefore, it is important to calibrate, read instruments, etc. correctly.

Gross errors are results in a value which is far different than either the true or the mean. They may be caused by sample inconsistencies or experimental error (i.e. reading measuring instruments wrong on one trial).

Accuracy and Precision

When experimental values are discussed it is important to know the information about the quality of the data. What exactly is meant by quality? How can the size of the random and systematic

errors be determined? To answer these questions, the terms accuracy and precision need to be defined.

Accuracy is a measure of the difference between the true value and measured value. The real, true value is not always known. Absolute error is the approximate error of a single measurement:

$$\text{absolute error} = \Delta = |\text{true value} - \text{observed value}| \quad (\text{EQ 1.1})$$

Accuracy is frequently described as a percent difference or percent error between the measured value and the actual value:

$$\% \text{ error} = \frac{\text{observed value} - \text{true value}}{\text{true value}} \times 100 \% \quad (\text{EQ 1.2})$$

The difficulty with determining the error for a measured (or calculated) value is that it is often difficult or impossible to determine the true value. For measurements taken in the undergraduate laboratory, we frequently compare our results with generally accepted results published in the literature as our known or true value. In such cases the percent error is calculated.

Precision is a measure of the reproducibility of a measurement. It is a measure of the amount of random error. If we were to take many measurements, how close would they be to each other?

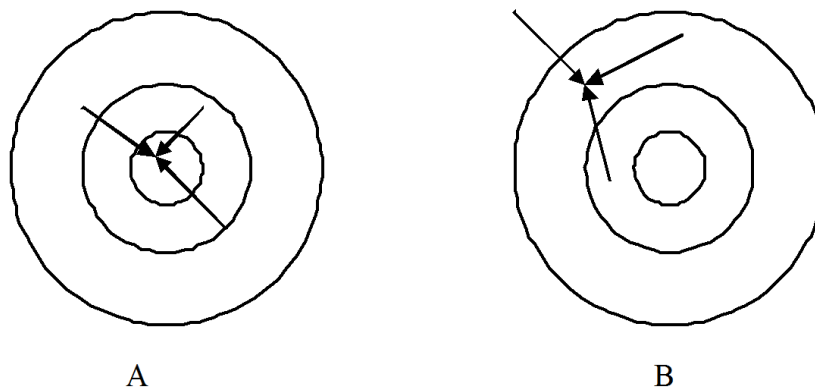
$$\text{deviation} = d = |\text{average value} - \text{observed value}| \quad (\text{EQ 1.3})$$

Precision is frequently described by the percent deviation:

$$\% \text{ deviation} = \frac{\text{observed value} - \text{average value}}{\text{average value}} \times 100 \% \quad (\text{EQ 1.4})$$

Unfortunately, precision cannot give much information regarding the accuracy of a measurement. A common illustration for these terms is a “bull’s-eye” target. Good accuracy means several arrows close to or in the middle of the target. Good precision means all the arrows are clustered in the same region of the target. Good precision does not guarantee good accuracy; all of the arrows can be grouped close together yet far from the center of the target. However, good precision often lends confidence to the experimentalist since it would appear that all measurements are consistently good in the absence of any obvious systematic errors.

FIGURE 1.1



Although, both sets of arrows represent a set of precisely thrown arrows, only picture A would be considered accurate and precise, while picture B would be considered precise, but not accurate.

How can the best possible results be obtained during an experiment?

- Perform experiments as precisely as possible to minimize random error.
- Analyze each of the measurements to identify possible sources of systematic error and minimize them.
- Determine the result using several entirely independent methods of measurements and compare. If these independent methods give the same final results it is a good indication of accuracy.

Treatment of Errors

Since a series of measurements will produce random errors, some positive and some negative values, the true value is best estimated by finding the **mean** value (\bar{x}). The mean is often called the average value and is found by summing all the values and dividing by the number of measurements:

$$\bar{x} = \frac{\sum M_n}{n} \quad (\text{EQ 1.5})$$

where M is the individual value and n is the total number of measurements

Closely related is the **median** value which is the value that has an equal number of measurements above and below the mean. Consider this set of percent chlorine data in a sodium chloride sample. The balance is good to four significant figures and five observations were taken:

TABLE 1.1

Trial #	Observed Value for Percent Chlorine
1	60.50
2	60.41
3	60.53
4	60.54
5	60.52
Mean	60.50
Median	60.52

Some questions may come to mind: Why wasn't the same value obtained for each trial? What value should have been obtained for the percent chlorine? One way to analyze the distribution of values is to report the spread or range which is defined as the difference between the highest and lowest values.

$$\text{range} = 60.54 - 60.41 = 0.13 \quad (\text{EQ 1.6})$$

The range is not particularly useful since it does not indicate anything about the distribution of data points about the mean value. The mean or average value is:

$$\bar{x} = \frac{60.50 + 60.41 + 60.53 + 60.54 + 60.52}{5} = \frac{302.50}{5} = 60.500 \quad (\text{EQ 1.7})$$

The median is found to be 60.52%. The true value for the percent chlorine in sodium chloride can be calculated:

$$\%Cl = \frac{35.45 \frac{g}{mol}}{35.45 \frac{g}{mol} + 22.99 \frac{g}{mol}} \times 100 \% = 60.66\%Cl \quad (\text{EQ 1.8})$$

Therefore, the true or calculated value is 60.66%. Then the absolute error for each measurement can be determined for each trial as shown for trial 1:

$$\text{Absolute error} = |60.66\% - 60.500\%| = 0.16\% \text{ for trial 1} \quad (\text{EQ 1.9})$$

The deviation for each measurement from the average can also be determined:

$$\text{Deviation} = |60.500\% - 60.50\%| = 0.00\% \text{ for trial 1} \quad (\text{EQ 1.10})$$

Tabulating these results:

TABLE 1.2

Trial #	Observed Value for Percent Chlorine	Absolute Error	Deviation
1	60.50	0.16	0.00
2	60.41	0.25	0.09
3	60.53	0.13	0.03
4	60.54	0.12	0.04
5	60.52	0.14	0.02
Average	60.50	0.16	0.04

Using the same data set, the deviation and absolute deviation can be tabulated for each value as shown in Table 1.1 on page 4. Notice that except for rounding errors, the mean deviation is nearly zero as one would expect if the errors in measurement were randomly distributed above and below the mean. The only significant information in this example is the average of the absolute deviation or simply the **average deviation**, \bar{d} .

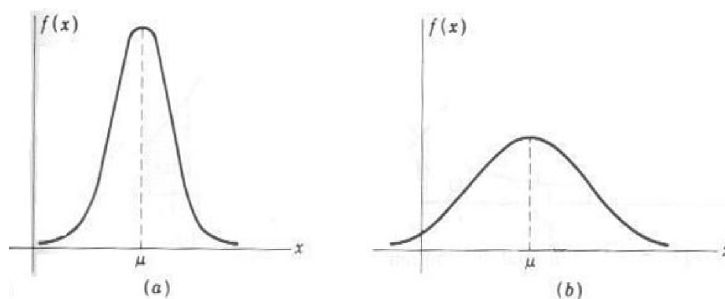
$$\bar{d} = \frac{\sum M_n - \bar{x}}{n} = \frac{0.00 + 0.09 + 0.03 + 0.04 + 0.02}{5} = 0.04 \text{ as seen in Table 1.2.} \quad (\text{EQ 1.11})$$

Notice that in this data the average deviation, a measure of the precision, is less than the average error. This indicates that there is some systematic error in the experiment resulting in inaccurate data. This example demonstrates how a student might be misled into believing their data was accurate based on good precision. Unfortunately, systematic error can not be described using any clean mathematical theories; So it is often ignored although, it is frequently found to be orders of magnitude larger than the random errors. In fact, many published papers have later been shown to be incorrect by amounts far greater than the claimed limits of error.

Given the fact that it is very difficult to identify and quantify all sources of systematic error statistical methods of analyzing random error are used as an indication of the error found in experimental data.

Although random errors cannot be corrected for, they can be treated statistically in an attempt to establish the reliability of the measurement. The analysis is based on the "normal" error curve.

FIGURE 1.2



The curve shows the relative frequency of deviation that can be expected to be found if a large number of measurements are made. The curve allows determinations about the magnitude of indeterminate errors to be made. Some of the main points of these curves are:

- The curves are symmetric about the midpoint, which is the arithmetic mean. Therefore, positive and negative deviations are equally likely.
- The curves rise to a maximum at the midpoint, indicating that small deviations occur more often than large deviations. In fact, if a large deviation is observed a systematic error is most likely involved.
- The shape of the curve is dependent on the inherent precision of the measurements. Sloppy or crude instrumentation give a high frequency of large deviations, as in curve (b). Refined measurements with improved precision show large deviations to be improbable, as in curve (a).

For reasons that will not be discussed here, the standard deviation is preferred over average deviation because it can be interpreted statistically. **Standard deviation** is the measure of the size of the random error in a set of data. The standard deviation gives information about the shape of the error curve that is associated with a set of experimental measurements. In order to measure the exact, theoretical value of the standard deviation of a measurement, the measurement must be taken many times. Therefore, the equation of standard deviation is technically only an approximation of the true standard deviation of a particular measurement. This estimation of the standard deviation, σ , is given as:

$$\sigma = \sqrt{\frac{\sum d^2}{n-1}} = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}} \quad (\text{EQ 1.12})$$

Returning to our example the standard deviation of the percent chlorine data can be determined. First the deviation squared is calculated as shown in Table 1.3 on page 6.

TABLE 1.3

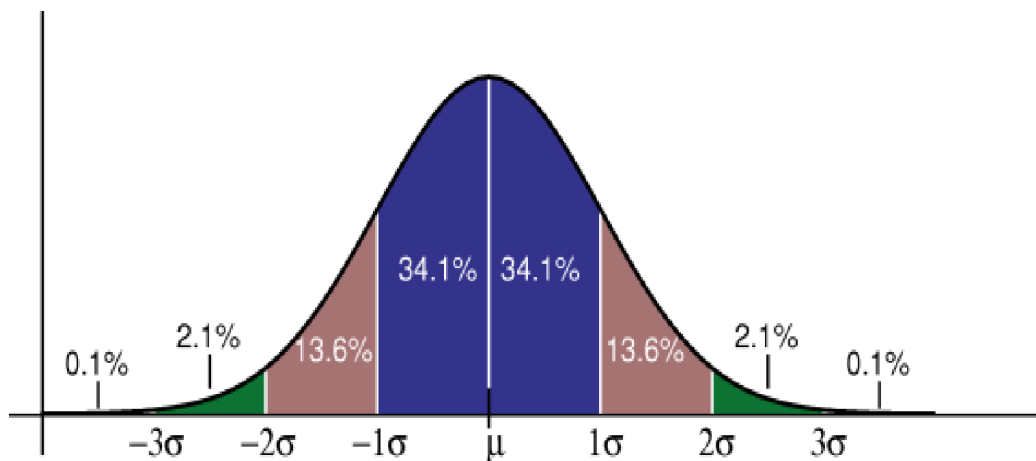
Trial #	Observed Value for Percent Chlorine	Deviation, d	d ²
1	60.50	0.00	0.00
2	60.41	0.09	0.0081
3	60.53	0.03	0.0009
4	60.54	0.04	0.0016
5	60.52	0.02	0.0004
Sum			0.011

The standard deviation is calculated to be:

$$\sigma = \sqrt{\frac{0.011}{5-1}} = 0.052 \quad (\text{EQ 1.13})$$

The standard deviation tells a lot about the error curve. A small value for sigma corresponds to a sharp, steeply rising curve, where deviations are close to zero. On the flip side, a broad, squat curve indicates that large deviations are highly probable.

FIGURE 1.3



The shaded area bound by $-\sigma$ and σ is proportional to the probability of an observation with a deviation within one unit of σ of the arithmetic mean (located at the midpoint of the curve). This shaded area represents about two-thirds of the total area, or more exactly 68.4% of the total area under the curve. This means that if a large number of measurements are made about two-thirds should fall within $\bar{x} - \sigma$ to $\bar{x} + \sigma$ or $\bar{x} \pm \sigma$ (i.e. the average plus or minus the standard deviation). So, about one-third of the trials should fall outside of these boundaries and hence, would show a larger deviation or be classified as “good”. Actually, $\pm 2\sigma$ covers most of the area under the curve or about 95%. This means that 95% of the trials fall within $\pm 2\sigma$ from the arithmetic mean, $\bar{x} - 2\sigma$ to $\bar{x} + 2\sigma$ or $\bar{x} \pm 2\sigma$. Therefore, these values would be classified as “fair.” This leaves about 5% of the measurements out of this range. In other words, about one-twentieth of the measurements will have a deviation of greater than $\pm 2\sigma$. Those falling within 3σ are classified as “poor.” Keep in mind the probability of where a measurement falls is valid when dealing with a large number of observations.

Looking at the percent chlorine data, the mean value is within a range of $60.500 \pm 0.052\%$. So, four out of five (80%) measurements are within one standard deviation 60.448% to 60.552% and all of the measurements are within two standard deviations 60.396% to 60.604% . Therefore, the measurements in this experiment have good accuracy since more than 68.4% fall within one standard deviation. Similarly, four of five measurements fall within one standard deviation of the median value. So, the measurements also have good precision.

In other words, the standard deviation indicates the distribution of values about the mean. To say this another way, the standard deviation is an indication of the precision involved with a certain set of measurements.

Procedure Part A: Glassware

For each piece of glassware, the volume will be determined by weighing the amount of DI water in each sample and then using the density to calculate the volume. For example, a beaker filled with water to the 50 mL mark contains approximately 50 mL of liquid. By weighing the beaker and its water, then subtracting the empty beaker weight, the actual mass of the water sample is known. The density of water is then used to calculate the true volume of that sample. Which piece of glassware do you expect to be the most accurate? The most precise?

Part I: Beaker Calibration

Use a 100 or 150 mL beaker that has a calibration line at the 50 mL point. Use the beaker in your drawer, not your partner's beaker. The aim is to determine the accuracy of your beaker so you know the reproducible volume of liquid that is delivered with your beaker. Check out a clean beaker from the stockroom if you do not have one that is suitable for this experiment. Wash your beaker and rinse with DI water. Do not dry the inside of your beaker. Dry the outside then follow the instructions below. Record your data in your laboratory notebook.

1. Fill the beaker to the 50 mL mark as carefully as possible. Adjust the level using an eye dropper if needed. What is the uncertainty of the beaker measurement?
2. Weigh the beaker and its contents. Do not use an analytical balance. Zero the balance first and continue to use the same balance for each measurement throughout this part of the experiment. What is the uncertainty of the balance?
3. Pour the water out of the beaker until it stops draining, then weigh the empty beaker (remember to use a glass stir rod, "glass-to-glass-to-glass" to ensure that as much of the liquid is transferred as possible). This is your tare weight. Do not dry out any remaining drops of water before it is weighed. This procedure will measure the volume of water delivered by the beaker, not the actual volume that it holds.
4. Repeat steps 1 – 3 for two more trials.
5. Determine the mass of water delivered by your beaker for each trial. This is simply done by subtracting the tare weight from the weight of the beaker plus the water.

Part II: Graduated Cylinder Calibration

Use a 10 mL graduated cylinder from your equipment drawer. Wash your glassware and rinse with DI water. As before, do not dry the inside of the cylinder; dry the outside. You will also need a plastic bottle with cap that can hold approximately 125 mL of liquid. Follow the steps below and record the data in your notebook.

1. Fill a clean 250 mL beaker with approximately 200 mL DI water. Record the temperature of the water. Use this water for the six trials that you will do in this part of the experiment.
2. Weigh the plastic bottle and its cap on an appropriate balance. The bottle should be empty but does not have to be completely dry. This is your tare weight for the plastic bottle.
3. Fill the graduated cylinder to the 10.0 mL mark. Make sure the meniscus is just even with the 10.0 mL mark. Use an eye dropper to adjust final volume if needed. What is the uncertainty of the graduated cylinder?
4. Pour the contents of the graduated cylinder into the plastic bottle ("glass-to-glass-to-glass"). Some drops of water will adhere to the inside of the cylinder which is fine. Remember, you want to determine the deliverable volume, not the actual volume. Place the cap on the plastic bottle and record the weight. What is the uncertainty of the balance?
5. Transfer another 10.0 mL of water from the graduated cylinder to the plastic bottle like you did in steps 3 and 4. Do not empty the water in the plastic bottle from the first transfer. You will add

each sample to the bottle in consecutive trials. By the end of this exercise, the bottle will be quite full.

6. Repeat steps 3, 4 and 5 until you have a total of seven measurements.
7. Add another column to the right of your data table and fill it with the mass of the water delivered in each transfer. You will need this value later when interpreting your results.

Part III: Pipet Calibration

Before the pipet can be used, it must be clean so that it drains freely (i.e wash three times with soapy water, rinse three time with tap water, rinse three times with D.I. water, and if necessary rinse three times with your solution.). After cleaning, practice with the pipet before you start the procedure. Use DI water to practice until you have mastered the skill needed to deliver an aliquot from the pipet. This exercise is similar to the procedure for the graduated cylinder except you will use the 10 mL pipet to deliver your samples into a small plastic bottle that has a 50 mL capacity. Follow the steps below and record your data in your notebook.

1. Obtain the tare weight of your plastic bottle on an appropriate balance. As before, the bottle does not have to be completely dry on the inside.
2. Fill the pipet to the 10 mL mark and deliver the contents to the plastic bottle. What is the uncertainty of the pipet?
3. Weigh the bottle plus its contents. What is the uncertainty of the balance?
4. Repeat steps 2 and 3 until you have data for four trials. Remember- don't empty the bottle between trials.

Calculations and Results



Remember to convert your masses to volumes since the beaker, graduated cylinder, and pipet are used to measure volumes and not masses.

Part I: Beaker Calibration

1. Calculate the mean and standard deviation for the mass of water contained in the beaker.
 - a. What does the standard deviation tell you about the precision of the beaker? Classify the precision as good, fair, or poor. Refer to Figure 1.3 on page 7 and the subsequent text. Remember that you will use your data to support your choice in your discussion.
2. Assuming that the density of water is 1.0 g/mL, what is the most likely volume contained in your beaker when filled to the 50 mL mark (i.e the "true value" for the volume)?
 - a. What is the percent error with respect to the volume? What does the percent error tell you about the accuracy of your measurements? Classify the accuracy as good, fair, or poor. Remember that you will use your data to support your choices in your discussion.

Part II: Graduated Cylinder

1. Calculate the mean and standard deviation for the mass of water contained in the cylinder.
2. Find the density of water at the temperature you recorded in the *Handbook of Chemistry and Physics*. Use this density to convert the mean value of the mass of water and its standard deviation to the corresponding volume.

- a. What does the standard deviation tell you about the precision of the beaker? Classify the precision as before. You will use your data to support your choices in your discussion.
3. What is the percent error? What does the percent error tell you about the accuracy of your measurements? Classify the accuracy as good, fair, or poor as you did before.

Part III: Volumetric Pipet

1. Do the same calculations as listed above for the graduated cylinder.
2. Classify the accuracy and precision of the volumetric pipet as good, fair or poor. Remember that you will use your data to support your choices in your discussion. .



NOTE: Your results and calculations section should include a table like the one below to summarize your major data.

TABLE 1.4 Analysis of Volume Instruments

Instrument	Uncertainty	Average Volume	Standard Deviation	Precision (good, fair, poor)	True Value	%error	Accuracy (good, fair, poor)
beaker							
graduated cylinder							
pipet							

SAMPLE

Part B: Measuring the Density of Coke and Diet Coke



Remember that the instrument was calibrated previously. Use that volume in your calculations.

Objective

Determine the density of each soft drink using 10 mL samples. From your results in Part A, you need to decide which piece of glassware is the best choice for measuring the density of each. .

Procedure

The student should develop and follow a procedure similar to that used in Part A. You should do a minimum of three trials on each soda.

Results

Report the mean density and standard deviation for each soft drink. Show your calculations.

References

Masterton and Slowinski: *Elementary mathematical preparation for General Chemistry*. Saunders Publishing, 1974.

Shoemaker, Garland, and Steinfeld: *Experiments in Physical Chemistry*. McGraw-Hill, 1974.

Kratchvil, H.: *Chemical Analysis*. Barnes and Noble, 1969.

Post Lab Questions

1. What factors did you consider in choosing the particular piece of glassware for Part B of the experiment? Include comments on the accuracy and precision of your glassware choice.
2. Is the density of the two soft drinks the same, greater or less than that of water? Suggest reasons for your answer (hint- examine the contents label on the aluminum cans).
3. Compare the density of Coke with the density of Diet Coke. Are they the same or different? Explain your answer.

Density: A Study in Precision and Accuracy (Part A)

Introduction

In this lab, you will be investigating the concepts of precision and accuracy. You will be doing an experiment in which you will be measuring the density of some glass beads. Although you will be learning a little bit about density measurements, the primary goal of the lab is for you to come to grips with the separate concepts of accuracy and precision.

In any scientific investigation, when the results are reported, it is standard practice that the investigating scientist carefully consider both the issues of accuracy and precision. Since these two concepts are often confused, we will begin with a careful definition of each.

Precision: A measure of the amount of random variation in the measurement of data.

Accuracy: A measure of how far an experimental result is from the true or correct value.

Whenever a scientist makes measurements, there will always be some random variation in the values recorded. If one were to use a stop watch to measure the time, t , it took an object to fall a certain distance, one might record data such as the following:

1.49 s, 1.48 s, 1.53 s, 1.48 s, 1.50 s, 1.47 s, 1.52 s, 1.52 s, 1.46 s

The random variation does not necessarily reflect an error on the part of the person doing the measurements, but rather it may reflect the limit of the precision of the time measuring device (and the ability of the person controlling the stopwatch to hit the button at the right time). The precision of the experiment is a measure of the size of the random variation in the experiment. In this experiment, you will learn to calculate the standard deviation of the measurement: the most common accepted statistical measure of precision.

Another way of thinking about precision is as a measure of the amount of random error in an experiment. Any experimental error is considered to be random if its result could make the calculated or measured value either too high or too low. Any potential error in an experiment which could have a predicted effect on the result, making it either definitely too high or too low, would be considered a systematic error (see below).

For the same experiment as described above, if the exact height from which the mass was dropped was known, the equations of motion from the basic physics course (assuming the acceleration due to gravity to be 9.80 m/sec^2) could be used to calculate the theoretical time it should take the mass to fall. In this case, the correct theoretical value could be compared to the results. For example, if the “true” or “theoretical” value for the time it should take the mass to drop were 1.45 seconds, the accuracy of the experiment could be calculated. In this experiment, you will measure the accuracy as the %-error of the measurement.

In general, scientists are always able to measure the random error of an experiment. There are situations in which there is no known “true” or “accepted” value for a measurement. In this case, the scientist may not be able to calculate the accuracy as a %-error. Normally, in such a situation, the scientist will do a very similar experiment to the one to be reported, only doing the very similar experiment on slightly different case in which the “true” value is known. The scientist will then calculate the %-error in this case as a check on the validity of the measurement they are reporting.

Another way of thinking of accuracy is to think of accuracy as a measure of the systematic error in an experiment. For example, in the mass-dropping experiment described above, if one were to anticipate the mass hitting the floor, and press the button just a little before the mass hit, that would definitely make the time measured too small. This would be an example of a systematic error. If the person doing the experiment were to consistently make such an error, it would effect the accuracy (and therefore the %-error), but not the precision (and therefore not the standard deviation).

Theory

For a set of measurements of a variable x , the standard deviation is calculated using the following equation:

$$\sigma = \sqrt{\frac{\sum(x - \bar{x})^2}{n - 1}} \quad \text{(EQ 2.1)}$$

Where σ is the symbol for standard deviation (sometimes the letter s is used to represent the standard deviation). The symbol x represents the individual measurements, while the symbol \bar{x} represents the average of the measurements in question. In this equation, n is the number of measurements. For example, one could calculate the standard deviation of the measurements of time listed above. The calculation is shown below:

TABLE 2.1

t (s)	$t - \bar{t}$ (s)	$(t - \bar{t})^2$ (s ²)
1.49	-0.004	0.000016
1.48	-0.014	0.000196
1.53	+0.036	0.001296
1.48	-0.014	0.000196
1.50	+0.006	0.000036
1.47	-0.024	0.000576
1.52	+0.026	0.000676
1.52	+0.026	0.000676
1.46	-0.034	0.001156

$$\bar{t} = \frac{13.45}{9} = 1.494 \text{ s} \quad \sum (t_i - \bar{t})^2 = 0.004824 \text{ s}^2 \quad (\text{EQ 2.2})$$

Therefore, the standard deviation is:

$$\sigma = \sqrt{\frac{0.004824}{9-1}} = 0.0245 \text{ s} \quad (\text{EQ 2.3})$$

The average and the standard deviation are combined to yield the result that the time it took the mass to fall is in the form $t = \bar{t} \pm \Delta t$:

$$t = 1.494 \pm 0.025 \text{ s} \quad (\text{EQ 2.4})$$

Note that both the average value and the standard deviation should end with the same number of digits past the decimal. Also note that the units label follows the standard deviation, not the average value.

The accuracy of the time measurement may be calculated as well. The equation for %-error is as follows:

$$\% \text{ error} = \frac{\text{measured value} - \text{theoretical value}}{\text{theoretical value}} \times 100 \% \quad (\text{EQ 2.5})$$

If the measured value is below the accepted or theoretical value, then there will be a negative %-error. Be sure to show the positive or negative sign (e.g. +5.67% or -5.67%) when reporting your answer. What does the sign tell you about the %-error?

For the time experiment described above, then, the %-error is calculated (assuming the true value to be 1.45 s) as:

$$\% \text{ error} = \frac{1.494 - 1.45}{1.45} \times 100 \% = 3.0 \% \quad (\text{EQ 2.6})$$

In general, a %-error is only reported to one or at most two significant figures.

In this experiment, you will be measuring both the mass and the volume of some glass beads. The density will be measured using the well-known equation:

$$d = \frac{m}{v} \quad (\text{EQ 2.7})$$

After calculating both the mass and the volume of some glass beads a number of times, you will calculate the average values and the standard deviations of both values. You will then calculate the density, the standard deviation of the density, and the %-error from the true value for the density of the glass beads.

What about the precision of your density measurement? In other words, you will be measuring the standard deviation of the mass measurement as well as of the volume measurement. The precision of the mass and volume measurements are determined when the standard deviation is measured. The question is how to use these results to estimate the size of the random error (precision) in the density when it is calculated by dividing the mass by the volume.

One way to do this would be to simply calculate the random error of the two measurements used to calculate the density and add the two errors. There are two problems with this approach. First, one cannot add apples to oranges. In other words one cannot add the error in the mass (with units grams) to the error in the volume (with units of milliliters). A partial solution to this problem would be to calculate the percentage of the two errors and adding them. In other words, if the standard deviation of the mass measurement was 5.2% of size of the average mass, and the standard deviation of the volume measurement was 8.4% of the size of the average volume, one could conclude that the random error in the density measurement was $5.2 + 8.4 = 13.6\%$.

The problem with this solution is that it overestimates the error. There is a significant probability that the error in the volume will have the opposite effect on the density as the error in the mass measurement. In other words, the errors can cancel. The correct statistical measurement of the combined error due to two measurements (x and y) being used to calculate a secondary value (z) is given by the following equation:

$$z = \frac{x}{y} \quad \text{or} \quad z = xy \quad \text{(EQ 2.8)}$$

The estimated error, Δz , can be calculated as follows,

$$\Delta z = z \sqrt{\left(\frac{\sigma_x}{x}\right)^2 + \left(\frac{\sigma_y}{y}\right)^2} \quad \text{(EQ 2.9)}$$

Where z is the calculated value and Δz is the estimated error in the calculated value. In this formula, σ_x and σ_y are the standard deviation in the measured values x and y . Therefore, the final result for the calculated value is $z = \bar{z} \pm \Delta z$.

Experimental Procedure

Part I: Measuring the mass of the glass beads

1. Using a balance, measure the mass of forty glass beads eight different times. It is most convenient to measure the beads in a weighing boat. Be sure to measure different beads each time to ensure that you are getting a random selection of the beads in the jar.
2. Record the eight values of the mass in a table in your lab book, being sure to get as much precision out of the balance as possible.
3. After recording the values, determine the average mass of the beads.
4. Go on to calculate the standard deviation of the mass measurements.
5. In addition, report the average \pm the standard deviation.
6. Be sure to report the units and the number of significant figures properly. Show all your calculations.

Part II: Measuring the volume of the glass beads

1. Fill a buret about one-third to one-half full with deionized water.
2. Carefully record the volume of water in the buret. If you are not sure how to record the volume measurement from a buret accurately to two places past the decimal, ask your instructor for help.

3. Now, add forty glass beads to the buret and record the volume again.
4. Repeat this process for a total of eight additions of forty beads, recording the final volume each time. Record the results in a table in your lab book.
5. When you are done, drain the water from the buret and dump the wet beads into the container provided marked "wet glass beads".
6. Calculate the volume of forty beads for each of the eight cases, and continue on to calculate the standard deviation of the volume measurements.
7. Report the average of the volume of forty beads \pm the standard deviation in the correct format.

Part III: Calculating the density and the error in the density

1. First, use the average mass and average volume from above to calculate the density of the glass beads.
2. Next, calculate the %-error of your measurement, assuming that the correct value for the density of the glass beads is $d = 2.35 \text{ g/mL}$.
3. In addition, calculate the random error in the density using Equation 2.9 for calculating the accumulated uncertainty for a calculation involving two measurements.
4. Finally, record the density of the glass beads from your measurements as $d = \bar{d} \pm \Delta d$.

Post Lab Questions

1. Is the size of your random error big enough to explain the difference between your measured value of density and the expected value of 2.35 g/mL? Explain.
2. Based on your answer to question #1, would you need to invoke some sort of systematic error to explain the difference between your calculated density and the expected value of 2.35 g/mL, or can all the error be assumed to be due to random error? Explain.
3. Give two examples of random error in this experiment.
4. Give two examples of systematic error in this experiment. In each case, would the proposed systematic error make the calculated density too high or too low when compared to the correct value?

Density: A Study in Precision and Accuracy (Part B)

Validity

In this part of the statistics lab, we will consider two additional aspects of statistical treatment of data which are very important to scientists. The first is validity. **Validity** is a measure of how well cause and effect are correlated. Testing claims of the validity of a cause and effect relationship between two variables is perhaps the most basic part of what scientists do. If the effect of a new drug in treating a particular disease is being tested, the drug must be tested on a set of patients as well as a control group which receives a “placebo.” The obvious question is whether or not there is a significant difference in symptoms of disease between those who took the drug and those who were given a placebo.

Validity is a measure of whether two different results are truly different statistically. For example, a scientist could study the colon cancer rates of those who eat Wheaties and those who do not. Let us imagine that the colon cancer rate of those who eat Wheaties is 24.5 per thousand, while those who do not eat Wheaties have a cancer rate of 24.0 per thousand. Is the scientist justified in reporting that eating Wheaties can increase your likelihood of getting cancer? The answer is almost certainly no!!! The two different results almost certainly do not differ enough to statistically justify concluding there is a relationship between eating Wheaties and getting colon cancer.

The problem of determining validity of a result is especially difficult in the biological sciences, and even more so in the medical sciences. For example, consider the following hypothetical study. A group of subjects was surveyed and it was discovered that people in the army have a 30% higher lung cancer rate than those not in the army. This 30% difference is certainly statistically valid. Conclusion: being in the army causes lung cancer. Wrong!!! What this study fails to do is to adjust the results for smokers. In fact, those in the army have a 40% higher rate of smoking. It was not being in the army which caused cancer, it was smoking.

The conclusion is that anyone doing a scientific study must very carefully consider all the relevant variables which could conceivably effect a given result. Once all the variable have been controlled for, the results must still be checked for statistical validity. In other words, is there a valid correlation between a change in a given variable and the result measured.

The t Test

The most common statistical test for whether a scientific measurement of an effect is valid is the t test. For a given set of data, one being the test, the other being the control, the question is whether the average value measured is statistically different. Is there a valid effect? To provide an example, consider the following data:

TABLE 3.1

measurement #	height of plant using just water	height of plant using "Mighty Grow"
1	58 cm	64 cm
2	62 cm	55 cm
3	53 cm	58 cm
4	61 cm	66 cm
5	54 cm	56 cm
6	57 cm	62 cm
average	57.5 cm	60.2 cm

Conclusion: "Mighty Grow" makes the plants grow faster. Not so fast! We must apply the t test. Look at Equation 3.1

$$t = \frac{\bar{x}_1 - \bar{x}_2}{s_p} \sqrt{\frac{N_1 N_2}{N_1 + N_2}} \quad (\text{EQ 3.1})$$

Where \bar{x}_1 is the average of the first set of data, \bar{x}_2 is the average of the second set of data, N_1 and N_2 are the number of measurements for each set of data, and s_p is the pooled standard deviation of the two sets of data. The pooled standard deviation is given by Equation 3.2.

$$s_p = \sqrt{\frac{\sum (x_{i1} - \bar{x}_1)^2 + \sum (x_{i2} - \bar{x}_2)^2}{N_1 + N_2 - 2}} \quad (\text{EQ 3.2})$$

The value of t is calculated and compared to a t table. If it is greater than the relevant t value in the table, then the difference between the two measurements is valid. A table of t values is included.

For example, from the data in Table 3.1 on page 22, one can calculate the t value to be:

TABLE 3.2

Set #1 $(x_i - \bar{x}_1)^2$	Set #2 $(x_i - \bar{x}_2)^2$
0.25	14.44
20.25	27.04
20.25	4.84
12.25	33.64
12.25	17.64
0.25	2.24
$\sum (x_i - \bar{x}_1)^2 = 65.50$	$\sum (x_i - \bar{x}_2)^2 = 99.84$

$$s_p = \sqrt{\frac{65.50 + 99.84}{6 + 6 - 2}} = 4.07 \quad (\text{EQ 3.3})$$

$$t = \frac{\bar{x}_1 - \bar{x}_2}{s_p} \sqrt{\frac{N_1 N_2}{N_1 + N_2}} = \frac{60.2 - 57.5}{4.07} \sqrt{\frac{6 \cdot 6}{6 + 6}} = 1.14 \quad (\text{EQ 3.4})$$

Now, checking the t table, the number of degrees of freedom is $N-1$. Critical values for t (two-tailed). Use these for the calculations of confidence intervals.

TABLE 3.3 T-test Table

Degrees of Freedom	50%	60%	70%	80%	90%	95%	98%	99%	99.5%	99.8%	99.9%
1	1.000	1.376	1.963	3.078	6.314	12.706	31.821	63.657	127.3	318.3	636.6
2	0.816	1.061	1.386	1.886	2.920	4.303	6.965	9.925	14.09	22.33	31.60
3	0.765	0.978	1.250	1.638	2.353	3.182	4.541	5.841	7.453	10.21	12.92
4	0.741	0.941	1.190	1.533	2.132	2.776	3.747	4.604	5.598	7.173	8.610
5	0.727	0.920	1.156	1.476	2.015	2.571	3.365	4.032	4.773	5.893	6.869
6	0.718	0.906	1.134	1.440	1.943	2.447	3.143	3.707	4.317	5.208	5.959
7	0.711	0.896	1.119	1.415	1.895	2.365	2.998	3.499	4.029	4.785	5.408
8	0.706	0.889	1.108	1.397	1.860	2.306	2.896	3.355	3.833	4.501	5.041
9	0.703	0.883	1.100	1.383	1.833	2.262	2.821	3.250	3.690	4.297	4.781
10	0.700	0.879	1.093	1.372	1.812	2.228	2.764	3.169	3.581	4.144	4.587
11	0.697	0.876	1.088	1.363	1.796	2.201	2.718	3.106	3.497	4.025	4.437
12	0.695	0.873	1.083	1.356	1.782	2.179	2.681	3.428	3.428	3.930	4.318

Since we had six measurements, the number of degrees of freedom is five. At the 90% confidence level, with 5 degrees of freedom, $t = 2.015$. Since our value for t was 1.14, there is not a valid correlation between use of the fertilizer and plant height. If we had used the 50% confidence level, $t = 0.727$, and the result would be valid. In other words, at a 50% confidence level, there is at least a small statistical effect of using the fertilizer.

Q test

Scientists use the **Q test**, an empirical evaluation, to determine whether a measurement should be rejected. In statistics, the **Q test** is used for identification and rejection of outliers. This test should be used sparingly and never more than once in a data set. To apply a Q test for bad data, arrange the data in order of increasing values and calculate Q as defined:

$$Q = \frac{\text{gap}}{\text{range}} \quad (\text{EQ 3.5})$$

If $Q_{\text{calculated}} > Q_{\text{table}}$ then reject the questionable point.

TABLE 3.4 Q-test Table

Number of Values	3	4	5	6	7	8	9	10
$Q_{90\%}$	0.941	0.765	0.642	0.560	0.507	0.468	0.437	0.412
$Q_{95\%}$	0.970	0.829	0.710	0.625	0.568	0.526	0.493	0.466

EXAMPLE 3.5 Evaluate the following data using the Q test:.

TABLE 3.6 A student does five trials on a substance to find its molar mass.

Trial #	Molar Mass (g/mol)
1	152.9
2	148.0
3	153.5
4	154.2
5	154.5

The student applies the proceeding steps:

1. First, arrange the values in increasing order:

$$148.0 \text{ g/mol}, 152.9 \text{ g/mol}, 153.9 \text{ g/mol}, 154.2 \text{ g/mol}, 154.5 \text{ g/mol}$$

2. Find the difference between the suspicious value and the value closest to it:

$$152.9 \text{ g/mol} - 148.0 \text{ g/mol} = 4.9 \text{ g/mol}$$

3. Calculate the difference between the highest and lowest value:

$$154.5 \text{ g/mol} - 148.0 \text{ g/mol} = 6.5 \text{ g/mol}$$

4. Obtain the quotient, Q, by dividing step 2's answer by step 3's answer:

$$Q = \frac{\text{gap}}{\text{range}} = \frac{4.9 \frac{\text{g}}{\text{mol}}}{6.5 \frac{\text{g}}{\text{mol}}} = 0.75 \quad (\text{EQ 3.6})$$

5. Finally, compare the value of $Q_{90\%}$ found in Table 3.4 .

$Q_{90\%}$ tells use the maximum values we can have for a 90% confidence. If the calculated result in step 4 is greater than the value for $Q_{90\%}$, we can reject the suspicious value. For this example, $Q_{90\%}$ for the five trials is 0.642 and 0.75 is greater than 0.642. Hence, the value for trial 2, 148.0 g/mol, can be rejected.

EXAMPLE 3.7 Evaluate the following data using the Q test:

$$0.189, 0.169, 0.187, 0.183, 0.186, 0.182, 0.181, 0.184, 0.181, 0.177$$

Arrange in increasing order:

$$0.169, 0.177, 0.181, 0.181, 0.182, 0.183, 0.184, 0.186, 0.187, 0.189$$

Outlier is 0.169. Calculate Q:

$$Q = \frac{\text{gap}}{\text{range}} = \frac{(0.177 - 0.169)}{(0.189 - 0.169)} = \frac{0.008}{0.020} = 0.400 \quad (\text{EQ 3.7})$$

With 10 observations at 90% confidence, $Q_{\text{calculated}} < Q_{\text{table}}$. Therefore keep 0.169 at 90% confidence.

The "Experiment"

Perform a t test to see if there is a statistically valid relationship between number of bean seeds sprouted per 100 and exposure to UV light.

TABLE 3.8

Experiment #	# sprouted without UV irradiation	# sprouted with UV irradiation
1	87	71
2	72	64
3	88	80
4	81	69
5	69	70
6	78	70
7	80	72
Average		

1. Calculate the average for each set of data and fill in the blank in the table above. Then do the calculations to find t for the two sets of data. Show your calculations in your lab book.
2. What is the number of "degrees of freedom" for the data above?
3. Find the value of t from Table 3.3 on page 23 using your number of degrees of freedom at the 90% confidence level. Compare to your t calculated above. According to your result, is there a significant difference in the seed-sprouting rate for seeds irradiated with UV light? If not, is the difference significant at the 50% confidence level? If yes to the 90% confidence level, what is the highest confidence level at which the result is valid according to the table?

Least Squares Analysis Of Data

Least squares analysis of data is a statistical method for determining the best fit straight line to a set of data. There is hardly any more common thing for a chemist to do than to fit a set of data to a straight line, be it in kinetic studies, absorbance/concentration studies and so forth. Chemists almost invariably use a canned program from excel or other software to determine the slope and intercept of the best straight line fit to a set of data. In this experiment, you will actually do a least squares analysis of a set of data by hand. The theory and equations of least squares analysis is provided in an attachment to this lab write-up. You will be doing a simple experiment to determine the density of a solution using least squares analysis of data.

Experiment

Using a 50.0 mL graduated cylinder, measure the mass of the cylinder empty as well as five sets of volume and mass data for the same cylinder and a solution provided. The volumes should be about 10, 20, 30, 40, and 50 mL. Measure both mass and volume with as much precision as the data allows. Record the data in your lab book. That is it!

Calculations

1. Perform a least squares fit to the five pairs of data, assuming that the volume is the independent (x -axis) data and the mass is the dependent (y -axis) data. Your analysis of the data should include finding both the slope and the intercept (see Equation 3.8 and Equation 3.9), as well as

the uncertainty in both numbers (see Equation 3.10, Equation 3.11, and Equation 3.12). Record the slope as $m = \text{slope} \pm \text{error in slope}$ and the intercept as $b = \text{intercept} \pm \text{error in intercept}$.

2. What is the physical interpretation of the slope of your graph? Does it agree with the correct answer (look it up) within the uncertainty? What is the %-error? Is a systematic error required to explain your %-error? (explain)
3. What is the physical interpretation of the intercept of your graph? Does this value agree with the correct value within the uncertainty you determined? Calculate your %-error. Is a systematic error required to explain your %-error?
4. Now, make a graph of your data and do a least squares fit to the same data using a canned program such as Vernier or Excel, available on the computers and compare to the values you got by hand.

$$m = \frac{\sum (x_i - \bar{x})(y_i - \bar{y})}{\sum (x_i - \bar{x})^2} = \frac{\sum x_i y_i - \left[\frac{\sum x_i \sum y_i}{n} \right]}{\sum x_i^2 - \left[\frac{(\sum x_i)^2}{n} \right]} \quad (\text{EQ 3.8})$$

$$b = \bar{y} - m\bar{x} \quad (\text{EQ 3.9})$$

$$s_y = \sqrt{\frac{\left[\sum y_i^2 - \frac{(\sum y_i)^2}{N} \right] - m^2 \left[\sum x_i^2 - \frac{(\sum x_i)^2}{N} \right]}{N - 2}} \quad (\text{EQ 3.10})$$

$$s_m = \sqrt{\frac{s_y^2}{\sum x_i^2 - \frac{(\sum x_i)^2}{N}}} \quad (\text{EQ 3.11})$$

$$s_b = s_y \sqrt{\frac{1}{N - \frac{(\sum x_i)^2}{\sum x_i^2}}} \quad (\text{EQ 3.12})$$

Conductivity and Net Ionic Equations

Objective

To use electrical conductivity as a way of determining the number of free ions present in a substance and to use this information to draw conclusions regarding the type of bonding present in the substance.

Introduction

Types of Bonding

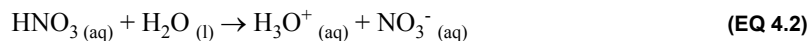
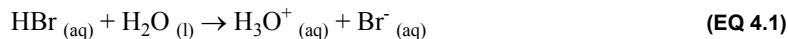
There are three basic types of bonds. They are ionic, covalent, and polar covalent, which is a hybrid of an ionic and a covalent bond. Ionic bonds are formed between elements with very different electronegativities. **Electronegativity** is the ability of an atom to draw electrons towards itself in a chemical bond. Generally, ionic compounds form between metals and non-metals and are identified by the transfer of an electron from the metal to the non-metal to form charged ions which are held together by electrostatic interactions known as ionic bonds. Covalent bonds form between elements with similar electronegativities. Generally, covalent bonds form between non-metals and are characterized by the sharing of electron pairs between the atoms. Polar bonds are formed between two elements with different electronegativities, but which still share the electrons albeit unevenly.

Electrolytes versus Non-electrolytes

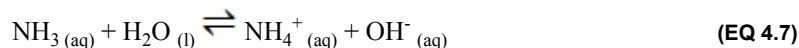
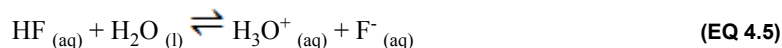
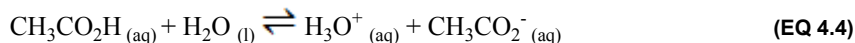
Substances may be classified by their electrical conductivity. **Electronic conduction** is a type of electrical conductivity that occurs in metals where charge is carried by electrons. In **ionic conduction** the charge is carried by ions. Substances which can conduct electricity are called **electrolytes**. When ionic compounds are melted or dissolved in water, they form mobile ions that are able to conduct electricity. Polar covalent compounds such as acids and bases will sometimes dissociate or break apart in aqueous solution to form ions as well. There are two types strong electrolyte and weak electrolytes.

Substances which do not conduct electricity are called **non-electrolytes**. Examples of non-electrolytes are covalent molecules such as sucrose or table sugar ($C_{12}H_{22}O_{11}$) and acetone (CH_3CO-CH_3). These substances are non-electrolytes because they are not composed of ions and cannot conduct an electric current. Ionic compounds in their crystalline form are also considered to be non-electrolytes because even though they are composed of ions, the ions are not able to move freely through the crystal and therefore are not able to conduct electricity.

Strong electrolytes dissociate ~100% in aqueous solution. In chemical equations where ions are included (total and net ionic equations) write the ionized components, since they are the major species present in the solution. Examples of these are shown below:



Weak electrolytes are substances that are able to conduct electricity, but conduct poorly. Examples of weak electrolytes are molecular substances that dissociate to a small extent such as weak acids and bases, and ionic compounds that have limited water solubility. They are **slightly ionizable substances**. In chemical equations where ions are included (total and net ionic equations) write the complete weak acid formula, not the ions. The ions are only a minor component in the total solution. Examples are shown below:



As you complete the experiment, notice the difference in conductivity between strong and weak acids and bases. What does this tell you about the relative degree of dissociation? What are the principal species present in the solution? How do we write these substances in ionic equations?

Writing Chemical Reactions

Reaction can be classified into two basic types: oxidation-reduction and double displacement.

1. Oxidation-Reduction (Redox) Reactions: Electrons are transferred from one reactant to another. Most simply oxidation is the loss of electrons and reduction is the gain of electrons.

a. Combination reactions where reactants combine to form a new substance:



b. Decomposition reactions where reactants break apart into new substances:

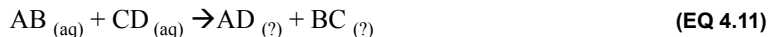


c. Single Replacement Reactions involve the reactivity of an element is related to its tendency to lose or gain electrons; that is, to be oxidized or reduced. Generally speaking:



where A is the more active element and replaces B in the compound.

2. Double Displacement Reactions (aka Ion Exchange Reactions) two aqueous solutions are mixed together to produce a precipitate, slightly ionizable substance, or a gas.



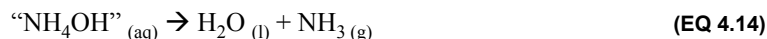
- a. Precipitate — formation of an insoluble compound. Solubility rules are given below:

FIGURE 4.1 Solubility Rules

- Alkali metals and NH_4^+ compounds are soluble (i.e. aqueous, (aq)), this means they completely dissociate in water.
- Nitrates (NO_3^-), acetates (CH_3CO_2^-) (except for acetates of Al^{3+} , and Ag^+), chlorates (ClO_3^-), perchlorates (ClO_4^-), and sulfates (SO_4^{2-}) are generally soluble (except for Sr^{2+} , Ca^{2+} , Ba^{2+} , Pb^{2+} , and Hg_2^{2+} sulfates).
- Chlorides (Cl^-), bromides (Br^-), and iodides (I^-) are soluble (except for silver (Ag^+), mercury(I) (Hg_2^{2+}), and lead(II) (Pb^{2+}) halides).
- Compounds containing the fluoride ion, F^- , are soluble except for group IIA cations and Pb^{2+} . These cations will precipitate out as a fluoride salt.
- Most compounds not included above are not soluble (i.e. precipitates/solids, (s)): i.e. sulfides (S^{2-}), carbonates (CO_3^{2-}), phosphates (PO_4^{3-}), chromates (CrO_4^{2-}), oxides (O^{2-}), and hydroxides (OH^-) ($\text{Ca}(\text{OH})_2$, CaO , $\text{Sr}(\text{OH})_2$, SrO , $\text{Ba}(\text{OH})_2$, and BaO are slightly soluble meaning that they dissociate some, but not completely in water.).

- b. Gas — bubbles or effervescence. Common gases include hydrogen gas, $\text{H}_2_{(g)}$, oxygen gas, $\text{O}_2_{(g)}$, hydrogen sulfide, $\text{H}_2\text{S}_{(g)}$, ammonia, $\text{NH}_3_{(g)}$, carbon dioxide, $\text{CO}_2_{(g)}$, and sulfur dioxide, $\text{SO}_2_{(g)}$.

When these compounds are “formed” they are unstable and decompose into gases and water:



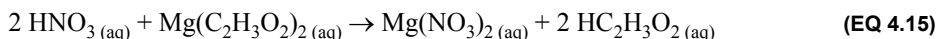
- c. Slightly ionized substance — heat usually accompanies the formation of water, H_2O , acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, or any other slightly ionized compound (weak acids, weak bases).

Writing Ionic Equations

When you write ionic equations, you need to show the principal species present in the solutions. By testing the conductivity of a variety of solutions you can determine whether the principal species are ions or undissociated or undissolved particles. For each of the substances test for electrical conductivity and determine the principal and minor species present in the solution.

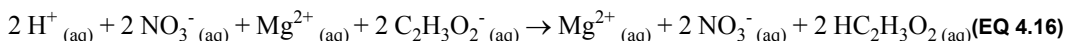
EXAMPLE 4.1 Write the balanced conventional equation for the reaction of nitric acid and magnesium acetate.

Remember that the conventional equation shows all species as neutral compounds.



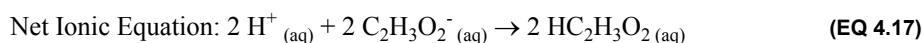
EXAMPLE 4.2 Write the total ionic equation for the reaction.

Remember that the total ionic equation shows all species as they appear in solution.

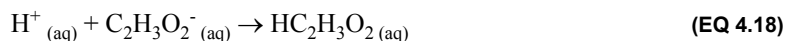


EXAMPLE 4.3 Write the net ionic equation for the reaction.

The net ionic equation shows only the species that undergo reaction. No spectator ions.



Remember to simplify the coefficients when necessary.



EXAMPLE 4.4 Complete the following table:

TABLE 4.5

	Conductivity	Ions (None, Few, Many)	Major species present in solution	Minor species in solution
Before Rxn: $\text{HNO}_3(\text{aq})$	Good	Many	$\text{H}^+(\text{aq}), \text{NO}_3^-(\text{aq})$	n/a
Before Rxn: $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2(\text{aq})$	Good	Many	$\text{Mg}^{2+}(\text{aq}), \text{C}_2\text{H}_3\text{O}_2^-(\text{aq})$	n/a
After Reaction	Good	Many	$\text{Mg}^{2+}(\text{aq}), \text{NO}_3^-(\text{aq}), \text{HC}_2\text{H}_3\text{O}_2(\text{aq})$	$\text{H}^+(\text{aq}), \text{C}_2\text{H}_3\text{O}_2^-(\text{aq})$

Note that water is omitted as a major species since it is a solvent.

Notice that the conductivity is good before and after the reaction due to the presence of ions in the solutions before and after the reaction.

Information to Include in the Introduction

- Name the three principal bond types.
- Define the following terms and tell what kind of bonding is expected in solutes that are:
 - Non-electrolyte
 - Strong electrolyte
 - Weak electrolyte
- What is the meaning of the term “hydration” when used to describe what happens to an electrolyte which is dissolved in water?
- What is meant by the term dissociation and what is an example of a substance that dissociates?
- What are the essential characteristics of a solution that is (include information regarding its behavior as well as the types of substances which indicate these types of solutions):
 - A nonconductor
 - A good conductor
 - A poor conductor

Procedure

Part 1 - Conductivity Classification

Test and record the conductivity of each substance and solution listed below using the method demonstrated by your instructor. Unless otherwise noted waste will go in the inorganic waste container. Then, after noting the range of conductivities measured, classify each as having essentially no ions, a few ions, or many ions. For each substance record also the major and minor species present in the sample. Your data table may be similar to the one shown below:

TABLE 4.6

Substance	Bond Type (Polar covalent, Ionic)	Conductivity	Ions (None, Few, Many)	Major species present in solution	Minor species in solution	Observations
HBr _(aq)	polar covalent, fully ionized	Good	Many	H ₃ O ⁺ _(aq) , Br ⁻ _(aq)	n/a	All three bulbs lit.
HF _(aq)	polar covalent, partially ionized	Poor	Few	HF _(aq)	H ₃ O ⁺ _(aq) , F ⁻ _(aq)	Two bulbs lit weakly.
Deionized water						
Tap water						
Methanol, CH ₃ OH _(l) (organic waste)						
CH ₃ OH _(aq) (organic waste)						
Glacial acetic acid CH ₃ CO ₂ H _(l)						
CH ₃ CO ₂ H _(aq) (Add water slowly to glacial acetic acid and record how the conductivity changes.)						
Sucrose C ₁₂ H ₂₂ O ₁₁ _(s)						
C ₁₂ H ₂₂ O ₁₁ _(aq)						
NaCl _(s)						
NaCl _(aq)						
KClO ₃ _(s) (Test in a crucible.)						
KClO ₃ _(l) molten (Heat crucible using a Bunsen burner.)						
0.1 M HgCl ₂						
0.1 M HCl						
0.1 M NaOH						
0.1 M CH ₃ CO ₂ H						
0.1 M NH ₃						
0.1 M NaCl						

Part 2 - Effect of Solvent

Test the conductivity of the following solvents and mixtures. Put all waste in the organic waste container. Your data table may be similar to the one shown below:

TABLE 4.7

Substance	Conductivity	Ions (None, Few, Many)	Major species present in solution	Minor species in solution	Observations
Xylene, C ₈ H ₁₀ (l) (premade)					
HCl in xylene (premade)					
Aqueous layer (after mixing water with HCl in xylene)					

Part 3 - Correlating Chemical and Conductivity Behavior

Be sure to use similar amounts of each solid and acid. You will compare the conductivity of the acids with their reaction rates. Compare the rates of reaction (fast, medium, slow, or no reaction) of:

- calcium carbonate, CaCO₃(s), with 6 M acetic acid and 6 M hydrochloric acid;
- zinc with 6 M acetic acid and 6 M hydrochloric acid.

TABLE 4.8

Acid	Conductivity Before rxn	Ions (None, Few, Many) Before rxn	Rxn Rate CaCO ₃ (s)	Rxn Rate Zn(s)	Observations
HCl _(aq)					
HC ₂ H ₃ O ₂ (aq)					

Part 4 - Observing Changes in Conductivity for Ionic Reactions

Measure the conductivities of the acid and base alone, and then titrate the acid with base using a pasteur pipet and observe the changes in conductivity. Add several drops of phenolphthalein to the acid before you begin the titration. Continue adding several more drops of base after the phenolphthalein turns pink. Note how the conductivity changes as you add base to the acid. Note the changes in conductivity as well as any other changes that may occur as you perform the titration.

- Perform the experiment with 0.1 M HCl with 0.1 M NaOH;
- Perform the experiment with 0.1 M CH₃COOH with 0.1 M NH₃;
- Perform the experiment with 0.1 M H₂SO₄ with 0.1 M Ba(OH)₂.

TABLE 4.9

	Conductivity	Ions (None, Few, Many)	Observations
Before Rxn: reactant 1			
Before Rxn: reactant 2			

*Procedure Questions***Part 1**

1. Write the equation for the reaction that forms the few (but important) ions in pure water.

2. Why is tap water more conductive than distilled water?

3. Answer the following questions about acetic acid.
 - a. Write an equation to describe the formation of ions in aqueous acetic acid.

 - b. Why does acetic acid form ions when it is dissolved in water, but not when it is in the pure (glacial) form?

4. The models of solid NaCl describe it as consisting of Na⁺ cations and Cl⁻ anions.
 - a. If this is the case, why is NaCl_(s) not an electrolyte?

 - b. Explain the distinctly different behavior in the conductivity of NaCl_(s) and NaCl_(aq).

5. Explain the difference in behavior in the conductivity of KClO_3 (s) and KClO_3 (l).

Part 2

1. Why is the conductivity of HCl different in the two solvents?

2. What causes this difference?

Part 3

1. Write the equation for the reactions of:
- calcium carbonate and acetic acid

 - calcium carbonate and hydrochloric acid;

 - zinc and acetic acid;

- d. zinc and hydrochloric acid.
-
- 2. Discuss any correlation between the rates of the chemical reactions of 6 M acetic and 6 M hydrochloric acid and the conductivities observed for acetic acid and hydrochloric acid in part 1.

Part 4

- 1. Describe what happened as you reacted 0.1 M HCl with 0.1 M NaOH.
 - a. Write the conventional, total ionic, and net ionic equations for the reaction.

 - b. Explain any changes in conductivity you detected for this reaction.

2. Describe what happened as you reacted 0.1 M CH_3COOH and 0.1 M NH_3 .
- Write the conventional, total ionic, and net ionic equations for the reaction.

 - Explain any changes in conductivity you detected for this reaction.
3. Describe what happened as you reacted 0.1 M H_2SO_4 with 0.1 M $\text{Ba}(\text{OH})_2$.
- Write the conventional, total ionic, and net ionic equations for the reaction.

 - Explain any changes in conductivity you detected for this reaction.

Post Lab Questions

1. Listed below are several substances and their conductivities when dissolved in water. Based on this information, write the formulas for all of the individual species present. Omit water from your list.

TABLE 4.10

Substance	Conductivity	Major Species Present	Minor Species Present
HF _(aq)	Poor	HF _(aq)	H ⁺ _(aq) , F ⁻ _(aq)
K ₂ SO _{4(aq)}	Good		
CH ₂ O _(l)	Non-conductive		
HCHO _{2(aq)}	Poor		

2. Recognition of ionic or molecular species present. For each substance, write the formula(s) of the principal species (molecular or ionic) present in major amounts in the aqueous solution if the substance is soluble; if it is only slightly soluble, use the molecular formula followed by (s). Also include the minor species where appropriate. The first three are done as examples.

TABLE 4.11

Substance	Major Species Present	Minor Species Present
BaSO _{4(s)}	BaSO _{4(s)}	-----
CH ₃ COOH _(aq)	CH ₃ COOH _(aq)	CH ₃ COO ⁻ _(aq) , H ⁺ _(aq)
NaCl _(aq)	Na ⁺ _(aq) , Cl ⁻ _(aq)	-----
Al(OH) _{3(s)}		
Fe ₂ (SO ₄) _{3(aq)}		
HBr _(aq)		
H ₃ PO _{4(aq)}		
Mg(OH) _{2(s)}		
NH ₄ C ₂ H ₃ O _{2(aq)}		
C ₂ H ₅ OH _(aq)		
HgCl _{2(aq)}		
CuS _(s)		

3. Separate solutions of 0.01 M barium acetate, $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$, and 0.01 M sulfuric acid, H_2SO_4 , are tested for electrical conductivity. Equal volumes of these solutions are then mixed and the conductivity tested again. Predict the result and justify your answer with an appropriate equation.
4. The electrodes of the conductivity apparatus of this experiment are immersed in 10 mL of 0.01 M barium hydroxide, $\text{Ba}(\text{OH})_2$, and the conductivity is noted. A student blows his breath through a glass tube dipped into the solution. Can the student “blow out the light”? Write equations for any reactions, and justify your conclusions. (HINT: $\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq})$)
5. Interpretation of Reactions by Ionic Type Equations. Aqueous solutions of the following substances or their mixtures with water if they are only slightly soluble, are mixed. Write first the conventional equation, second the total ionic equation, and lastly the net ionic equation. If you predict no appreciable reaction, indicate this, and state why.
- Magnesium chloride and sodium carbonate
 - Aqueous ammonia and acetic acid

c. Nitric acid and magnesium acetate

d. Ammonium chloride and sodium hydroxide

e. Barium chloride and calcium nitrate

f. Potassium hydrogen carbonate and sulfuric acid

g. Aluminum hydroxide and nitric acid

h. Aqueous ammonia and sulfuric acid

i. Magnesium nitrate and zinc chloride

Objective

To gain a better understanding of the processes of oxidation and reduction by balancing oxidation-reduction, redox, reactions.

Introduction

The **oxidation state** is the imaginary charge an atom would have if shared electrons were divided equally between identical atoms bound to one another, or, for different atoms, if electrons were all assigned to the atom in each bond that has the greater attraction for electrons. **Oxidation** corresponds to an increase in the oxidation number. The compound being oxidized is the **reducing agent**. The reducing agent causes a gain in electrons, a loss of oxygen atoms, or a gain of hydrogen atoms. **Reduction** corresponds to a decrease in oxidation number. The compound being reduced is the **oxidizing agent**. The oxidizing agent causes a loss of electrons, a gain of oxygen atoms, or a loss of hydrogen atoms.

Oxidation States for Common Reagents

Much useful information about the behavior of oxidizing and reducing agents under various conditions can be summarized in the form of charts. Such charts for some common elements are presented in Table 5.1 on page 42 and are repeated again in later experiments where these elements are studied in greater detail. The charts, with their comments on the behavior of the various compounds, will help you predict the probable changes in oxidation state in a particular reaction. Note that the oxidation state is given just before each formula in the chart.

TABLE 5.1

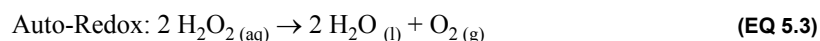
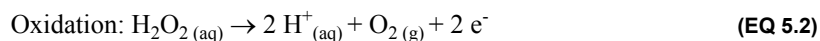
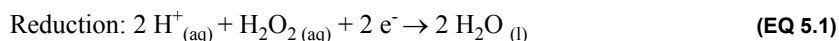
		Oxidation State	Formulas	Comments
Sulfur Compounds				
		+6	SO ₃ , H ₂ SO ₄ , SO ₄ ²⁻	Concentrated acid is a strong oxidizing agent.
		+4	SO ₂ , H ₂ SO ₃ , SO ₃ ²⁻	Active either as oxidizing agent or reducing agent.
		+2	S ₂ O ₃ ²⁻	Thiosulfate ion decomposes to S and H ₂ SO ₃ in acid solution. Oxidized to S ₄ O ₆ ²⁻ (tetrathionate ion) by free I ₂ .
		0	S	
		-1	S ₂ ²⁻ or S _x ²⁻	Polysulfide ion decomposes to S and H ₂ S in acid solution.
		-2	H ₂ S, S ²⁻	Strong reducing agent, usually oxidized to S.
Oxygen Compounds, Peroxides				
			Acidic Basic	
		0	O ₂	
		-1	H ₂ O ₂ HO ₂ ⁻	
		-2	H ₂ O OH ⁻	
Chlorine Compounds				
		+7	(Cl ₂ O ₇), HClO ₄ , ClO ₄ ⁻	Cl ₂ O ₇ is unstable. HClO ₄ is a very strong oxidizing agent reduced to Cl ⁻ .
		+5	HClO ₃ , ClO ₃ ⁻	Strong oxidizing agent. Reduced to Cl ⁻ .
		+4	ClO ₂	Explosive.
		+3	HClO ₂ , ClO ₂ ⁻	Good oxidizing agent. Reduced to Cl ⁻ .
		+1	Cl ₂ O, HClO, ClO ⁻	Good oxidizing agent. Reduced to Cl ⁻ .
		0	Cl ₂	Good oxidizing agent. Reduced to Cl ⁻ .
		-1	Cl ⁻	
Nitrogen Compounds				
		+5	N ₂ O ₅ , HNO ₃ , NO ₃ ⁻	Strong oxidizing agent, usually reduced to NO ₂ and NO (in dilute. acid). With strong reducing agent may go to NH ₃ .
		+4	NO ₂ , (N ₂ O ₄)	A heavy brown gas.
		+3	(N ₂ O ₃ , HNO ₂), NO ₂ ⁻	N ₂ O ₃ and HNO ₂ are unstable. Nitrites are usually stable. Oxidizing or reducing agents.
		+2	NO	Oxidized by air to NO ₂ .
		+1	N ₂ O	Supports combustion vigorously.
		0	N ₂	
		-3	NH ₃ , NH ₄ OH, NH ₄ ⁺	

		Oxidation State	Formulas	Comments
Chromium Compounds				
			Acidic Basic	
		+6	Cr ₂ O ₇ ²⁻ CrO ₄ ²⁻	Strong oxidizing agents. Dichromate ion is orange and chromate ion is yellow.
		+3	Cr ³⁺ Cr(OH) ₄ ²⁻	Amphoteric. Cr ³⁺ is green to violet. Cr(OH) ₄ ²⁻ is green.
		+2	Cr ²⁺	An uncommon ion, because it is a strong reducing agent that reduces water to hydrogen gas.
		0	Cr	The metal.
Manganese Compounds				
		+7	MnO ₄ ⁻	Purple. Strong oxidizing agent, reduced to Mn ²⁺ in acid solution or to MnO ₂ (sometimes MnO ₄ ²⁻) in neutral or basic solution.
		+6	MnO ₄ ²⁻	Green. Easily reduced to MnO ₂ .
		+4	MnO ₂ , MnO(OH) ₂	Brown as precipitated from solution.
		+3	Mn ³⁺ , Mn(OH) ₃	Mn ³⁺ is unstable, gives Mn ²⁺ and MnO ₂ .
		+2	Mn ²⁺ , Mn(OH) ₂	Colorless in solution, pale pink as solid Mn(II) salts. Mn(OH) ₂ is oxidized by air to Mn(OH) ₃ .
		0	Mn	The metal.

Let us comment briefly on the charts for sulfur and oxygen compounds.

It should be obvious from the chart of sulfur compounds that since H₂S represents the lowest possible oxidation state it can act only as a reducing agent in an oxidation-reduction, redox, process. In such a process it can be oxidized to free sulfur or to some higher state, such as a sulfate, its extent of oxidation, depending on the conditions and the strength of the oxidizing agent. Sulfuric acid, H₂SO₄, representing the highest oxidation state, can act only as an oxidizing agent, its reduction products being any lower states of sulfur. However, since sulfurous acid, H₂SO₃, represents an intermediate state of sulfur, it can act either as a reducing agent with substances that can take on electrons, or as an oxidizing agent with substances that can lose electrons.

Hydrogen peroxide and the peroxides are important oxidizing agents, both commercially and in the laboratory. Note, from Table 5.1 on page 42, that when hydrogen peroxide acts as an oxidizing agent it is reduced to water or, in basic solution, to hydroxide ion. It is oxidized to free oxygen only when it acts as a reducing agent, in the presence of certain catalysts, is due to the ability of one molecule to oxidize another molecule of the same substance (auto-oxidation-reduction). The half-reactions corresponding to these statements are



Listed below are some important categories of common oxidizing and reducing agents.

Some Common Oxidizing Agents

1. The halogens and oxygen-reduced to their negative ions, such as the following:

F_2 reduced to F^-	Cl_2 reduced to Cl^-	O_2 reduced to O^{2-}
------------------------	--------------------------	---------------------------

2. Ions in which the metal ion has a stable lower oxidation state such as the following:

Ce^{4+} reduced to Ce^{2+}	Mn^{3+} reduced to Mn^{2+}	Co^{3+} reduced to Co^{2+}
--------------------------------	--------------------------------	--------------------------------

3. Oxygen containing complex ions, where the central atom is in a high oxidation state:

MnO^- reduced to Mn^{2+}	ClO_3^- reduced to Cl^-
$Cr_2O_7^{2-}$ reduced to Cr^{3+}	NO_3^- reduced to NO

Some Common Reducing Agents

1. The metal oxidized to their positive ions - such as these

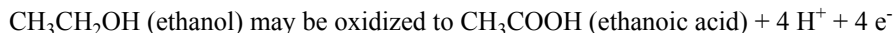
Sn oxidized to Sn^{4+}	Zn oxidized to Zn^{2+}
----------------------------	----------------------------

2. Ions in which the metal has another higher oxidation state, such as the following:

Sn^{2+} oxidized to Sn^{4+}	Fe^{2+} oxidized to Fe^{3+}	Hg_2^{2+} oxidized to Hg^{2+}
---------------------------------	---------------------------------	-----------------------------------

3. Carbon and organic compounds may be oxidized to CO or CO_2 and H_2O :

- C (coke, much used in industry) oxidized to CO or to CO_2
- alcohols \rightarrow carboxylic acids



- aldehydes \rightarrow carboxylic acids.

**Balancing of Oxidation-Reduction (Redox) Equations**

In balancing any oxidation-reduction, redox, reaction, you must first know all of the reactants and products. If you do not, you will not be able to balance it correctly. Once the reactants and products are known, balance the reaction by keeping in mind that, in a redox reaction which is essentially an electron-transfer reaction, relative amounts of reactants must be taken in such a way that all the electrons supplied by the oxidation process are used in the reduction process. There are several methods for doing this, each differing in mechanics of operation, but all based on the same principle.

The Half-Reaction Method

Separated half-reactions, or electron reactions, are written for the oxidation and for the reduction processes. In developing these, we can first determine the number of electrons required from the change in oxidation number, then insert H^+ (or OH^- if the solution is basic) to balance the charges, and finally add H_2O to balance the atoms.

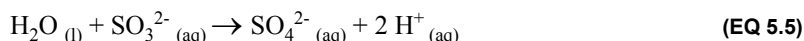
The reverse process is sometimes used. First, balance the atoms in half-reactions by inserting H^+ and H_2O as needed, then insert as many electrons as needed to balance the charges. Study the following example:

EXAMPLE 5.2

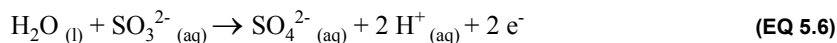
Let us consider the oxidation of potassium sulfite, K_2SO_3 , by potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, in an acid solution (assume hydrochloric acid for this example). Referring to the charts of oxidation states for sulfur compounds, we find that sulfite ions will be oxidized to sulfate ions ignoring the spectator ions of potassium:



We need another oxygen atom on the left; this is supplied by water, and we write the hydrogens as 2H^+ on the right. (Note that we keep oxidation states of oxygen -2 and hydrogen +1 on both sides of the equation, since they are not the substances oxidized and reduced.) Our partial equation then becomes:



We still need to balance the charges so they are the same on both sides of the equation. To do so we add two electrons to the right:

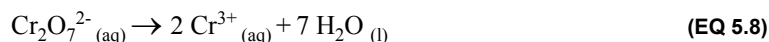


Thereby completing the oxidation half-reaction, and demonstrating the fact that in an oxidation process, electrons are lost.

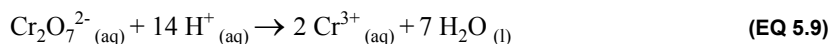
Referring to the charts of oxidation states for chromium compounds, we find that the dichromate ion will be reduced to the chromic ion, Cr^{3+} , as will be evidenced by the green color of the solution. The several steps are as follows. First balance the number of chromium atoms by putting a 2 in front of Cr^{3+} :



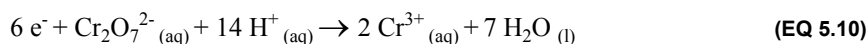
Next, balance the oxygen atoms by adding 7 H_2O :



Then balance the hydrogen atoms and oxygen by inserting 14 H^+ to react with the 7 oxygen atoms to form the 7 H_2O :



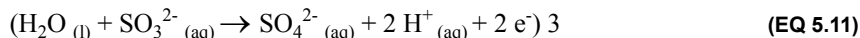
Finally, we balance the charges. As above written, we have 12 positive on the left and 6 positive on the right, or a net charge of +6 on the left. We therefore need 6 electrons on the left to complete the reduction half-reaction:



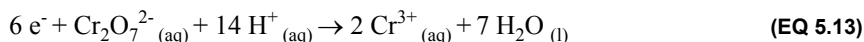
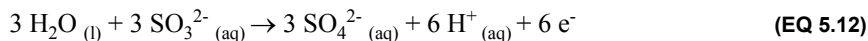
This emphasizes the fact that in a reduction process electrons are gained. Note the requirement of 6 electrons corresponds to the change in oxidation state of chromium from +6 to +3, so two chromium atoms decrease by a total of 6 charges.

Finally, we may combine the two processes in such a way that we balance electrons gained against electrons lost.

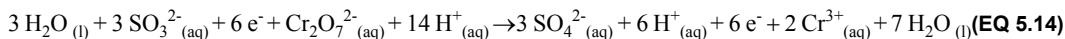
To do this we multiply the oxidation half-reaction by 3 and add algebraically to the reduction half-reaction:



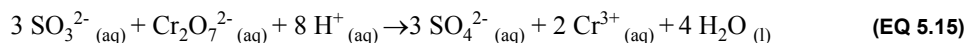
Now that the number of electrons transferred for the oxidation and reduction half-reactions are equal, 6e^- , the two half-reactions are:



Adding the two half-reactions together:

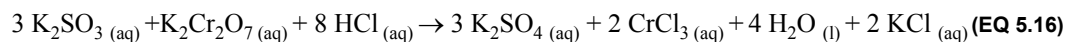


Canceling like terms, $\text{H}_2\text{O}_{(l)}$, e^- , and $\text{H}^+{}_{(aq)}$, from both sides of the equation the balanced net ionic equation is:



Always check your results to make certain that both atoms and charges are balanced in the equation.

Adding back the potassium and chloride counterions for the reaction gives the balanced molecular equation of:



Post Lab Questions

1. As a review, in the following equations for familiar reactions, underline the reducing agent once and oxidizing agent twice. At the right, indicate the change in oxidation number per atom for each element concerned. If there is no change write no valance change "NVC."

TABLE 5.3

Reactions	Element Oxidized	Oxidation Number increase per atom	Element Reduced	Oxidation number decrease per atom
$2 \text{Al}_{(s)} + 3 \text{Cl}_{2(g)} \rightarrow 2 \text{Al}^{3+}_{(aq)} + 6 \text{Cl}^{-}_{(aq)}$				
$\text{Ag}^{+}_{(aq)} + \text{Cl}^{-}_{(aq)} \rightarrow \text{AgCl}_{(s)}$				
$\text{Mg}_{(s)} + 2 \text{H}^{+}_{(aq)} \rightarrow \text{Mg}^{2+}_{(aq)} + \text{H}_{2(g)}$				
$\text{Cu}^{2+}_{(aq)} + \text{H}_2\text{S}_{(g)} \rightarrow \text{CuS}_{(s)} + 2 \text{H}^{+}_{(aq)}$				
$\text{Ba}_{(s)} + 2 \text{H}_2\text{O}_{(l)} \rightarrow \text{Ba}^{2+}_{(aq)} + 2 \text{OH}^{-}_{(aq)} + \text{H}_{2(g)}$				
$3 \text{Na}_2\text{O}_2_{(s)} + \text{Cr}_2\text{O}_3_{(s)} + \text{H}_2\text{O}_{(l)} \rightarrow 6 \text{Na}^{+}_{(aq)} + 2 \text{CrO}_4^{2-}_{(aq)} + 2 \text{OH}^{-}_{(aq)}$				
$\text{H}_2\text{O}_2_{(aq)} \rightarrow \text{H}_2\text{O}_{(l)} + \frac{1}{2} \text{O}_{2(g)}$				
$\text{CO}_2_{(g)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{CO}_3_{(aq)}$				
$\text{CO}_2_{(g)} + \text{C}_{(s)} \rightarrow 2 \text{CO}_{(g)}$				
$\text{HCl}_{(g)} + \text{NH}_3_{(g)} \rightarrow \text{NH}_4\text{Cl}_{(s)}$				
$2 \text{ZnS}_{(s)} + 3 \text{O}_2_{(g)} \rightarrow 2 \text{ZnO}_{(s)} + 2 \text{SO}_2_{(g)}$				
$4 \text{H}^{+}_{(aq)} + 2 \text{Cl}^{-}_{(aq)} + \text{MnO}_2_{(s)} \rightarrow \text{Mn}^{2+}_{(aq)} + \text{Cl}_{2(g)} + 2 \text{H}_2\text{O}_{(l)}$				
$10 \text{H}^{+}_{(aq)} + \text{SO}_4^{2-}_{(aq)} + 8 \text{I}^{-}_{(aq)} \rightarrow 4 \text{I}_2_{(s)} + \text{H}_2\text{S}_{(g)} + 4 \text{H}_2\text{O}_{(l)}$				

2. Show the change in oxidation number (give the number of electrons gained or lost *per atom*) in the following:

TABLE 5.4

Reaction	Number of e- lost or gained per atom
$\text{PO}_3^{3-}(\text{aq}) \rightarrow \text{PO}_4^{3-}(\text{aq})$	P lost $2 e^-$
$\text{NO}_2^-(\text{aq}) \rightarrow \text{NO}_3^-(\text{aq})$	
$\text{SO}_2(\text{g}) \rightarrow \text{S}_2^{2-}(\text{aq})$	
$\text{MnO}_4^-(\text{aq}) \rightarrow \text{MnO}_2(\text{s})$	
$\text{KClO}_2(\text{s}) \rightarrow \text{KCl}(\text{s})$	
$\text{NH}_3(\text{g}) \rightarrow \text{NH}_4^+(\text{aq})$	
$\text{HCOOH}(\text{aq}) \rightarrow \text{HCHO}(\text{aq})$	

3. Give the formula of a product (derived from the first substance in the statement) that may be formed in the following reactions. (Note: in the example any lower oxidation state compound is possible; but not any higher one. Some are more probable than others.)

TABLE 5.5

Reaction	Possible Products
H_2SO_3 is treated with a reducing agent	$\text{S}(\text{s})$, $\text{S}_2^{2-}(\text{aq})$, or $\text{H}_2\text{S}(\text{g})$
HClO_2 is treated with a reducing agent	
H_2SO_3 is treated with an oxidizing agent	
SnCl_4 is treated with zinc dust	
$\text{Cr}_2\text{O}_7^{2-}$ is treated with SnCl_2	
KMnO_4 is treated with FeSO_4	
MnO_2 is treated with concentrated HCl	

4. Write the half-reaction equation for the oxidation of:

TABLE 5.6

Reaction	Balanced Net Ionic Equation
NO_2^- (aq) to NO_3^- (aq) (acidic)	
H_2S (g) to SO_4^{2-} (aq) (acidic)	
NH_4^+ (aq) to NO_3^- (aq) (acidic)	
H_2O_2 (aq) to O_2 (g) (basic)	
$\text{Cr}(\text{OH})_4^-$ (aq) to CrO_4^{2-} (aq) (basic)	
ClO^- (aq) to ClO_4^- (aq) (acidic)	
HCOOH (aq) to CO_2 (g) (acidic)	

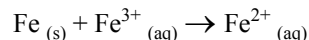
5. Write the half-reaction equation for the reduction of:

TABLE 5.7

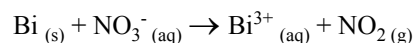
Reaction	Balanced Net Ionic Equation
SO_3^{2-} (aq) to H_2S (g) (acidic)	
MnO_4^{2-} (aq) to MnO_2 (s) (basic)	
HO_2^- (aq) to OH^- (aq) (basic)	
HCOOH (aq) to CH_3OH (aq) (acidic)	
ClO_3^- (aq) to Cl^- (aq) (acidic)	
$\text{Cr}_2\text{O}_7^{2-}$ (aq) to Cr^{3+} (aq) (acidic)	
CH_3NO_2 (aq) to CH_3NH_2 (aq) (acidic)	

6. Given the reactants and products, write balanced net ionic equations for the following reactions. Supply H_2O , H^+ , or OH^- as needed.

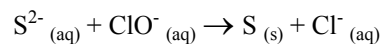
a. Iron filings are added to an aqueous iron(III) chloride solution.



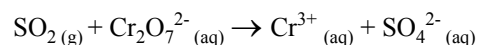
b. Bismuth metal is dissolved in hot, concentrated nitric acid, HNO_3 , giving off a brown gas.



c. A mixture of sodium sulfide, Na_2S , sodium hypochlorite, NaClO , and sodium hydroxide, NaOH , solutions is warmed, giving a suspended precipitate.



d. Sulfur dioxide gas, SO_2 , is bubbled into an acidic potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, solution.



7. Predict the products and write a balanced net ionic equation for the following reactions:

a. Tin(II) chloride is added to potassium permanganate solution in acidic conditions.

b. Zinc dust is treated with dilute nitric acid, forming ammonium ions.

c. Potassium permanganate oxidizes the oxalate ions in calcium oxalate to carbon dioxide in an acidic solution.

Redox Reactions – The Activity Series

Objective

In this experiment you will perform several reactions between various metals and solutions of ionic compounds. The goal is to determine the relative reactivity of the elements. By observing the reactions that occur (or do not occur), an activity series will be created.

Introduction

Redox reactions are defined as reactions in which electrons are transferred from one element to another. The element that gains one or more electrons is said to be reduced and the element that loses one or more electrons is said to be oxidized. There are many types of redox reactions but in this experiment, we will limit our examination to **single displacement reactions**. These are reactions in which an ion in solution gets replaced by some other ion. The ion originally in solution gets reduced or oxidized to the elemental form. The ion that ends up in the final solution is formed by oxidation of a metal atom, oxidation of a metal cation or reduction of a nonmetal.

EXAMPLE 6.1

- $$\text{Cu}_{(s)} + 2 \text{AgNO}_{3(aq)} \rightarrow 2 \text{Ag}_{(s)} + \text{Cu}(\text{NO}_3)_{2(aq)}$$

In this reaction, copper metal is oxidized to the Cu^{2+} ion and replaces the silver ion, which is reduced to silver metal.
- $$\text{Fe}(\text{NO}_3)_{2(aq)} + 3 \text{AgNO}_{3(aq)} \rightarrow 3 \text{Ag}_{(s)} + \text{Fe}(\text{NO}_3)_{3(aq)}$$

In this example, the Fe^{2+} ion is oxidized to the Fe^{3+} ion. Here the Fe^{3+} ion replaces the Fe^{2+} ion in solution while silver ion gets reduced to the metal.
- $$\text{Zn}_{(s)} + 2 \text{HBr}_{(aq)} \rightarrow \text{ZnBr}_{2(aq)} + \text{H}_{2(g)}$$

Acids can also oxidize metals: notice that zinc metal gets oxidized by the hydrogen ion. Hydrogen ion gets reduced to form H_2
- $$2 \text{KI}_{(aq)} + \text{F}_{2(g)} \rightarrow \text{I}_{2(s)} + 2 \text{KF}_{(aq)}$$

In this reaction, the nonmetal anion, iodide ion, is being oxidized to elemental iodine while fluorine gets reduced to the fluoride anion.

In each case in Example 6.1 the overall process is the same: one species gets oxidized while another species gets reduced. Or to say this another way: one species replaces another in solution.

Referring to Example 6.1, determine which species in each pair is more active:

1. copper or silver?

Answer: copper

2. silver ion or iron(II) ion?

Answer: iron(II) ion

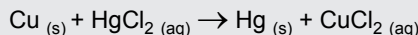
3. iodide or fluorine?

Answer: fluorine

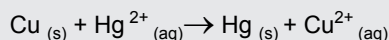
In this experiment, the student will perform several redox reactions and determine the relative ease of oxidation for each element. An activity table will be constructed based upon the results. For example:

EXAMPLE 6.2

If a strip of copper metal is placed into a solution of mercury(II) chloride, the solution will become blue over time and a small pool of liquid mercury will collect at the bottom of the container. The reaction written below is occurring.



Copper is more easily oxidized than mercury because we observe that the copper replaces the mercury as the more oxidized substance. If we were to try the reverse reaction, that is to pour some liquid mercury into a solution of copper chloride, there would be no reaction. Again we would conclude that copper is more easily oxidized because mercury is not able to replace copper as the more oxidized substance. We state that copper is more active than mercury because it is the most easily oxidized. The actual reaction that occurs is called the net ionic reaction:



If the reaction proceeds to the right, copper is more active than mercury. If the reaction proceeds to the left, mercury is more active than copper. Because the reaction proceeds to the right, copper is the more active metal.

EXAMPLE 6.3

A strip of copper metal is dropped into a solution of lead(II) chloride. There is no visible reaction.

Which is more active, copper or lead?

Answer: lead

Combining the results of this experiment with the results from the reaction between copper and mercury ion (Example 6.2), can you determine whether lead is more or less active than mercury?

Answer: lead is more active than mercury.

Therefore, the activity series for Pb, Cu, and Hg from most active to least is $\text{Pb} > \text{Hg} > \text{Cu}$.

Procedure

You will mix the following sets of substances and determine the more easily oxidized species in each case. From the relative oxidizability of each set, you will develop a comprehensive activity series. Be sure the data is clearly organized, and that clear and complete observations are made for each reaction. Observations should include color changes, temperature changes, gas formation, and precipitate formation.

In this procedure, there are various combinations of reactants to observe:

Reactions between a metal and a salt solution. The student must determine whether the metal or the salt cation is more active. *The actual comparison is to determine which metal is more easily oxidized (more active).*

Reactions between a metal and an acid solution. The student must determine whether the metal or the hydrogen ion is more active. *The actual comparison is between a metal and hydrogen.*

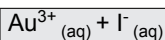
Reactions between a halogen (I₂ and Br₂) and a halide ion. The student must determine which halide ion is more active. *The actual comparison is that between halogens.*

Reactions between a halide ion and a metal ion. The student must determine whether the halide ion or metal ion is more active. *The actual comparison is between a metal and a nonmetal.*

As you perform each reaction, keep in mind the following:

1. Be sure to sand all of the metal pieces to provide a clean metal surface.
2. Watch the reactions for at least 15 minutes before deciding whether or not a reaction has occurred. Some of the reactions are slow.
3. Describe the reactions that occur in such a manner that you could identify it from your lab notebook. Describe texture, color, location of precipitate (i.e., bottom of test tube or a deposit on the metal strip), etc. Be detailed in these descriptions, they are your observations and therefore your data.
4. Note that some of the metals are reacted with acids. Here, the cation is H⁺, which will be reduced to H_{2(g)} if a reaction occurs.

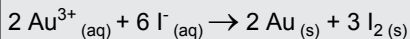
EXAMPLE 6.4 Sample Data Log



Log: Mixed with 1 mL of KI with about 1 mL of gold(III) nitrate.

Observations: The solution became darker and it was difficult to determine what was happening. After the reaction had progressed for about 10 minutes, I poured some of the supernatant into another tube and added hexane. A pink color was extracted into the hexane layer.

The net ionic reaction would be:



Analysis: Stronger oxidizing agent is Au. More active element is I.

Reactions:

Metal + salt solution.

1. Place a strip of copper metal into a 3 mL sample of 0.1 M ZnSO₄.

2. Place a strip of copper metal into a 3 mL sample of 0.1 M FeSO_4 .
3. Place a strip of zinc metal into a 3 mL sample of 0.1 M CuSO_4 .
4. Place a strip of zinc metal into a 3 mL sample of 0.1 M FeSO_4 .
5. Place a piece of steel wool (iron) into a 3 mL sample of 0.1 M CuSO_4 .
6. Place a piece of steel wool (iron) into a 3 mL sample of 0.1 M ZnSO_4 .

Metal + acid solution.

1. Place a strip of copper metal into a 3 mL sample of 1.0 M H_2SO_4 (or what the stockroom has available for this experiment).
2. Place a strip of zinc metal into a 3 mL sample of 1.0 M H_2SO_4 (or what the stockroom has available for this experiment).
3. Place a piece of steel wool (iron) into a 3 mL sample of 3.0 M H_2SO_4 (or what the stockroom has available for this experiment).

Halogen + halide solution. For reactions involving the halogens, a two-phase system will be used. The halide ion is soluble in water and the halogen will be partitioned between an aqueous layer and an organic (hexane) layer. The student must first be able to recognize what happens when a halide ion is oxidized to the halogen: When a halide gets oxidized, the resulting halogen dissolves into the organic layer and the hexane becomes colored. Hexane is a colorless liquid. The appearance of a colored hexane layer is evidence for oxidation of a halide ion to the halogen.



NOTE: This simple procedure must be done before the halogen reactions are performed so that the student easily recognizes what happens when the halides are oxidized.

1. Add a few drops of I_2 (in methanol) to a mixture of 3 mL of water and 1 mL of hexane.
2. Shake well and record the color of the organic, hexane, layer and the color of the aqueous layer. The halogen will dissolve into the organic layer.
3. Repeat with the Br_2 (in water). Now you know how to detect the presence of a halogen.



CAUTION: When you are finished working with the halogen solutions, dispose of them in the appropriate container in the hood.

1. Mix 3 mL of 0.1 M KBr with 1 mL of hexane (this may be already prepared for you by the stockroom). Add a few drops of I_2 .
2. Mix 3 mL of 0.1 M KI with 1 mL of hexane (this may be already prepared for you by the stockroom). Add a few drops of Br_2 .

Halogen/Halide + metal/metal ion. You will examine the redox chemistry of iron(III) ions and copper metal with the halogen/halides. Use the information gained in these experiments to get a complete activity series.

All balanced equations should be redox equations. Do not include the reactions of copper with ammonia or the reactions to detect halides with silver nitrate. Note that the Fe^{3+} ion will be reduced to Fe^{2+} ion if a reaction occurs. Also remember that the hexane is used only to detect the presence of either I_2 or Br_2 .

1. Mix 1 ml of 0.1 M FeCl₃ with 2 mL of 0.1 M KBr.
2. Mix 1 ml of 0.1 M FeCl₃ with 2 mL of 0.1 M KI.
3. Add some copper turnings to 10 mL of Br₂ water. Shake well for several minutes. Allow any precipitate that forms to settle and pour off some of the liquid phase into each of two new test tubes.

To the first tube add a few drops of 0.1M AgNO₃, does a AgBr precipitate form?

To the second tube add 1 mL of 6 M NH₃, does a blue Cu(NH₃)₄²⁺ (tetraamminecopper(II) ion) complex form?

4. Add some copper turnings to 15 mL of 0.05 M I₂ methanol. Shake well for several minutes. Allow any precipitate that forms to settle and pour off some of the liquid phase into each of two new test tubes.

To the first tube add a few drops of 0.1M AgNO₃, does a AgI precipitate form?



NOTE: You may see a precipitate of CuI₂ here, do the test for Cu²⁺ to be sure that the expected reaction occurred.

5. To the second tube add 1 mL of 6 M NH₃, does a blue Cu(NH₃)₄²⁺ (tetraamminecopper(II) ion) complex form?

Results and Calculations

In your lab book create a table like Table 6.5 on page 56. Be sure to write balanced equations for each reaction that occurred. If no reaction occurs state that by writing NO RXN. Do not write out reactions that will not occur. Remember that you can determine relative activity from a null result as well as a positive result. For each experiment note which of the two elements is more active.

Be careful when you start working with the halogens. All of the balanced equations should be redox equations. Do not include the reactions of copper with ammonia or the reactions to detect halides with silver nitrate in your report.

Note that Fe³⁺ will be reduced to Fe²⁺ if a reaction occurs. Also remember that hexane is used only to detect the presence of either I₂ or Br₂.

From the data you have gathered in this experiment, develop an activity series for Br, Cu, Fe, Fe³⁺, H, I and Zn, as was done for Pb, Cu, and Hg in the introduction.

- Did you have any difficulties determining the activity series?
- If so, what species are you unsure of the relative activities?
- What additional experiments might help you to make a better assessment of the relative activities?

TABLE 6.5

	Reactants		Observation	Net Ionic Reaction	Element Oxidized	Element Reduced	Stronger Oxidizing Agent	More Active
1	Cu	Zn ²⁺						
2	Cu	Fe ²⁺						
3	Zn	Cu ²⁺						
4	Zn	Fe ²⁺						
5	Fe	Cu ²⁺						
6	Fe	Zn ²⁺						
7	Cu	H ⁺						
8	Zn	H ⁺						
9	Fe	H ⁺						
10	I ₂	Br ⁻						
11	Br ₂	I ⁻						
12	Fe ³⁺	Br ⁻						
13	Fe ³⁺	I ⁻						
14	Cu	I ₂						
15	Cu	Br ₂						

Objective

Seven reactions are carried out, and their qualitative features are carefully observed and recorded. The basic objectives of this investigation are to illustrate the following:

1. the four reaction categories;
2. some of the signs which indicate that a chemical reaction has occurred or is in progress;
3. the wide variety of stoichiometric ratios featured in chemical reactions;
4. transform copper into various copper compounds and reclaim pure copper.

Introduction

Several interesting concepts may be demonstrated by studying a sequence of reactions involving compounds of copper. Included in this series are double displacement, decomposition, acid-base, and oxidation-reduction processes.

A quantity of copper metal, issued to each student, is reacted in the first of several procedures to be given. The experiment will guide you in transforming copper into various copper compounds and back to pure copper.

In the final step, copper metal is recovered and weighed. A comparison of the mass of reclaimed copper with the mass of the original sample provides evidence of how carefully the experiment has been performed by calculating the percent recovery of the copper.

$$\% \text{ recovery} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100$$

(EQ 7.1)

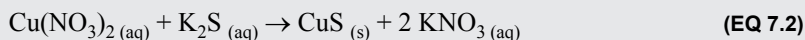
For each reaction, you will write a balanced chemical equation, calculate a theoretical yield, and classify the type of reaction. Example 7.1 below illustrates possible one transformation. It is not done in this experiment, but could be.

EXAMPLE 7.1

How would you prepare and isolate copper(II) sulfide from copper(II) nitrate?

Answer: You would mix it with a solution of potassium sulfide. The copper(II) sulfide would precipitate and you could filter the solution and the precipitate would contain pure copper sulfide. The potassium nitrate would remain in solution and be discarded with the filtrate.

Balanced chemical reaction:



Theoretical yield:

$$0.578 \text{ g Cu}(\text{NO}_3)_2 \times \frac{187.57 \text{ g Cu}(\text{NO}_3)_2}{65.38 \text{ mol Cu}(\text{NO}_3)_2} \times \frac{1 \text{ mol CuS}}{1 \text{ mol Cu}(\text{NO}_3)_2} \times \frac{95.61 \text{ g CuS}}{1 \text{ mol CuS}} = 0.294 \text{ g CuS} \quad (\text{EQ 7.3})$$

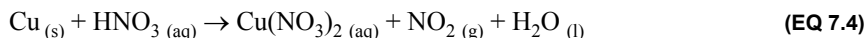
Reaction Type: *Double displacement/precipitation*

Procedure



NOTE: You should have a clearly written log of what you did and saw. Be sure to note any unusual or unexpected observations in your running log. Good descriptions are important here.

Step 1: Preparation of copper(II) nitrate from copper metal



1. Place the weighed sample of copper in a 250 mL beaker and slowly add 2 mL of 16 M HNO₃(aq). The brown gas evolved is nitrogen dioxide, NO₂. Be sure to describe the appearance of your original piece of copper.
2. The reaction mixture may be heated on a hot plate to facilitate the reaction; do not boil the mixture to dryness.
3. Allow the mixture to stand until all the metal has reacted, and then slowly dilute the solution that remains with 20 mL of distilled water.

Step 2: Preparation of copper(II) hydroxide from copper(II) nitrate



4. To the solution from “Step 1: Preparation of copper(II) nitrate from copper metal” on page 58, add 8 M NaOH(aq) solution drop by drop, with constant stirring. The solid that forms is copper(II) hydroxide.
5. Continue the addition of the 8 M NaOH(aq), frequently testing the solution with red litmus paper. This is readily done by touching a clean stirring rod to the solution and transferring a

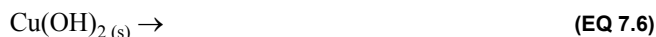
drop of liquid to a piece of litmus paper. When the solution becomes basic, the litmus paper will turn blue.

- At this point, discontinue the addition of NaOH (aq) since the precipitation of the hydroxide is essentially complete.



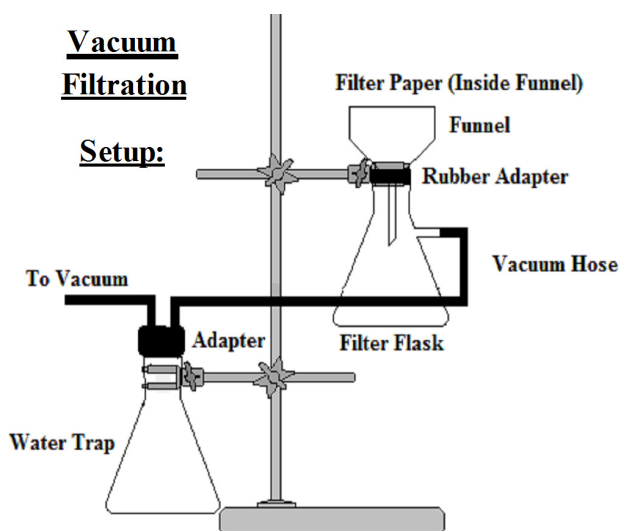
Be careful not to transfer any of the blue precipitate during this procedure since it can produce a blue coloration of the paper even though the solution is not alkaline.

Step 3: Preparation of copper(II) oxide from copper(II) hydroxide



- Add 30 mL of deionized water to the mixture from “Step 2: Preparation of copper(II) hydroxide from copper(II) nitrate” on page 58.
- Stirring constantly, gently boil the mixture until the solid copper(II) hydroxide is completely converted to copper(II) oxide.
- The precipitate should settle to the bottom of the beaker as it boils. It may be stored until the next lab period at this point.
- Perform a suction filtration and collect the copper(II) oxide in a Büchner funnel. A *fiberglass* pad filter paper should be used. Be sure to place the rough side up and wet it with water before beginning the filtration.

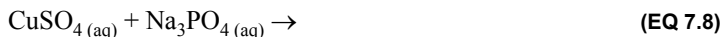
FIGURE 7.1



- The filtrate may be discarded if it is free of black copper(II) oxide; otherwise it must be poured back into the funnel and filtered again.
- Remove the suction from the filter flask and wash the solid in the funnel with a small volume of deionized water; apply suction in order to remove the wash liquid.
- Repeat this operation and then discard all the wash solutions.
- Do not store the solid collected here until the next lab period!

Step 4: Preparation of copper(II) sulfate from copper(II) oxide

15. Rinse the filter flask several times with distilled water. Reassemble the filtration apparatus, but do not apply suction during this step, a reaction with sulfuric acid is occurring.
16. Slowly add 2 M $\text{H}_2\text{SO}_{4(aq)}$ drop by drop to the funnel. Allow sufficient time for the solid to react in order to avoid using a large excess of the acid.
17. A total of 4 to 5 mL of the acid solution is required.
18. The contents of the funnel may be swirled, but this should be done carefully to avoid spillage.
19. There is a tendency for filter paper to lift off the surface of the funnel during this operation. This should cause no problem as long as any oxide which passes through the filter undergoes reaction in the filtration flask.
20. Continue the addition of 2 M $\text{H}_2\text{SO}_{4(aq)}$ until the oxide has completely reacted and all that remains is an aqueous solution containing copper(II) sulfate.
21. Apply suction to the filtration apparatus to draw the solution into the filter flask.
22. Rinse the funnel and filter paper with several small portions of deionized water and collect this wash liquid in the flask.
23. Carefully pour the contents of the filter flask into a clean 250 mL beaker.
24. Rinse the flask with a stream of deionized water, allowing the liquid to flow into the beaker.

Step 5: Preparation of copper(II) phosphate from copper(II) sulfate.

25. Add 8 M $\text{NaOH}_{(aq)}$ drop by drop, with constant stirring, to the solution from “Step 4: Preparation of copper(II) sulfate from copper(II) oxide” on page 60. This addition is continued until a blue precipitate of copper(II) hydroxide just begins to persist.
26. Then introduce 20 mL of 0.5 M $\text{Na}_3\text{PO}_{4(aq)}$ and stir the mixture thoroughly.
27. Allow any precipitate of copper(II) phosphate to settle and test the supernatant liquid with litmus paper.
28. If the liquid is acidic (indicator color is red), carry out a dropwise addition of 8 M $\text{NaOH}_{(aq)}$, with constant stirring, until it is just basic, and allow the precipitate to settle.
29. Carefully decant the supernatant, if possible, and dispose of it. Use an eye-dropper to remove as much of the remaining supernatant as possible without removing any precipitate.
30. Save all of the precipitate (note the color in your lab book) for “Step 6: Preparation of copper(II) chloride from copper(II) phosphate” on page 60.

Step 6: Preparation of copper(II) chloride from copper(II) phosphate

31. Add sufficient 6 M HCl with stirring to the beaker containing the copper(II) phosphate precipitate to dissolve all of the precipitate.

Step 7: Preparation of copper from copper(II) chloride

32. To the solution from “Step 6: Preparation of copper(II) chloride from copper(II) phosphate” on page 60 add a piece aluminum foil about the size of your filter paper and stir.
33. Two chemical reactions are evident: (a) the principal one in which a deposit of elemental copper appears; and (b) a side reaction in which hydrogen gas is evolved.
34. It may be necessary to introduce an additional small quantity of aluminum in order to complete the principal reaction.
35. Additional 6 M HCl also may be needed to react with any excess aluminum. The completion of the principal reaction is indicated by the disappearance of the blue color of the solution and the absence of further copper formation.



36. To test for completeness of the reaction withdraw a 1-2 mL sample of the solution and add 6 M ammonia until you have a solution which is basic to litmus.
37. If copper is present you should observe the formation of a bright blue copper ammonium complex.
38. During the final stages of the reactions, weigh a piece of Whatman No. 4 filter paper. This paper should be suitable for gravity filtration of the copper metal product.
39. Proceed with the filtration once the formation of copper metal is complete and there are no pieces of aluminum remaining.
40. Fine particles of copper tend to pass through the filter paper, but usually the quantity is not significant and can be ignored.
41. Wash the copper with deionized water and then a few mL of acetone, a volatile liquid that permits the copper to dry rapidly.
42. Remove the filter paper from the funnel and spread it out on a dry watch glass so that the copper product may dry.
43. Meanwhile, weigh a clean, dry sample bottle. Be sure to describe the appearance of your reclaimed copper.
44. Place the dried, reclaimed copper and the filter paper in the sample bottle and reweigh.
45. Put a label on the bottle containing your name and the mass of the recovered copper.
46. Give the sample to your lab instructor for further evaluation.
47. The quality of the product depends on color and dryness as well as absence of visible impurities.

Calculations and Results

1. For each reaction you will:
 - a. Write a description of what you did and what you observed.
 - b. Write a balanced equation for the reaction and identify its type as double displacement, decomposition, acid-base, and/or redox.
 - c. Calculate the theoretical yield (expected yield) of the product based upon the theoretical yield of the preceding step.

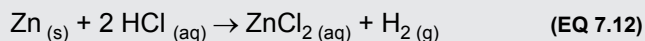


NOTE: You need to summarize your major data. This may be done several ways including: a list or a table

2. Obtain the mass of copper reclaimed in “Step 7: Preparation of copper from copper(II) chloride” on page 60.
3. Calculate the actual yield of the copper metal.
4. Calculate the percent recovery of the copper metal.
5. Calculate the percent error for the theoretical and actual amount of copper obtained.

EXAMPLE 7.2

A 0.250 g sample of zinc metal was dissolved in 10.0 mL of 6.0 M HCl. When the shiny zinc was added to the HCl, it dissolved with the production of considerable gas to yield a colorless solution. The reaction was highly exothermic.



Reaction Type: Redox

$$\text{theoretical yield} = 0.250 \text{ g Zn} \times \frac{136.26 \text{ g ZnCl}_2}{65.38 \text{ g Zn}} = 0.521 \text{ g ZnCl}_2$$

If 0.4632 g of zinc chloride was recovered, what is the percent recovery?

$$\% \text{ recovery} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100 = \frac{0.4632 \text{ g}}{0.521 \text{ g}} \times 100 = 88.9\%$$

Post Lab Questions

1. If you need to produce 3.50 kg of copper metal from a contaminated sample of reclaimed copper wiring, which is 68.3% copper, how many kg of reclaimed copper wiring would you need to buy if your percent yield at each step is 90%? Assume that you will isolate the copper wiring by going through the steps in this lab. Be sure to show all stoichiometry used.

2. How might you prepare (in one step) copper(II) nitrate from copper(II) chloride? Include in your answer: the reagent that you would add, a description of the equation that would take place, and an explanation of how you would then isolate the pure copper(II) nitrate from the reaction mixture.
-
-
-
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-
3. How might you prepare (in one step) copper(II) hydroxide from copper(II) sulfate? Include in your answer: the reagent that you would add, a description of the equation that would take place, and an explanation of how you would then isolate the pure copper(II) hydroxide from the reaction mixture.

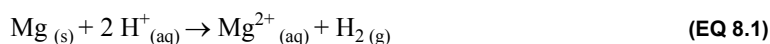
Analysis of a Two-Component Alloy

Objective

The goal in this experiment is to determine the mass percentage of each metal present in a sample of zinc-aluminum alloy.

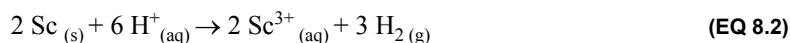
Introduction

Some of the more active metals, such as magnesium, will react readily with solutions of strong acids. The products from this reaction are hydrogen gas and a solution of a salt of the metal.



From this equation it is clear that a mole of magnesium produces one mole of hydrogen gas. If the hydrogen was collected under known conditions, it would be possible to calculate the mass of magnesium in a pure sample by measuring the amount of hydrogen gas produced by reaction with acid.

Scandium reacts spontaneously with strong acids in a manner similar to that shown by magnesium.



Using this reaction, it is possible to find the amount of scandium in a pure sample by measuring the amount of hydrogen produced by its reaction with an acid solution. In this reaction one and a half moles of hydrogen are produced by each mole of scandium that reacts.

Since the amount of hydrogen produced by a gram of Mg is not the same as the amount produced by a gram of Sc, it is possible to react an alloy of Mg and Sc of known mass with excess acid, determine the amount of hydrogen gas evolved, and calculate the percentages of Mg and Sc in the alloy using reaction equation 8.1 and 8.2 above.

In this experiment, you will react a weighed sample of a two-metal alloy with excess acid and collect the hydrogen gas evolved over water. If you measure the volume, temperature, and total pressure of gas and use the Ideal Gas Law, taking into account the pressure of water vapor in the system, you can calculate the number of moles of hydrogen gas produced by the sample.

$$PV = nRT \quad n = \frac{PV}{RT} \quad (\text{EQ 8.3})$$

where P is the partial pressure of hydrogen gas. The volume, V , and the temperature T of the hydrogen are easily obtained from the data. The pressure of the *dry* hydrogen, P_{H_2} , requires more attention. The total pressure P_{bar} is, by Dalton's Law, equal to the partial pressure of the hydrogen, P_{H_2} , plus the partial pressure of the water vapor, $P_{\text{H}_2\text{O}}$, plus or minus the water head pressure (as explained below), $P_{\Delta h}$. For this experiment P_{bar} is equal to the measured barometric pressure.

$$P_{\text{bar}} = P_{\text{H}_2\text{O}} + P_{\text{H}_2} \pm P_{\Delta h} \quad (\text{EQ 8.4})$$

The water vapor in the bottle is present with liquid water so the gas is saturated with water vapor; the pressure $P_{\text{H}_2\text{O}}$ under these conditions is equal to the vapor pressure of water at the temperature of the experiment. This value is constant at a given temperature, and can be found in your textbook. Once the water vapor pressure is known it can be subtracted from equation 8.4. Now, the pressure, P_{bar} is equal to the pressure of the dry hydrogen and the head pressure.

The head pressure is measured by taking the difference in the heights of the liquid levels in the large bottle and beaker (not the reaction flask). This level represents the pressure difference in mm H_2O between atmospheric pressure, P_{bar} , and the pressure inside the large bottle and reaction flask. It is important to note that this difference must be converted to mmHg before it can be added to or subtracted from the atmospheric pressure. Since the density of Hg is 13.6 times as dense as water, the height difference values in mm must be divided by 13.6 to convert them to mmHg.

If the water level in the beaker is higher than the level in the large bottle then the pressure in the bottle is *greater* than atmospheric pressure. If the level in the beaker is below the level of the liquid in the large bottle, then the pressure in the bottle is *less than* atmospheric pressure. This will help you determine whether this difference is added to, or subtracted from the atmospheric pressure reading.

Now we know the pressure of the dry hydrogen. We now calculate the weight of each metal in the alloy as a mixture problem as the following equations illustrate:

$$\text{mass Mg} + \text{mass Sc} = \text{mass sample} = \text{mass M} \quad (\text{EQ 8.5})$$

$$\text{mol H}_2 \text{ from Mg} + \text{mol H}_2 \text{ from Sc} = \text{mol H}_2 \text{ collected} \quad (\text{EQ 8.6})$$

Now we have two equations and two unknowns. These can be solved simultaneously:

$$\text{mass Sc} = \text{mass M} - \text{mass Mg} \quad (\text{EQ 8.7})$$

$$\text{mol H}_2 \text{ from Sc} = \text{mass Sc} \times \frac{1 \text{ mol Sc}}{44.96 \text{ g Sc}} \times \frac{3 \text{ mol H}_2}{2 \text{ mol Sc}} \quad (\text{EQ 8.8})$$

$$\text{mol H}_2 \text{ from Mg} = \text{mass Mg} \times \frac{1 \text{ mol Mg}}{24.31 \text{ g Mg}} \times \frac{1 \text{ mol H}_2}{1 \text{ mol Mg}} \quad (\text{EQ 8.9})$$

$$\text{Substituting Equation 8.8 and Equation 8.9 into Equation 8.6 yields:} \quad (\text{EQ 8.10})$$

$$\left(\text{mass Mg} \times \frac{1 \text{ mol Mg}}{24.31 \text{ g Mg}} \times \frac{1 \text{ mol H}_2}{1 \text{ mol Mg}}\right) + \left(\text{mass Sc} \times \frac{1 \text{ mol Sc}}{44.96 \text{ g Sc}} \times \frac{3 \text{ mol H}_2}{2 \text{ mol Sc}}\right) = \frac{PV}{RT} \quad (\text{EQ 8.11})$$

Using Equation 8.7 we can substitute for the mass of Sc into Equation 8.11:

$$\left(\text{mass Mg} \times \frac{1 \text{ mol Mg}}{24.31 \text{ g Mg}} \times \frac{1 \text{ mol H}_2}{1 \text{ mol Mg}}\right) + \left((\text{mass M} - \text{mass Mg}) \times \frac{1 \text{ mol Sc}}{44.96 \text{ g Sc}} \times \frac{3 \text{ mol H}_2}{2 \text{ mol Sc}}\right) = \frac{PV}{RT} \quad (\text{EQ 8.12})$$

Solving for the mass of Mg in Equation 8.12 gives the grams of metal, M , in the alloy sample. Substituting this into Equation 8.7 gives the grams of Sc in the original sample. The percentages of each of the metals can be calculated in the following manner.

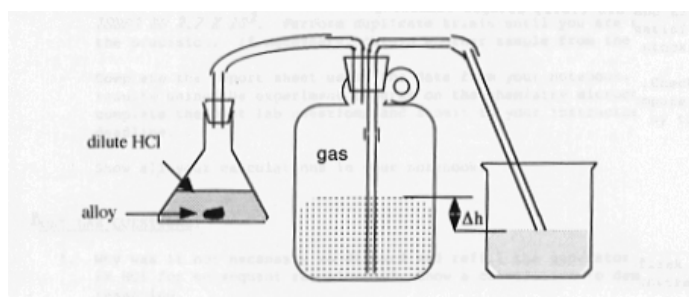
$$\frac{\text{mass Mg}}{\text{mass sample}} \times 100 = \% \text{Mg} \quad (\text{EQ 8.13})$$

$$\frac{\text{mass Sc}}{\text{mass sample}} \times 100 = \% \text{Sc} \quad (\text{EQ 8.14})$$

Procedure

1. Obtain an unknown Zn-Al alloy sample and requisite apparatus from the stockroom. Assemble the apparatus illustrated in Figure 8.1 :

FIGURE 8.1



2. A demonstration apparatus should also be displayed on your instructor's bench. The generator flask is a 250 mL Erlenmeyer flask fitted with a one-hole stopper; the beaker is a 1000 mL beaker. Insert the glass tubes in the two-hole stopper of the large bottle with equal treatment and care. The generator flask should be placed in a beaker.



CAUTION: Remember to lubricate the hole of the stopper with glycerin prior to inserting the glass tube.

3. Determine the mass of a piece of weighing paper to the maximum precision of the electronic balance (this is called the "tare"). Do the same for a second piece of weighing paper and place one piece of your unknown on the first paper and another piece on the second paper. Weigh each again and record these values.
4. Fill the large bottle to near the top with water. Determine the mass of the bottle and water on a balance of adequate capacity. Assemble the apparatus for the first experimental run.

5. Add 50-75 mL of dilute (6 M) HCl to the generator flask.
6. Add your first alloy sample to the generator flask and immediately insert the stopper. The gas will flow through the tubing and displace the water from the large bottle. Swirl the flask as needed to continue the reaction until all of the alloy is reacted. Allow the system to equilibrate for 10 minutes after the reaction is complete.
7. Measure the difference in mm of the water level in the bottle and beaker. Remove the stopper from the large bottle and measure the temperature of the remaining water and reweigh it on the balance. The difference between the initial and final mass of the bottle and water is the mass of water displaced by the gas. Using the density for water (look up the value in the CRC handbook of Chemistry and Physics), the volume of the gas displaced can be determined.
8. Take the temperature of the water and the temperature of the gas above the water.
9. Repeat the experiment with the second sample of alloy using the acid solution from the previous trial. When you are completely finished with the experiment, dump the bottle full of water in the planter outside.



NOTE: For an approximate quick check of the precision of your results, determine the ratio of the mL of H₂ produced to the grams of alloy used for each trial. Excellent precision should give ratio values that are equal to two significant figures. For example, the values, 818 and 823, both round to 8.2×10^2 . Perform duplicate trials until you are satisfied with the precision of your results.

Results and Calculations

In the calculations show:

1. how you derived the equation to determine the amount of zinc in the sample from the mass of the alloy and the total number of moles of hydrogen gas from the reaction. Do this without putting the **actual mass** of alloy or **number of moles** of gas from the data;
2. a sample calculation using this equation on one of your trials;
3. create a table summarizing your major data.

Post Lab Questions

1. Why was it not necessary to discard and refill the generator flask with fresh 6 M HCl for subsequent reactions? Show a calculation to demonstrate your reasoning.

2. In an experiment similar to yours, students were given an unknown sample that produced H₂S or NH₃ gas. What problem(s), if any, might arise if the same procedures as this experiment were followed?

3. Why is it not necessary to consider the amount of air that was in the generator flask at the start of the reaction?

4. If there was a leak in the rubber tubing that allowed approximately 150 mL of H₂ to escape, how would it affect the relative amounts (% values) that you calculated as the results? Would the %zinc in the sample appear to be high, low, or remain the same? Show a calculation to justify your answer.

5. What assumptions do we make regarding the temperatures of the generator and collection flasks? Are they valid?
6. How would the calculated number of moles of H₂ collected change if the generator flask were not given time to fully equilibrate?

Calorimetry—Measuring Heat of Formation

Part A: Introduction to Calorimetry

The goal in Part A of this experiment is to determine the heat capacity of a calorimeter. Once this value is known, your calorimeter can be used in Part B of the experiment to determine the heat of formation of magnesium oxide.

All chemical and physical processes are accompanied by heat changes. The measurement of heat changes in physical and chemical processes is called **calorimetry**. Heat changes may be measured by carrying out the process in an insulated vessel where the heat exchange between the system being observed and its surroundings is minimized. This type of system is called a **calorimeter**. The insulated vessel contains a temperature measuring device and a magnetic stirring bar.

The energy associated with the temperature changes in a substance can be expressed two ways. **Specific heat**, C_{sp} , is defined as the amount of energy in joules required to raise the temperature of one gram of that substance by one degree Celsius:

$$\text{specific heat} \quad C_{\text{sp}} = \frac{q}{m(\Delta T_{\text{°C}})} \quad (\text{EQ 9.1})$$

Where q is the quantity of heat, $\Delta T_{\text{°C}}$ is the temperature change in degrees Celsius, and m is the mass of the substance in grams.

The term **heat capacity**, C_s , is used if a particular object, such as a particular calorimeter, is being used repeatedly. Heat capacity is defined as the amount of energy required to raise the temperature of that object one degree Celsius:

$$\text{heat capacity} \quad C_s = \frac{q}{\Delta T_{\text{°C}}} \quad (\text{EQ 9.2})$$

The heat capacity of your calorimeter will be determined in this part of the experiment so that you can use your calorimeter in the following experiment, “Determination of Enthalpy of Formation”. The following example illustrates this procedure to determine the heat capacity of a calorimeter.

EXAMPLE 9.1

A 50.0 mL sample of warm tap water at 50.2 °C is mixed with 62.0 mL of cooler tap water in the calorimeter, which is at 21.4 °C. The final temperature of the system after mixing is 33.7 °C. The density of the water is 1.00 g/mL, and the specific heat of the tap water is 4.184 J/g°C. Determine the heat capacity, C_p , of the calorimeter system.

If there was no heat transfer from the hot water to the calorimeter, all of the heat would be conserved in the liquid. Therefore, all of the heat lost by the warm water would equal the heat gained by the cool water. This, however, is not what is observed because some of the heat from the warm water is used to raise the temperature of the calorimeter system.

The change in temperature is simply

$$\Delta T = T_{\text{final}} - T_{\text{initial}} \quad (\text{EQ 9.3})$$

As mentioned, the heat, q , lost by the warm water is gained by both the cool water and the calorimeter, hence the negative sign represents a heat loss and a positive sign is a heat gain

$$-q_{\text{warm}} = q_{\text{cool}} + q_{\text{calorimeter}} \quad (\text{EQ 9.4})$$

By substituting the expressions for specific heat (equation 9.1) and heat capacity (equation 9.2), equation 9.4 can be expressed as

$$-(\Delta T_{\text{warm}})(m_{\text{warm}})(C_{\text{sp}}) = [(\Delta T_{\text{cool}})(m_{\text{cool}})(C_{\text{sp}})] + C_p(\Delta T_{\text{cool}}) \quad (\text{EQ 9.5})$$

Using the data from this example gives:

$$\Delta T_{\text{cool}} = 33.7\text{ °C} - 21.4\text{ °C} = 12.3\text{ °C} \quad (\text{EQ 9.6})$$

$$\Delta T_{\text{warm}} = 33.7\text{ °C} - 50.2\text{ °C} = -16.5\text{ °C} \quad (\text{EQ 9.7})$$

$$-[-16.5\text{ °C})(50.0\text{ g})\left(4.184\left(\frac{\text{J}}{\text{g}\text{ °C}}\right)\right)] = [(12.3\text{ °C})(62.0\text{ g})\left(4.184\frac{\text{J}}{\text{g}\text{ °C}}\right)] + C_p(12.3\text{ °C}) \quad (\text{EQ 9.8})$$

Now the heat capacity of our calorimeter can be calculated:

$$3452\text{ J} = 3191\text{ J} + C_p(12.3\text{ °C})$$

$$C_p = 21.2\frac{\text{J}}{\text{°C}} \quad (\text{EQ 9.9})$$

Procedure: Part A

The following operations are typical for determining the heat capacity of a calorimeter. The temperature of a known mass of water is recorded; the temperature should be approximately room temperature. Another sample of water, whose mass and temperature is measured, is added to the first water sample. The second water sample should be approximately 50 °C higher than the original sample. By carefully monitoring the temperature changes upon mixing the hot and cool water samples, we can determine how much of the heat was transferred to the cool water and how much of the heat was transferred to the calorimeter; refer to equation Equation 9.4.

We will use a temperature probe called a thermistor to measure the temperature changes during this experiment. Your instructor will assist you in setting up and operating the thermistor. After you have collected your data with the thermistor, we will use it to help analyze the data.

Obtain a calorimeter, a magnetic stir bar, a stirring plate and a thermistor. The temperature throughout the experiment as a function of time will be tabulated during the experiment. Measure all masses to the nearest 0.1 g and all temperatures to the nearest 0.1°C.

1. While one partner is performing Step 2 the other should be preparing the thermistor apparatus as directed by your instructor.
2. Wipe out any water or solid debris from the inside of the calorimeter. Measure 50.0 mL of tap water into a graduated cylinder and pour this into a dry, tared calorimeter cup. Weigh the contents of the calorimeter after the water has been added to obtain the mass of water actually transferred to the cup. Add a stir bar and place the cover on the calorimeter then insert the thermistor. Click **Start** on the apparatus screen. Turn on the stirring plate and allow the system to reach a constant temperature.
3. Measure approximately 50 mL of tap water and pour it into a clean 250 mL beaker. Weigh the beaker and its water and record this mass. Gently heat the water to approximately 50-55 °C. Remove from heat and place your thermometer in the beaker and record the temperature of the hot water. It is essential that you obtain the actual temperature of the hot water just before you add the hot water to the calorimeter.
4. Add the hot water without splashing to the calorimeter. Stir gently to prevent splashing.
5. The thermistor apparatus will commence temperature and time measurements automatically. Observe the temperature and time measurements until a maximum temperature has been reached. Continue recording temperature and time readings until the temperature decreases by 2 °C below the maximum temperature or after 10 minutes have elapsed since the maximum temperature was observed.
6. While you are waiting for the maximum temperature to be reached, weigh the empty (wet) beaker to obtain the actual mass of hot water that was added to the calorimeter. Be sure to use the same balance each time that you weigh a particular piece of glassware. **Compare this mass to the mass of the water in the calorimeter.**
7. Weigh the water in the calorimeter.
8. Repeat steps 2-6 at least two more times and calculate the average heat capacity and the standard deviation for your calorimeter.
9. Consult with your instructor to determine if you have good precision for your calorimeter heat capacity.

Part B: Introduction to Measuring the Heat of Formation of Magnesium Oxide

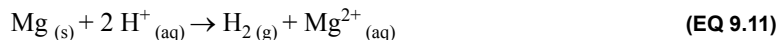
In Part B, the heat of formation of magnesium oxide will be determined. The heat capacity of your calorimeter that you calculated from Part A will be used in this part of the experiment.

The **enthalpy of formation**, ΔH_f , of a substance is the heat absorbed when one mole of it is formed from the elements in their most stable forms at constant pressure. In some cases, elements may be combined in a calorimeter to form the desired product and thus the ΔH_f may be measured directly. In other cases, the elements may not combine completely to form the desired product, or there may be other difficulties with the direct determination. In these cases, ΔH_f may be obtained indirectly by combining results from reactions that may be successfully measured:

$$\Delta H_{\text{rxn}} = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants} \quad (\text{EQ 9.10})$$

A direct determination of the ΔH_f for Mg^{2+} ion and an indirect determination for MgO will serve to illustrate the possibilities.

Consider the reaction of magnesium and HCl:



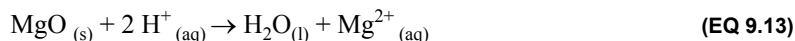
Since the ΔH_f for H^+ and H_2 are zero by definition under these conditions, the ΔH for this reaction is the ΔH_f for Mg^{2+} . The variations in temperature, pressure, and concentration occurring during this experiment will not cause significant errors. So, the ΔH_{rxn} would be the sum of the heat from the reaction of Mg and HCl and the heat from the calorimeter:

$$\Delta H_{\text{rxn}} = \frac{-(q_{\text{solution}} + q_{\text{calorimeter}})}{n} \quad (\text{EQ 9.12})$$

Using Equation 9.1, Equation 9.2, and Equation 9.12 allows one to calculate ΔH_{rxn} .

For MgO , the elements will combine directly, but the reaction is not easily accomplished and measured in a calorimeter, so an indirect approach will be followed.

Consider the reaction of MgO with 1 M HCl:



The ΔH for this reaction will be measured in your calorimeter. When this information is combined with known values for ΔH_f of Mg^{2+} and $\text{H}_2\text{O}_{(l)}$, the desired ΔH_f value for MgO can be determined.

Calorimetry

If a reaction occurs in a calorimeter, the heat released during the reaction will be detected as an increase in temperature, and the amount of heat will be the total heat capacity of the calorimeter and its contents multiplied by the temperature change. The temperature change should be obtained by taking data and graphing the temperature as a function of time from before the reaction until well after the reaction is complete. A thermistor apparatus will be used to capture the temperature changes during this process; the set-up and operations will be similar to that used in previously.

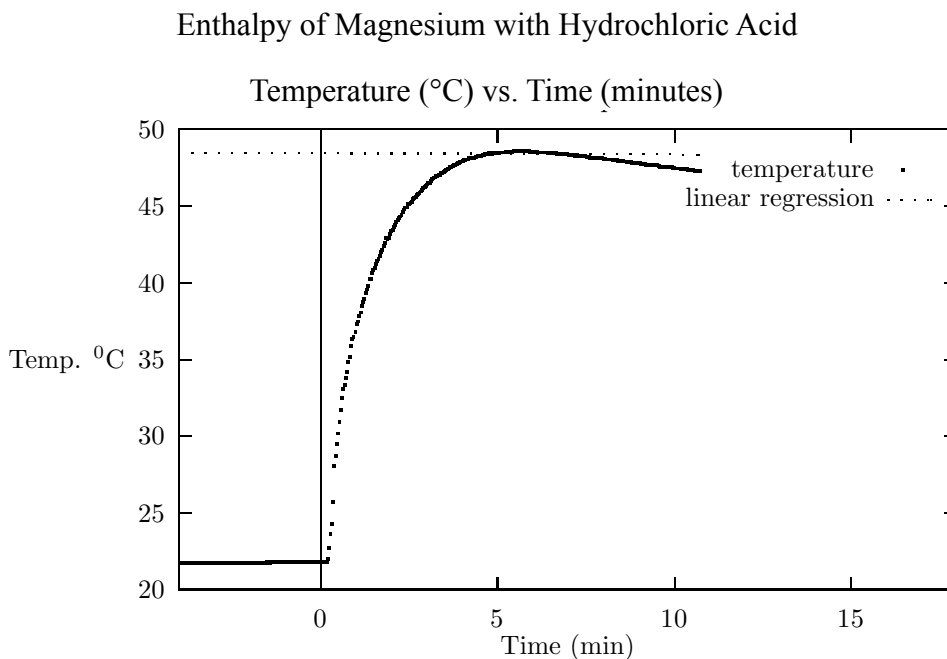
The calorimeter has a heat capacity of approximately 18 J/°C. If your calculated heat capacity from Experiment 9 is close to this value, then use your determined value for heat capacity. If you calculated a heat capacity much different than this value, use 18 J/°C for your heat capacity. The heat capacities of Mg and MgO are negligibly small and can be ignored. The 0.8 M HCl (the average value during reaction) has a specific heat of 4.07 J g⁻¹°C⁻¹, and a density of 1.01 g/mL.

Procedure: Part B

Reaction of Mg with HCl

1. Calibrate the thermistor as you did in “Heat Capacity of the Calorimeter.”

2. Weigh approximately 0.5 g of Mg to the maximum precision; record this mass in your notebook.
3. Add 100.0 mL of 1.0 M HCl to the calorimeter and begin stirring. Click the `Start` button to begin data collection. At this point you want to see the temperature stabilize and produce a nearly straight line on the graph of the thermistor apparatus screen. This may take 2-5 minutes.
4. Add the Mg and continue to stir. It is important that you add the metal into the solution. Any material that sticks to the sides of the calorimeter will introduce error into your results. You will notice the temperature increase on the display as the Mg reacts with the acid.
5. After the temperature remains constant or begins to drop slowly (5-10 minutes), click `Stop` and then `Save Data`.
6. Name your file with a **unique name** and save it to a flash drive. You want to obtain a graph in which the final temperature has been obtained by extrapolation of the first-order line-fit (see Figure 9.1 on page 75).

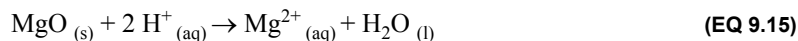
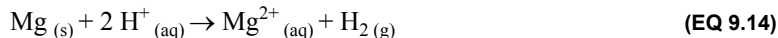
FIGURE 9.1

Reaction of MgO with HCl

Weigh out approximately 0.8 g of MgO. Clean out the calorimeter from the previous reaction and be sure to use a new aliquot of HCl for this reaction. Then repeat the procedure given above for the first reaction of Mg and HCl. Obtain a graph with the final temperature calculated from the curve-fit function as before.

Calculations and Data Treatment

1. By definition ΔH_f° for H^+ , O_2 and H_2 are zero. Therefore, the ΔH for reaction 9.14 is equal to the ΔH_f for Mg^{2+} . The ΔH for reaction 9.17 can now be determined using the data from reactions 9.14-9.16. ΔH for reaction 9.16 can be found in your text.



2. Make graphs and determine the corrected temperatures for each run. Be sure to completely and correctly label all graphs.
3. Calculate ΔH for each reaction using the amounts of reagents that you measured for your reactions.
4. Calculate ΔH per mole of Mg and MgO for each trial.
5. Calculate the percent error for each of your values.
6. Tabulate your values for ΔH_f for Mg^{2+} and MgO along with the literature values for each and their percentage errors.

Objective

In this experiment, we will be investigating a number of emission spectra in a qualitative manner. The hydrogen emission spectrum in particular will be examined in greater detail. The visible wavelengths in the hydrogen line spectrum will be measured with a spectroscope. These experimental values will be analyzed graphically to determine the principle quantum number associated with the Balmer Series of hydrogen and to calculate a value for the Rydberg constant.

Introduction

An **emission spectrum** is electromagnetic radiation emitted by a substance. The emission spectrum of sunlight is a **continuous spectrum**; in other words, all wavelengths of visible light are represented in the spectrum and these can be observed if the beam of sunlight is split with a prism. The emission spectrum for an atom can also be observed if the sample absorbs energy in the form of heat or, for a gas, an electrical current. However, the emission spectra for atoms in the gas phase are not continuous; only a few colors are observed which correspond to different wavelengths in the visible region of the electromagnetic spectrum. Light emission that occurs only at specific wavelengths are called a **line spectrum**. Every element has a unique line spectrum and the characteristic lines are like fingerprints used for identification of unknown atoms.

There is a fundamental link between atomic spectra and atomic structure. Beginning with Thomson's discovery of the electron, the structure of the atom was revealed and a *planetary* model was proposed in which the electrons were thought to be in circular orbits around the nucleus. Although this model is no longer considered to be an accurate description of the atom, the notion of orbits survives. Modern interpretation of atomic structure still uses the idea of orbits which we refer to as energy levels or electronic shells. Niels Bohr presented an explanation for atomic spectra based on this idea of electrons orbiting a nucleus but he imposed a restriction on these orbits: For the hydrogen atom, the single electron can only be located in specific orbits. Therefore, the electron can only possess certain fixed energy values which correspond to the energies of the allowed orbits. In other words, the energy of the electron is **quantized**. Bohr had embraced the idea of **quantization** con-

ceived by his contemporaries, Max Planck and Albert Einstein and was awarded the Nobel Prize in Physics in 1922 for his theory explaining the spectrum of the hydrogen atom.

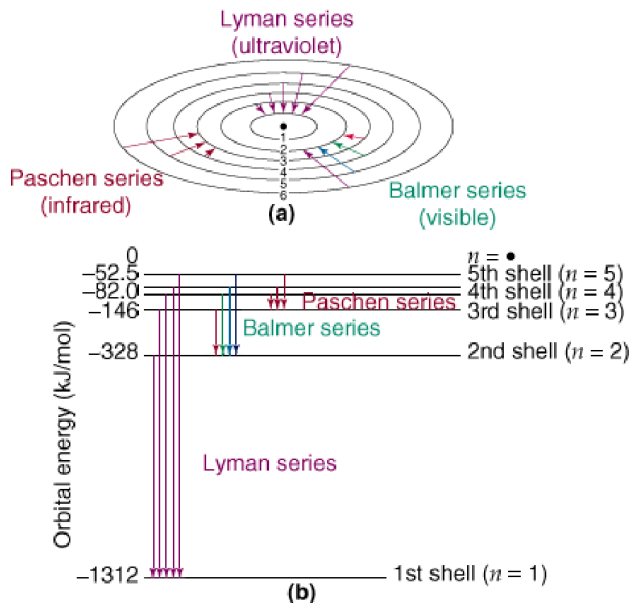
According to Bohr's theory, the energy values of an electron in a hydrogen atom are expressed by the equation

$$E = -B\left(\frac{1}{n^2}\right) \quad \text{(EQ 10.1)}$$

where B is a constant equal to 2.18×10^{-18} J and n is an integer called the principal quantum number with values equal to 1, 2, 3, ... etc. By convention, the negative sign signifies that the energy of an electron is less than the energy of a *free electron*, that is, an electron infinitely distant from the nucleus. The energy of a free electron is arbitrarily given a value of zero; this corresponds to n equal to infinity in the equation and E approaches zero. As the electron moves closer to the nucleus (as the value for n decreases), E becomes larger and more negative. The largest negative value is when $n = 1$ which is the lowest energy state or **ground state** for the hydrogen electron. When n is greater than 1, the hydrogen atom is said to be in an **excited state**. Since the radius of each circular orbit depends on n^2 , the size of the orbit increases as n gets larger and the electron is located further from the nucleus in any excited state.

Think about a hydrogen atom that absorbs energy. The energy absorbed causes the electron to move from a low energy state (small n) to a higher energy state (larger n). When the electron falls back to a lower energy state this energy is released as a photon. This quantized movement between energy states is like a ball moving up and down a stairway. The ball can rest on any step but is never located between steps. The energy associated with movement from one step to another is determined by the distance between the steps. For the hydrogen atom, the energy required to move an electron between energy levels depends on the difference in energy between the initial and final state. Movement of an electron between two energy states is called an **electronic transition** or simply a **transition**. When an electron is promoted to an excited state, there exists more than one emission pathway: The electron may return directly to the ground state by emitting a photon of frequency ν which is equal to the energy difference between the ground state and excited state, or the electron may return to the ground state stepwise, emitting a photon for each successive movement to a lower energy level. These energy transitions are illustrated in Figure 10.1 on page 79.

FIGURE 10.1



Now consider a hydrogen atom in an excited state characterized by principal quantum number n_i . When the electron returns to a lower energy state, the energy of transition is simply the difference between the initial and final state (symbolized by subscripts i and f)

$$\Delta E = E_f - E_i \quad (\text{EQ 10.2})$$

and by substituting into equation 10.1, the energy for initial and final states can be calculated as

$$E_f = -B\left(\frac{1}{n_f^2}\right) \quad \text{and} \quad E_i = -B\left(\frac{1}{n_i^2}\right) \quad (\text{EQ 10.3})$$

where n_i refers to the shell number of the excited state and n_f refers to the shell number of the lower energy state. Remember that n_f is not necessarily the ground state shell number. An excited electron does not always return to the ground state in one step, therefore, we typically observe more than one wavelength for atomic emission spectra. Thus, the total energy change for a transition is given by

$$\Delta E = \left(\frac{-B}{n_f^2}\right) - \left(\frac{-B}{n_i^2}\right) \quad \text{or} \quad \Delta E = -B\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \quad (\text{EQ 10.4})$$

Using the relationships, $E = h\nu = hc/\lambda$, we can derive the familiar form of the Rydberg equation:

$$\Delta E = h\nu = \frac{hc}{\lambda} = -2.18 \times 10^{-18} \text{ J} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \quad (\text{EQ 10.5})$$

where $B = 2.18 \times 10^{-18} \text{ J}$

Using the values of the constants, we have:

$$\frac{1}{\lambda} = \frac{-2.18 \times 10^{-18} \text{ J}}{hc} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = \frac{-2.18 \times 10^{-18} \text{ J}}{6.626 \times 10^{-34} \text{ J} \cdot \text{s} (3.0 \times 10^8 \text{ m/s})} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (\text{EQ 10.6})$$

Multiplying through gives

$$\frac{1}{\lambda} = 1.097 \times 10^{-2} \text{ nm}^{-1} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (\text{EQ 10.7})$$

Equation 10.7 is called the Rydberg equation where $1.097 \times 10^{-2} \text{ nm}^{-1}$ is the value of the **Rydberg constant for hydrogen** (R_H).

Finally, the Rydberg equation can be written as:

$$\frac{1}{\lambda} = -R \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \quad (\text{EQ 10.8})$$

which is a useful expression since it is an equation for a line ($y = mx + b$). Thus, by graphing reciprocal wavelength versus the correct values for $1/n_i^2$ a straight line should be obtained and from the graph, the slope can be determined which is of course the value for R , the Rydberg constant. Reciprocal wavelengths are also called wavenumbers symbolized by $\bar{\nu}$:

$$\bar{\nu} = -R \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \quad (\text{EQ 10.9})$$

factoring in R gives the equation:

$$\bar{\nu} = -R \frac{1}{n_i^2} + \frac{R}{n_f^2} \quad (\text{EQ 10.10})$$

where $y = \bar{\nu}$, $x = 1/n_i^2$, the slope, $m = -R$, and the y-intercept, $b = R/n_f^2$.

Which wavenumbers and which values of n_i^2 should be used? Wavenumbers are calculated from the observed wavelengths that are measured with the spectroscope. As for the n values, each wavelength corresponds to a transition from energy level n_i to level n_f . Energy level n_f is the same for all wavelengths in a particular series (Balmer, Paschen, Lyman) and n values are always integers. (As you know, the principle quantum number is always an integer). These are the spectral series are shown in Figure 10.1 on page 79 and the wavelengths for each series are illustrated in Table 10.1 on page 81.

TABLE 10.1

n_i	Pashen Series (Infrared light)	Brackett Series	Pfund Series	Humphreys Series
	$n_f = 3$	$n_f = 4$	$n_f = 5$	$n_f = 6$
	λ (nm)	λ (nm)	λ (nm)	λ (nm)
4	1870			
5	1280	4050		
6	1090	2630	7460	
7	1000	2170	4650	12370
8	954	1940	3740	7503
9	820	1820	3300	5910
10		1460	3040	5130
11			2280	4670
12				3280

Procedure

1. Your instructor will explain the operation of the spectroscopes.
2. Take precautions so that you ...



DO NOT attempt to change a discharge tube while it is connected to a power supply. The system generates up to 15,000 volts.

DO wear the special protective tinted glasses which filter the ultraviolet radiation that comes from the discharge tubes. Your eyes may be damaged if left unprotected.

3. For purposes of comparison, observe and *sketch* the spectra of: sunlight (do not aim the spectroscope directly at the sun!), an incandescent bulb, a fluorescent bulb, and at least three elements (one of these must be the hydrogen discharge tube) Draw a rough scale below each sketch to identify the approximate wavelengths in each spectrum.
4. Carefully measure the visible wavelengths in the hydrogen line spectrum. Create a Table of wavelengths then convert these values into wavenumbers.

Results and Calculations

1. Use a graphing program to plot these wavenumbers versus $1/n_i^2$, selecting the appropriate values for n_i for the visible wavelengths. The correct set of integer values will produce a straight-line plot $\bar{\nu}$ vs. $1/n_i^2$ as show in Equation 10.10.



NOTE: What is the ground state, n_f , for the visible spectrum? Refer to Figure 10.1 on page 79.

You may want to create a table like the one below:

TABLE 10.2

λ (nm)	n_i	$1/\lambda$ (1/nm)	$\bar{\nu}$ (nm ⁻¹)	$1/n_i^2$

2. From your graph, determine the slope and compare your value of the Rydberg constant with the accepted value of $1.097 \times 10^{-2} \text{ nm}^{-1}$. Calculate the percent difference.
3. From your graph, find (and explain) the value of n_f from the y-intercept of your plot.
4. Also make graphs and analyze:
 - a. $1/\lambda$ vs. $1/n_i^2$ for the UV lines of Hydrogen (121.6 nm, 102.6 nm, 97.3 nm, 95.0 nm, 93.8 nm);



NOTE: What is the ground state, n_f , for the ultraviolet spectrum? Refer to Figure 10.1 on page 79.

- b. $1/\lambda$ vs. $1/n_i^2$ for the visible lines of Hydrogen from literature (656.3 nm, 486.1 nm, 434.1 nm, 410.2 nm).
5. Determine what electronic transitions were responsible for each of the spectral lines in both the UV and visible spectra.

Post Lab Questions

TABLE 10.3

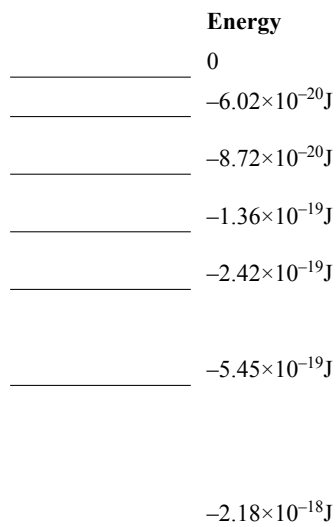
Quantity	Symbol	Value
atomic mass unit	amu	1.660565×10^{-27} kg
Avogadro's constant	N or N_A	6.022094×10^{23} mol ⁻¹
electronic charge	e	$1.6021892 \times 10^{-19}$ C
Faraday constant	F	9.648456×10^4 C/mol
gas constant	R	$0.0820568 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}$
		$8.314510 \frac{\text{J}}{\text{mol} \cdot \text{K}}$
mass of electron	m_e	9.109534×10^{-31} kg
mass of neutron	m_n	$1.6745943 \times 10^{-27}$ kg
mass of proton	m_p	$1.6726485 \times 10^{-27}$ kg
Planck's constant	h	6.626176×10^{-34} J s
Rydberg constant	R_H	1.0967758×10^7 m ⁻¹
speed of light in vacuum	c	2.997924×10^8 m/s

1. Determine the frequency of a photon of 5.0×10^{-7} meter wavelength.

2. What is the energy (in joules) of the photon in question 1?

3. If the threshold frequency, ν_0 , for a metal is $1.0 \times 10^{14} \text{ s}^{-1}$, what would be the velocity of an electron ejected from the metal surface by a photon of $6.0 \times 10^{14} \text{ s}^{-1}$ frequency striking the metal? (kinetic energy = $\frac{1}{2}mv^2$)
4. Find the wavenumber of the photon in question 1.
5. Find the wavelength (in nm) of the light emitted by the $n = 8$ to $n = 2$ electronic transition in a hydrogen atom.

6. A stream of laser photons with a frequency of 3.0×10^{15} Hz excited electrons in the lowest energy of the hydrogen atom shown in the energy level diagram below



a. Show to what level the photon excited the electron.

b. Show all the possible emission transitions as the electron returns from the $n = 3$ energy level to the ground state.

c. Calculate ΔE for each line produced in b.

- d. What is the wavelength of the photon that would just ionize the ground-state atom to H^+ ?

7. An energy of 1.09×10^3 kJ/mol is required to convert gaseous carbon atoms to gaseous C^+ ions and electrons. What is the maximum wavelength, in nm, of electromagnetic radiation with sufficient energy to cause ionization to a single carbon atom? In what region of the electromagnetic spectrum is this photon found?

8. Answer the following questions about the ground-state electron configuration of a neutral uranium atom.
- Write out the outer-shell ground-state electron configuration of the for the six electrons beyond the radon configuration of a neutral uranium atom.
 - Give the four quantum numbers that correspond to each of the six electrons beyond the radon configuration of a neutral uranium atom. Put your answers in Table 10.4 .

TABLE 10.4

Electron	n	l	m_l	m_s

9. What is the maximum number of electrons that can be accommodated in each representation below?

$2p$ _____ $l = 3$ _____ $m_l = 3$ _____

$n = 3$ _____ $4f$ _____ $n = 3, l = 2$ _____

Periodicity of Chemical Properties

Objective

The astute student can predict chemical behavior for the elements based on their position in the periodic table. In this experiment the student will explore the chemistry of selected elements and discern periodic trends based on graphical analysis of periodic trends.

Introduction

The Grossmont College Chemistry Department and the World Wide Web have available a variety of computer programs which demonstrate the properties of the chemical elements. Some of these are as follows:

Chemistry software

- An Excel spreadsheet has data from Periodic Table Alive on it, so that you can graph any property against any other. (Spreadsheet available on your instructor's website.) Choose the elemental properties option. Note that this first page contains all of the elements and subsequent pages contain only the elements in specific groups or periods.

Internet sites - The following sites are interesting. Try them out...

- <http://www.webelements.com/> This site has a periodic table and you can click on any element to learn about it. Notice especially here the crystal structures in the right margin. They may be useful.
- <http://www.chemeddl.org/resources/ptl> This site has a periodic table and you can click on any element to learn about it. It includes information of price of elements. It is an electronic version of the Periodic Table Alive software.
- <http://chemcollective.org/applets/pertable.php> This site shows the electron configurations of all the elements including the orbital diagrams.

- <http://chemicalelements.com/> This site has periodic table with clickable elements to show properties. You can also customize the chart to add different kinds of data under the symbol on the chart. This could be useful for determining trends.
- <http://www.chemicool.com/Chemicool/> Another site with elemental data appearing when you click on the element on the periodic table.

Procedure

Graphical Analysis

Using the graph option in Periodic Table Alive or the data in the Excel spreadsheet investigate two of the following:

1. Graph atomic number versus first ionization energy;
2. Graph atomic number versus number of isotopes (Is there a relationship between odd and even numbers of protons and neutrons?);
3. Graph atomic number versus electron affinity;
4. Graph atomic number versus atomic radius;
5. Graph atomic number versus electronegativity and look for trends in groups 1, 3, 6, and 7;
6. Graph atomic number versus atomic radius for groups 2, 3, 7, and 8 and for periods 2, 3, and 4;
7. Graph second ionization energy for groups 1, 2, 7, and 8 and for periods 2, 3, and 4.

Discussion

For the two relationships you investigated write a short report of your findings including the following:

1. Name of the trend you examined.
2. Definition - A short definition of the property you've studied.
3. Summary - The summary should be a brief description of the trend or grouping you observed. Describe the general trend, not every small "glitch" in the trend. A table summarizing your data would be useful here.
4. Graph - The pictorial representation of the trend you examined.
5. Discussion - In this section, you should discuss why the trends you observed behave in the manner illustrated by the programs. For example, if a certain property appears to decrease in value going across a period, you should explain why (in an atomic sense) the value is decreasing. A one or two paragraph discussion per relationship is sufficient.
6. References - You may use any book or journal article as a reference to help write your discussion. However, make sure you give proper credit for this reference at the end of your report. A basic sample report is shown below; the one you write should be more comprehensive.

Sample Report

- Boiling point for groups 6, 7, and 8.
- Definition

The boiling point of a liquid under a given pressure is the temperature at which its vapor pressure is just equal to the applied pressure. The normal boiling point is the temperature at which the vapor pressure of the liquid is equal to exactly one atmosphere of pressure (1).

A group is a vertical column on the periodic table, which contains elements that have similar chemical properties (2).

- Summary

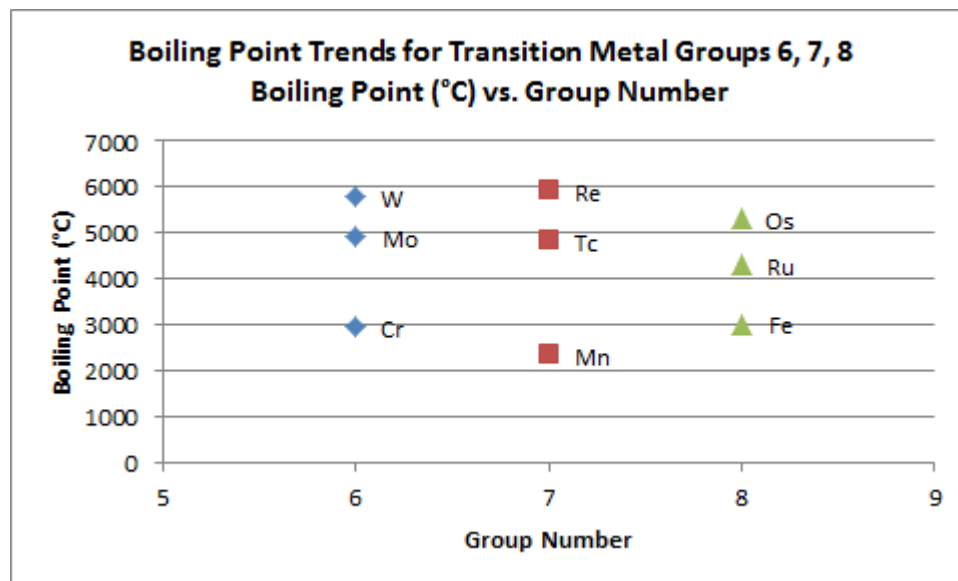
The boiling points of the elements increase as you go down groups 6, 7 and 8. There is not a regular trend for boiling point across a period.

TABLE 11.1

Element	Group Number	Boiling Point (°C)	Element	Group Number	Boiling Point (°C)	Element	Group Number	Boiling Point (°C)
Cr	6	2963	Mn	7	2333	Fe	8	3023
Mo	6	4923	Tc	7	4840	Ru	8	4823
W	6	5773	Re	7	5923	Os	8	5298
Sg	6	?	Bh	7	?	Hs	8	?

- Graph

FIGURE 11.1



- Discussion

The boiling points of the elements increase as you go down groups 6, 7 and 8. There is not a smooth trend for boiling point across a period. The boiling point depends on two factors: the molar mass of the particles and the cohesive forces holding the atoms or molecules together

making them more difficult to separate into individual gas particles; Going down a group both become greater. Each factor will be discussed separately.

As we go down a group, the size of the atom increases because shells of electrons are added. As the nuclear charge decreases the positive charge felt by the electrons decreases so that electrons are not held as closely to the nucleus increasing the size of the atom. In multi-electron systems there is also a repulsion between electrons, which also slightly increases the atomic size. The boiling point does not follow a trend across a period for transition metals because when electrons are added across a row the d electrons are added to the inner shell (n-1) and do not change the size of the atoms greatly (3).

Cohesive interactions between atoms and molecules (intermolecular forces) increase with increasing size and increasing number of electrons. As you go down a column there are more electrons, causing an increase in the cohesive interactions. Melting involves a change of state from the liquid state to the gaseous state. There are two types of energy involved in changing state: potential energy and kinetic energy. When a substance is in one phase adding energy to the system changes the potential energy, but not the average kinetic energy of the particles. During the change from a liquid to a gas, the temperature remains constant, but the potential energy of the particles is increasing (4). The larger the particle the more cohesive interactions are present, thus, it takes more energy to pull atoms or molecules away from the liquid to the gas phase, which results in a higher boiling point. Across a period the change in cohesive interactions does not change as much resulting in an uneven trend.

6. References

- (1) Whitten, Kenneth W., Gailey, Kenneth D., and Davis, Raymond E. *General Chemistry* 3rd ed. Philadelphia: Saunders College Publishing, 1988, p. 308.
- (2) Gilbert, Thomas, Kirss, Rein V., Foster, Natalie, Davies, Geoffrey *Chemistry: The Science in Context* 2nd ed. New York: W. W. Norton & Company, Inc., 2009, p. A-33.
- (3) Gilbert, Thomas, Kirss, Rein V., Foster, Natalie, Davies, Geoffrey *Chemistry: The Science in Context* 2nd ed. New York: W. W. Norton & Company, Inc., 2009, p. 338-339.
- (4) Dahm, Donald J., Nelson, Eric A., *Calculations in Chemistry: An Introduction*, 1st ed. New York: W. W Norton & Company, Inc. 2013, p. 361.

Post Lab Questions

Using the Excel data or KC discover sort though the data to answer the questions below:

1. Which elements are

a. Orange

b. Yellow

c. Liquids

2. When were the elements discovered? Using a periodic table color elements discovered between BC and 1600 AD green, elements discovered between 1601 and 1900 blue, and elements discovered between 1901 and the present red.

FIGURE 11.2

										NOBLE GASES							
IA											VIIA						
1 H 1.008											1 H 1.008	2 He 4.002					
IIA												3 B 10.81	4 C 12.01	5 N 14.01	6 O 16.00	7 F 19.00	8 Ne 20.18
		Transition Metals															
3 Li 6.941	4 Be 9.012											13 Al 27.00	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
11 Na 23.00	12 Mg 24.30	III B	IV B	V B	V I B	V II B	V III B			IB	IIB						
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.70	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (99)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.0	89 Ac 227.0	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (268)	110 Ds (271)	111 Rg (272)	112 ?? (???)	113 ?? (???)	114 ?? (???)	115 ?? (???)	116 ?? (???)		118 ?? (???)

Lanthanide series

Actinide series

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

3. List the five most and least expensive pure elements.

TABLE 11.2

Rank	Most Expensive	Cost	Least Expensive	Cost
1.				
2.				
3.				
4.				
5.				

4. Select the best element that meets all of the following: _____
- Reacts mildly with 6 M HCl.
 - Has no reaction with base or water at 25 °C.
 - Has an electrical conductivity of at least 200 m/cm.
 - Costs less than \$5 per 100 g pure.
5. Zirconium and hafnium occur together in nature. It is ever so difficult to obtain the pure elements.
- Why do you think this is so?
- b. If you had two ingots of equal size, one Hf and the other Zr, how could you determine which is which?
6. A mystery element is expensive because it is not readily available on the surface of the earth. It has a high density and can be scratched by glass and iron. It can be melted in a chromium or vanadium crucible. It forms the chloride MCl_3 . Predict the identify of the mystery element and state your reasons for making this conclusion.

7. Copper is used for electrical wiring. If copper became scarce, what element would make the best substitute? Explain your reasoning.
8. Answer the questions below using a plot of ionization energy versus atomic number.
- Define ionization energy.
 - Explain why the ionization energy increases from Al to Ar.
 - Explain why there is a decrease in ionization energy from Mg to Al.
 - Explain why the ionization energy of S slightly lower than P when we would expect it to be higher based on the general trend.
 - Explain why there is a decrease in ionization energy form Zn to Ga.

9. Answer the questions below using plots of electron affinity for groups IA, IIIA, and VIIA.

a. Define electron affinity.

b. Explain why the electron affinities for groups IIA and VIIIA are ~ 0 kJ/mol.

c. Explain why the electron affinities for group VIIA is so high compared to the other groups.

d. Explain why the electron affinity for F is less than for Cl.

Objective

The purpose of this experiment is to use molecular models to build and study structures of molecules and ionic species. In addition we will use molecular modeling software to analyze the bonding in a variety of compounds.

There are a number of theoretical models concerning the bonding between atoms in chemical compounds. We can explain bonding based upon empirical evidence and trends, as well as by applying fundamental physical principles to the particles in question. We must keep in mind that the efficacy of a model, however, is based upon its ability to predict and explain chemical phenomena. While a specific model may provide a very reasonable interpretation of certain characteristics exhibited by a system, it is never possible to say that this representation is complete or absolute. The failing of a model in one aspect or another preceded some of the most interesting events in science.

We shall use ball and stick models to show correct molecular geometries. They offer no information concerning atomic sizes or bond lengths. Wooden spheres represent atoms of various elements according to a color code. A number of holes drilled into each of these units are positioned so that proper bond angles are portrayed when the spheres are connected. The connections represent chemical bonds (shared electron pairs) and are made by means of wooden or plastic dowels (single bonds) or flexible springs (multiple bonds).

*Procedure***Part I**

Create models and draw Lewis structures for the molecules and ions in Table 12.2, Table 12.3, and Table 12.4 examples of each step are shown in Example 12.1:

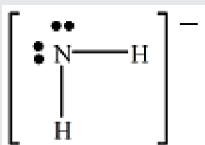
EXAMPLE 12.1 NH_2^-

- Determine the total number of valence electrons that must be included in the Lewis dot structure. For molecules (neutral species) this equals the sum of the valence electrons for all atoms as determined by the group number for each element. For ionic species, this equals total valence electrons plus (or minus for cations) the ionic charge. This will include all of the valence electrons of each atom as determined by the group number of the element on the periodic table.

Two atoms of hydrogen (Group IA) each contribute one valence electron, 1 atom of nitrogen (Group VA) contributes five valence electrons, the minus one charge indicates one additional electron, yielding a total of eight electrons for the Lewis structure.

2 H	$2e^-$
1 N	$5e^-$
<u>-1 ion charge</u>	<u>$1e^-$</u>
Total	$8e^-$

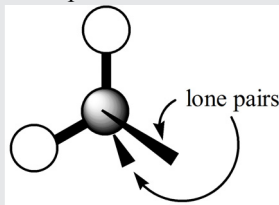
- Draw a Lewis electron dot structure for the species.



- Build the model. If using the wooden balls and sticks, follow these conventions.

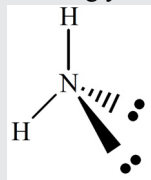
Valence Electrons on Central Atom	Ball Color (Number of Holes)
2	dark blue (2)
3	light green (3)
4	black (4)
5	brown (5)
6	silver (6)

For the atoms surrounding the central atom use the same conventions but include the yellow balls for hydrogen (one hole) which can only form one bond. Represent each non-bonding (unshared) pair of electrons in the Lewis structure with a dowel. This will help you to visualize the positions of the non-bonding pairs:



EXAMPLE 12.1 NH_2^-

4. Study carefully the model that you have constructed. Note the geometry of the connected atoms and of all the electron pairs about the central atom. Now draw in the space provided, a three-dimensional representation using your model as a guide:



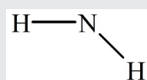
The wedges represent a bond or electron pair coming out of the plane of the page. A dotted line represents a bond behind the plane of the page, and the solid lines are in the plane of the page.

5. Determine the orbital (electron pair) geometry about the central atom using VSEPR theory and indicate the hybridization of the central atom.

The orbital geometry of NH_2^- is tetrahedral and the hybridization is sp^3 .

6. Determine the molecular shape of the molecule or ion. This is based on the atomic geometry about the central atom. The molecular shape structure often excludes unshared pairs. Ionic charge is often included using brackets around the species.

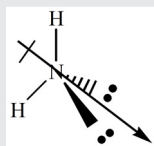
NH_2^- has bent molecular geometry:



7. Now list the electronegativities of the bonded atoms and calculate the differences in their electronegativities. Determine from this which bonds are polar and which are nonpolar:

H	2.2
N	3.0
ΔEN	0.8

8. If the molecule has all nonpolar bonds, write 'nonpolar'. If polar bonds are present draw another structure as in part (d) and add the dipole arrow to indicate the net dipole of the species. If the bond dipoles cancel due to the symmetry, show this and label the diagram as "nonpolar". A compound may have polar bonds and still



be nonpolar, if the bond dipoles cancel due to symmetry (as in boron trifluoride).

EXAMPLE 12.1 NH_2^-

9. Give the oxidation number for each element in the compound.

For NH_2^- the H's have an oxidation number of +1 and the nitrogen must have an oxidation number of -3. Remember that the sum of the oxidation numbers must be equal to the charge on the particular species. Refer to your text for the rules for assigning oxidation numbers.

10. Give the formal charge for each atom in a compound. Remember that the formal charge is nothing more than a means to make a better guess at the correct Lewis structure of a compound or ion. Formal charge does not have any real physical significance.

For NH_2^- there really isn't any reason to calculate formal charges since there is only one possible way to put these atoms together. That is, if we do not force H to bond more than once. Formal charge on an atom is equal to the group number minus the number of electrons surrounding atom (all lone pairs plus $\frac{1}{2}$ shared pairs). NH_2^- is shown:


$$\begin{array}{rcl} \text{N} & 5 - \left[4 + \frac{1}{4}(4) \right] & = -1 \\ \text{H} & 1 - \frac{1}{2}(2) & = 0 \end{array} \qquad \text{(EQ 12.1)}$$

Molecular Polarity. The polarity of a molecule can be determined by looking at the shape of the molecule and the bonds within the molecule. A polar molecule occurs when there is a net dipole moment on the molecule as determined by electronegativity differences between atoms. A nonpolar molecule will not have a net dipole moment. There are some visual indicators that can help determine if a molecule is polar. For example, a molecule can usually be classified as polar if: there is a lone pair (or lone pairs) on the central atom, or there are different types of atoms (or groups of atoms) on the central atom with different electronegativity values. Be careful using these rules especially with expanded octets and molecules with multiple central atoms.

Part II

Use Spartan to build the molecules. Measure bond lengths and bond angles with MMFF calculations. Then use semi-empirical calculations (AM1) to measure dipole moments, surfaces and investigate molecular orbitals. Complete Table 12.5 and Table 12.6 .

Spartan Molecular Modeling. When you open the Spartan application you see a blank screen with menus on top and along the side. To build a molecule, select an atom from the menu and click on the screen. The atom appears on the screen. Select another atom and click. The new atom is bonded to the first one. Continue adding one atom at a time until the molecule is complete. The computer adjusts the bond angles and bond lengths to give the correct molecular shape.

Now click on the "Energy" button"  That's it! What you see on the screen is a ball-and-stick representation of your molecule. You can change the structure to a space-filling model, a wire frame, or other choices by selecting options under the MODEL menu.

The energy button. The energy button performs a calculation to determine the most stable arrangement of atoms in your molecule. Using Hooke's Law, the bond lengths and bond angles are adjusted until the structure with the lowest potential energy is produced. In the parlance of molecular modeling, we say "the structure is minimized", in terms of its potential energy.

Once the molecule is built, you have several methods to investigate your structure:

- You can rotate the structure to see the 3-D arrangement of atoms; click and drag with the mouse.
- Click on the menu buttons to inspect bond length or bond angle, use menu options to view properties such as dipole moment or heat of formation.
- Use the calculation menu to generate an electron density surface for the molecule.

One of the more useful applications of Spartan is the **electron density surface** (electron cloud). The size and shape of the electron cloud defines the size and shape of an atom or molecule. You can make the surface transparent and view the atoms within. If you make the surface opaque, you get a structure that is very similar to a space-filling model. A space-filling model illustrates the van der Waal volumes for each atom, showing how the atomic orbitals penetrate into each other.

FIGURE 12.1



Menu options allow you to calculate the electrostatic potential for all points on the electron density surface. The electrostatic potential is defined as the energy of interaction between a point-positive charge and the nuclei and/or electrons in a molecule.

If the point charge is placed in a region of high electron density, the interaction is attractive, the potential is negative, and Spartan colors these regions red. If the point charge is placed near low electron density regions, the interaction is repulsive, the potential is positive and Spartan colors these regions blue. Yellow and green regions represent intermediate values for the potential.

You must use higher-level calculations (semi-empirical or ab initio methods) to view dipole moment, heat of formation and density surfaces. All these choices are available under the setup menu. Below are some basic directions for using Spartan:

Spartan and Electron Density Viewing:

1. Go to **START** and select **PC SPARTAN PLUS**.
2. Build molecule.
3. Drop down **SET UP** menu and click on **CALCULATIONS**.
4. Click **OK**.
5. Drop down **SET UP** menu and **SURFACES**.
6. Click **ADD: Surface DENSITY** and Property **DENSITY**.
7. Click **OK** and leave screen on the desktop.
8. Click **SET UP** again and select **SUBMIT**.
9. Be patient, the calculations can take a few minutes.
10. Save your file when prompted.

11. After Spartan says it has completed the save, click **DISPLAY**.
12. Select **PROPERTIES**.
13. On the Surfaces List screen put a check mark in the yellow density box.
14. Click on a part of the molecule. The property screen will toggle between molecule properties and surface properties.
15. Have fun looking at the molecules in a new way!

Spartan and Molecular Orbitals:

1. Using the same programs, create a model for the formate ion, HCO_2^- . Be sure to designate when you set up the calculations that the molecule has a minus one charge.
2. This time, have the program show the molecular orbitals for the molecule by checking the appropriate model.
3. Select **SET UP** then **SURFACES** check **ADD** under **SURFACE** select **HOMO** and click **OK**. Select **SET UP** then **SUBMIT**.
4. Repeat with **LUMO**, etc.
5. Draw the three molecular orbitals, labeling them as pi, n (nonbonding), and pi^* orbitals. Note which is the highest occupied molecular orbital (HOMO) and which is the lowest unoccupied molecular orbital (LUMO).

Prelaboratory Sheet

1. Complete the following table:

Valence shell electron pairs	Bonding electron "clouds"	Lone pairs	Formula	Orbital geometry	Approximate bond angles	Molecular geometry	Hybridization
			AX				
			AX ₂				
			AX ₃				
			$\ddot{A}X_2$				
			AX ₄				
			$\ddot{A}X_3$				
			$:\ddot{A}X_2$				
			AX ₅				
			$\ddot{A}X_4$				
			$:\ddot{A}X_3$				
			$:\ddot{A}X_2$				
			AX ₆				
			$\ddot{A}X_5$				
			$:\ddot{A}X_4$				

Report Sheet

TABLE 12.2 Inorganic Compounds - Be sure to show the proper geometries!

Species	Lewis Dot Structure and Resonance structures including formal charge	VSEPR Theory and Valence Bond Theory Classifications
HCN Indicate the hybridization of both the C and N Total Valence Electrons	H-C-N bond angle Polarity	Molecular Geometry Hybridization Carbon _____ Nitrogen _____ Orbital Geometry
H ₂ O Total Valence Electrons	H-O-H bond angle Polarity	Molecular Geometry Hybridization Orbital Geometry
SO ₂ Show all resonance structures and formal charges. Total Valence Electrons	O-S-O bond angle Polarity	Molecular Geometry Hybridization of central atom Orbital Geometry

TABLE 12.2 Inorganic Compounds - Be sure to show the proper geometries!

Species	Lewis Dot Structure and Resonance structures including formal charge	VSEPR Theory and Valence Bond Theory Classifications
CHCl ₃ Total Valence Electrons	H-C-Cl bond angle Polarity	Molecular Geometry Hybridization of central atom Orbital Geometry
PF ₃ Total Valence Electrons	F-P-F bond angle Polarity	Molecular Geometry Hybridization of central atom Orbital Geometry
NH ₄ ⁺ Total Valence Electrons	H-N-H bond angle	Molecular Geometry Hybridization of central atom Orbital Geometry

TABLE 12.2 Inorganic Compounds - Be sure to show the proper geometries!

Species	Lewis Dot Structure and Resonance structures including formal charge	VSEPR Theory and Valence Bond Theory Classifications
<p>CS₂</p> <p>Total Valence Electrons</p>	<p>S-C-S bond angle</p> <p>Polarity</p>	<p>Molecular Geometry</p> <p>Hybridization of central atom</p> <p>Orbital Geometry</p>
<p>O₃</p> <p>Show all the resonance structures and formal charges. This is a non-cyclic molecule.</p> <p>Total Valence Electrons</p>	<p>O-O-O bond angle</p> <p>Polarity</p>	<p>Molecular Geometry</p> <p>Hybridization of central atom</p> <p>Orbital Geometry</p>
<p>AsCl₅</p> <p>Are the Cl atoms equatorial, axial, or both?</p> <p>Total Valence Electrons</p>	<p>Cl-As-Cl bond angles _____ and _____</p> <p>Polarity</p>	<p>Molecular Geometry</p> <p>Hybridization of central atom</p> <p>Orbital Geometry</p>

TABLE 12.2 Inorganic Compounds - Be sure to show the proper geometries!

Species	Lewis Dot Structure and Resonance structures including formal charge	VSEPR Theory and Valence Bond Theory Classifications
<p>XeF₄</p> <p>Are the F atoms equatorial, axial, or both?</p> <p>Total Valence Electrons</p>	<p>F-Xe-F bond angle</p> <p>Polarity</p>	<p>Molecular Geometry</p> <p>Hybridization of central atom</p> <p>Orbital Geometry</p>
<p>ICl₃</p> <p>Are the Cl atoms equatorial, axial, or both?</p> <p>Total Valence Electrons</p>	<p>Cl-I-Cl bond angle</p> <p>Polarity</p>	<p>Molecular Geometry</p> <p>Hybridization of central atom</p> <p>Orbital Geometry</p>
<p>SO₃²⁻</p> <p>Show all resonance structures and formal charges.</p> <p>Total Valence Electrons</p>	<p>O-S-O bond angle</p>	<p>Molecular Geometry</p> <p>Hybridization of central atom</p> <p>Orbital Geometry</p>

TABLE 12.2 Inorganic Compounds - Be sure to show the proper geometries!

Species	Lewis Dot Structure and Resonance structures including formal charge	VSEPR Theory and Valence Bond Theory Classifications
<p>SF₆</p> <p>Are the F atoms equatorial, axial, or both?</p> <p>Total Valence Electrons</p>	<p>F-S-F bond angle</p> <p>Polarity</p>	<p>Molecular Geometry</p> <p>Hybridization of central atom</p> <p>Orbital Geometry</p>
<p>P₄</p> <p>All of the phosphorus atoms are equivalent with no multiple bonds or expanded octets. Draw the entire molecule.</p> <p>Total Valence Electrons</p>	<p>P-P-P bond angle</p> <p>Polarity</p>	<p>Molecular Geometry</p> <p>Hybridization of central atom</p> <p>Orbital Geometry</p>
<p>I₃⁻</p> <p>Don't forget the formal charges!</p> <p>Are the I atoms equatorial, axial, or both?</p> <p>Total Valence Electrons</p>	<p>I-I-I bond angle</p>	<p>Molecular Geometry</p> <p>Hybridization of central atom</p> <p>Orbital Geometry</p>

TABLE 12.2 Inorganic Compounds - Be sure to show the proper geometries!

Species	Lewis Dot Structure and Resonance structures including formal charge	VSEPR Theory and Valence Bond Theory Classifications
<p>AsCl₃F₂</p> <p>Are the F atoms equatorial, axial, or both?</p> <p>Are the Cl atoms equatorial, axial, or both?</p> <p>Total Valence Electrons</p>	<p>Cl-As-Cl bond angle</p> <p>F-As-F bond angle</p> <p>F-As-Cl bond angle</p> <p>Polarity</p>	<p>Molecular Geometry</p> <p>Hybridization of central atom</p> <p>Orbital Geometry</p>
<p>SO₄²⁻</p> <p>Look for some resonance structures that expand the valence of sulfur. Remember to show the formal charges.</p> <p>Total Valence Electrons</p>	<p>O-S-O bond angle</p> <p>Polarity</p>	<p>Molecular Geometry</p> <p>Hybridization of central atom</p> <p>Orbital Geometry</p>
<p>SF₄</p> <p>Are the F atoms equatorial, axial, or both?</p> <p>Total Valence Electrons</p>	<p>F-S-F bond angles _____ and _____</p> <p>Polarity</p>	<p>Molecular Geometry</p> <p>Hybridization of central atom</p> <p>Orbital Geometry</p>

TABLE 12.2 Inorganic Compounds - Be sure to show the proper geometries!

Species	Lewis Dot Structure and Resonance structures including formal charge	VSEPR Theory and Valence Bond Theory Classifications
<p>BF_3</p> <p>Show <u>all</u> possible resonance structures. Indicate which structures are likely to form and why. Be sure to include formal charges.</p> <p>Total Valence Electrons</p>	<p>F-B-F bond angle</p> <p>Polarity</p>	<p>Molecular Geometry</p> <p>Hybridization of central atom</p> <p>Orbital Geometry</p>
<p>NO_2</p> <p>Show all four resonance structures and charges. Identify the advantages of each.</p> <p>Total Valence Electrons</p>	<p>O-N-O bond angle</p> <p>Polarity</p>	<p>Molecular Geometry</p> <p>Hybridization of central atom</p> <p>Orbital Geometry</p>
<p>BeCl_2</p> <p>Show <u>all</u> possible resonance structures. Be sure to include formal charges.</p> <p>Total Valence Electrons</p>	<p>Cl-Be-Cl bond angle</p> <p>Polarity</p>	<p>Molecular Geometry</p> <p>Hybridization of central atom</p> <p>Orbital Geometry</p>

TABLE 12.3 Organic Compounds - Fill in the missing bonds, atoms, and/or lone pairs.

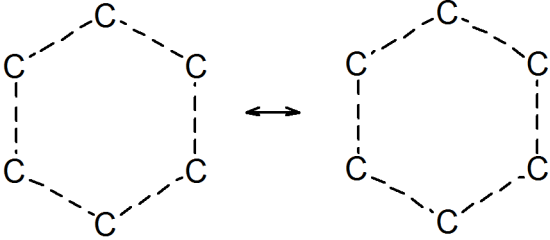
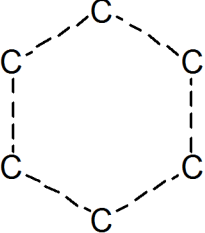
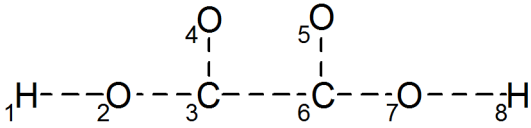
Species	Lewis Dot Structure	VSEPR Theory and Valence Bond Theory Classification
<p>C_6H_6 is benzene. Show the two resonance structures for this cyclic molecule</p> <p>Total Valence Electrons</p>		<p>Hybridization of carbon atoms</p> <p>C-C-H bond angle</p> <p>Polarity</p>
<p>C_6H_{12} is cyclohexane. There will be one large ring formed out of the carbon atoms.</p> <p>Total Valence Electrons</p>		<p>Hybridization of carbon atoms</p> <p>C-C-H bond angle</p> <p>Polarity</p>
<p>$H_2C_2O_4$ Oxalic acid aka Ethanedioic acid</p> <p>Total Valence Electrons</p>	<p>Complete Lewis Structure on the skeleton below:</p>  <p>Redraw with the proper geometry:</p>	<p>Orbital Geometry</p> <p>C_3</p> <p>O_2</p> <p>Hybridization of specified atom</p> <p>C_3</p> <p>O_2</p>

TABLE 12.3 Organic Compounds - Fill in the missing bonds, atoms, and/or lone pairs.

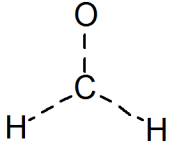
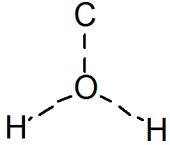
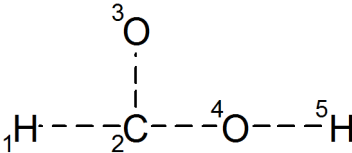
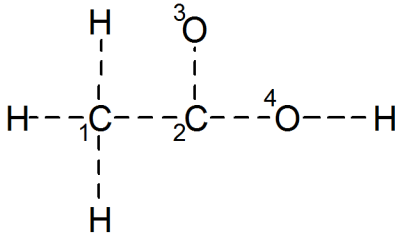
Species	Lewis Dot Structure	VSEPR Theory and Valence Bond Theory Classification
<p>CH₂O</p> <p>HCHO is formaldehyde. Determine the best structure by completing the structures to the right.</p> <p>Total Valence Electrons</p>	<p>Structure 1</p>  <p>Structure 2</p> 	<p>Which structure makes the most sense and why?</p>
<p>HCO₂H</p> <p>Complete the structure for formic acid aka methanoic acid.</p> <p>Total Valence Electrons</p>		<p>Give the bond angles for</p> <p>H₁-C₂-O₃</p> <p>C₂-O₄-H₅</p> <p>Polarity</p>
<p>CH₃CO₂H</p> <p>Complete the structure for acetic acid aka ethanoic acid.</p> <p>Total Valence Electrons</p>		<p>Give the hybridization of the numbered atoms</p> <p>1</p> <p>2</p> <p>3</p> <p>4</p>

TABLE 12.4 Isomers of Organic Compounds

Species	Lewis Dot Structures
<p data-bbox="181 327 237 359">C_3H_6</p> <p data-bbox="181 411 318 527">C_3H_6 has two distinct isomers. Draw each one.</p> <p data-bbox="181 621 318 674">Total Valence Electrons</p>	
<p data-bbox="181 768 237 800">C_4H_8</p> <p data-bbox="181 852 342 989">C_4H_8 has many possible variations. Draw 5 distinct possibilities.</p> <p data-bbox="181 1209 318 1262">Total Valence Electrons</p>	
<p data-bbox="181 1314 269 1346">C_4H_9OH</p> <p data-bbox="181 1398 342 1650">Draw 4 distinct variations; each will have an OH group attached. Do not try to create any isomers without a hydroxyl, OH, group!</p> <p data-bbox="181 1703 318 1755">Total Valence Electrons</p>	

TABLE 12.5 Spartan Molecular Modeling

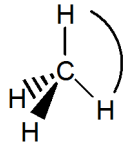
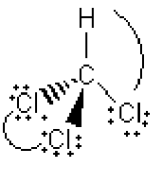
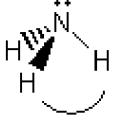
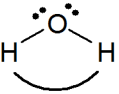
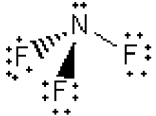
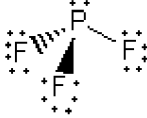
Draw Arrow Representing the Dipole Moment where appropriate on Structure	Bond Angle	Magnitude of Dipole Moment	Electrostatic Potential Surface (Use colored pencils) Several orientations for each molecule are possible.
	$\text{H}-\text{C}-\text{H}$	Polarity	
	$\text{H}-\text{C}-\text{Cl}$ $\text{Cl}-\text{C}-\text{Cl}$	Polarity	
	$\text{H}-\text{N}-\text{H}$	Polarity	

TABLE 12.5 Spartan Molecular Modeling

Draw Arrow Representing the Dipole Moment where appropriate on Structure	Bond Angle	Magnitude of Dipole Moment	Electrostatic Potential Surface (Use colored pencils) Several orientations for each molecule are possible.
	H—O—H	Polarity	
	F—N—F	Polarity	
	F—P—F	Polarity	

Draw the three molecular orbitals, labeling them as pi, n (nonbonding), and pi* orbitals. Note which is the highest occupied molecular orbital (HOMO) and which is the lowest unoccupied molecular orbital (LUMO).

TABLE 12.6 Spartan Molecular Orbitals

Species	Molecular Orbital Drawings
nitrite ion NO ₂ ⁻	

What is the significance to the stability of the nitrite ion of the fully occupied pi orbital?

Post Lab Questions

1. Explain why the bond angles increase or decrease in the following series H-C-H bond in methane, CH_4 , H-N-H bond in ammonia, NH_3 , H-O-H bond in water, H_2O .

2. Explain the differences between the H-C-H bond angle in methane, CH_4 , and the bond angles in trichloromethane, CHCl_3 (Be sure to consider both the Cl-C-Cl and H-C-Cl bonding in trichloromethane, CHCl_3).

3. Compare the dipole moments and bond angles for ammonia, NH_3 , nitrogen trifluoride, NF_3 , and phosphorus trifluoride, PF_3 . Does each dipole point in the same direction? Explain.

TABLE 12.7

	NH_3	NF_3	PF_3
Dipole Moment			
Bond Angles			

Propagation of Error: An Error Analysis Activity

Objective

More often than not, quantities that are measured are used to determine derived quantities. For instance, mass and volume measurements are used to make density determinations. These measurements have a certain error associated with them. This lab will introduce a method of statistical analysis to propagate error through calculations.

Introduction

Errors of a Calculated Result

If a balance with a ± 0.0001 g error and a pipet with a ± 0.01 mL error are used, how should these errors be combined to determine the error in the density? The use of significant figures is an approximation of error, but for a more exact representation the following methods are used.

Absolute error (Δ) is the approximate error of a single measurement. The absolute error is best estimated as the standard deviation for a measurement. Absent this data an estimation should be made based upon the confidence the experimenter has with their ability to read the measuring device.

Relative error is the ratio of the size of the absolute error to the size of the measurement being made.

$$\text{Relative Error} = \frac{\text{absolute error}}{\text{experimental value}} = \frac{\Delta}{\text{measurement}} \quad (\text{EQ 13.1})$$

$$\% \text{Relative Error} = \frac{\text{absolute error}}{\text{experimental value}} \times 100 \% = \frac{\Delta}{\text{measurement}} \times 100 \% \quad (\text{EQ 13.2})$$

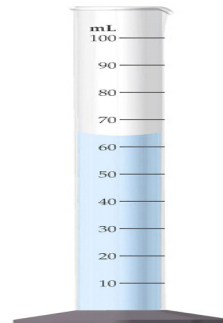
EXAMPLE 13.1

When reading the volume of liquid in the graduated cylinder to the right, you would estimate 64 mL, but it might be 63 or 65 mL. So, the value would be reported as 64 ± 1 mL and the absolute error in the volume measurement, $\Delta V = 1$ mL.

The relative error for the example would be:

$$\text{Relative Error} = \frac{1 \text{ mL}}{64 \text{ mL}} = 0.016$$

or reported as 1.6% relative error.



Using these values we can approximate the error in calculated values. For addition and subtraction the absolute value of the sum or difference can be roughly approximated as the sum of the absolute values.

EXAMPLE 13.2

If the volume of a rock is measured by the displacement of water two volume measurements will be found:

$$\text{Volume water} = 2.5 \pm 0.3 \text{ mL (range 2.2 - 2.8 mL)}$$

$$\text{Volume water + rock} = 6.8 \pm 0.4 \text{ mL (range 6.4 - 7.2 mL)}$$

$$\text{Volume rock} = (\text{Volume water + rock}) - (\text{Volume water})$$

$$= 6.8 \text{ mL} - 2.5 \text{ mL} = 4.3 \text{ mL}$$

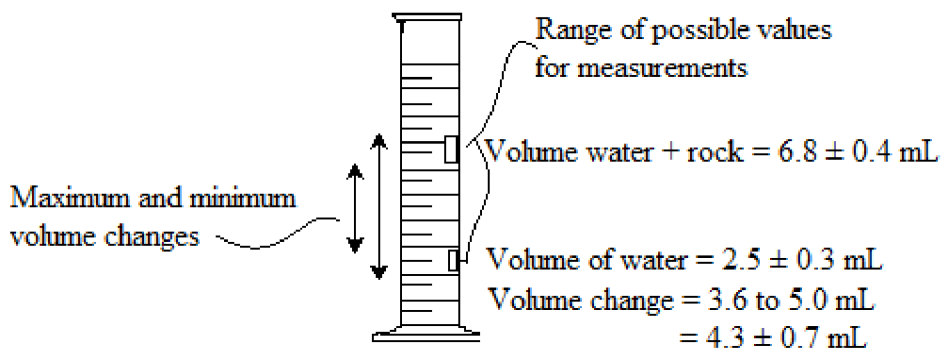
But, the two volume measurements may range over a variety of values. Subtracting the high value for water volume from the low value for water + rock will give a low value for the rock volume:

$$6.4 \text{ mL} - 2.8 \text{ mL} = 3.6 \text{ mL}$$

Subtracting the low value for water volume from the high value for the rock volume gives a high volume for the rock volume:

$$7.2 \text{ mL} - 2.2 \text{ mL} = 5.0 \text{ mL}$$

The range of values for the rock volume is 3.6 - 5.0 mL or 4.3 ± 0.7 mL. The absolute error in this measurement of 0.7 mL is equal to the sum of the absolute errors for the two original volumes. This idea is illustrated in the picture below.

FIGURE 13.1


This method of error propagation overestimates the combined error because of the possibility that errors can cancel when more than one measurement is made.

In fact, if this process is looked at statistically, a better approximation of error in a sum or a difference is given by the formula:

$$\Delta R = \sqrt{\Delta a^2 + \Delta b^2 + \dots} \quad (\text{EQ 13.3})$$

When performing multiplication and division, the propagation of error must use relative rather than absolute errors. This is illustrated when density is calculated. The error in mass is in grams, while the error in volume is in mL. Grams and milliliters cannot be added together to calculate the total error; The relative error is unitless. The sum of the relative errors is an approximation of the total relative error (although it is an overestimation as before. Again, if the simple idea of using statistics is applied a better approximation of error results from the following:

$$\text{Relative Error} = \frac{\Delta R}{R} = \sqrt{\left(\frac{\Delta a}{a}\right)^2 + \left(\frac{\Delta b}{b}\right)^2 + \left(\frac{\Delta c}{c}\right)^2 + \dots} \quad (\text{EQ 13.4})$$

where R is a calculated value and the final absolute error in the result is given by:

$$\Delta R = (\text{relative error})(R) \quad (\text{EQ 13.5})$$

TABLE 13.3

Operation	Example	Error
Addition	$S = A + B$	$\Delta S = \sqrt{\Delta A^2 + \Delta B^2}$
Subtraction	$D = A - B$	$\Delta D = \sqrt{\Delta A^2 + \Delta B^2}$
Multiplication	$P = A \times B$	$\frac{\Delta P}{P} = \sqrt{\left(\frac{\Delta A}{A}\right)^2 + \left(\frac{\Delta B}{B}\right)^2}$
Division	$Q = \frac{A}{B}$	$\frac{\Delta Q}{Q} = \sqrt{\left(\frac{\Delta A}{A}\right)^2 + \left(\frac{\Delta B}{B}\right)^2}$

EXAMPLE 13.4

A chemist analyzes a compound containing only H, C, and O. What is the uncertainty in the %O? The C-H analysis results are:

$$\%C = 54.80 \pm 0.05$$

$$\%H = 6.92 \pm 0.05$$

Answer:

$$\%O = 100.00\% - 54.80\% - 6.92\% = 38.28\%$$

Applying the rule for subtraction:

$$\Delta O \% = \sqrt{(\Delta \%C)^2 + (\Delta \%H)^2} = \sqrt{(0.05)^2 + (0.05)^2} = 0.07$$

So, $\%O = 38.28 \pm 0.07\%$

EXAMPLE 13.5

A student finds the density of a liquid by allowing a 10.00 mL volumetric pipet filled with liquid to drain into a previously weighed Erlenmeyer flask. The following data was recorded:

$$\text{Volume liquid} = 10.04 \pm 0.01 \text{ mL}$$

$$\text{Mass empty flask} = 22.452 \pm 0.002 \text{ g}$$

$$\text{Mass flask + liquid} = 33.629 \pm 0.002 \text{ g}$$

Answer:

$$m = 33.629 - 22.452 \text{ g} = 11.177 \text{ g}$$

$$V = 10.04 \text{ mL}$$

$$d = \frac{m}{V} = \frac{11.177 \text{ g}}{10.04 \text{ mL}} = 1.113 \frac{\text{g}}{\text{mL}}$$

For the error in mass, use the addition rule:

$$\Delta m = \sqrt{(\Delta m_{\text{flask}})^2 + (\Delta m_{\text{flask} + \text{liquid}})^2} = \sqrt{(0.002 \text{ g})^2 + (0.002 \text{ g})^2} = 0.003$$

For the error in density, use the rule for division:

$$\frac{\Delta d}{d} = \sqrt{\left(\frac{\Delta m}{m}\right)^2 + \left(\frac{\Delta V}{V}\right)^2} = \sqrt{\left(\frac{0.003 \text{ g}}{11.177 \text{ g}}\right)^2 + \left(\frac{0.01 \text{ mL}}{10.04 \text{ mL}}\right)^2} = 0.035$$

$$\Delta d = 0.035 (d)$$

$$\Delta d = (0.035)(1.113 \text{ g/mL}) = 0.039 \text{ g/mL}$$

However, normally error is only reported to one significant digit because generally speaking, as demonstrated in the above example, error is the least accurate quantity and therefore determines the magnitude of the overall error.

$$\Delta d = 0.04 \text{ g/mL}$$

Therefore, the student can now report the error in density as:

$$d = 1.12 \pm 0.04 \text{ g/mL}$$

Note that the final density and the error in the density end at the same decimal place.

See the following web sites for a good discussion of error propagation:

<http://www.rit.edu/cos/uphysics/uncertainties/Uncertaintiespart2.html>

<http://www.itl.nist.gov/div898/handbook/mpc/section5/mcp55.htm>

http://teacher.nsl.rochester.edu/phy_labs/AppendixB/AppendixB.html

Procedure

Density is a physical property of matter. It is defined as the ratio of the mass of an object divided by its volume:

$$d = \frac{m}{V} \quad \text{(EQ 13.6)}$$

For solids and liquids, density is usually expressed in units of g/cm^3 . It is evident that the mass and volume of an object must be known to determine its density. A cylindrical shaped metal slug will be used. Its mass will be determined by simple weighing. The volume, however, will be determined by two different methods. An estimate of error will then be made for each method, and then the method or methods with the highest degree of precision will be decided

1. Prepare a data table in your lab book, so that there is space to record the quantities indicated in each part. Be sure to estimate and record the uncertainty of each measurement as you are making the measurements.
2. Obtain the metal cylinder assigned to you. Weigh the cylinder, be sure to record the uncertainty of the measurement.

Vernier Calipers

1. Use Vernier calipers to measure the diameter and length of the metal cylinder to the 0.01 cm. Your instructor will demonstrate how to use these calipers. Make your measurements in centimeters and don't forget to include the uncertainty of your measurements. This will give a volume measurement in cm^3 .
2. Using the dimensions of the cylinder determine the volume:

$$V = \pi r^2 l \quad \text{(EQ 13.7)}$$

3. Obtain the actual density of your cylinder from your instructor.

Volume by Water Displacement

1. Partially fill a 50 mL graduated cylinder with water and read the volume. Don't forget to record the uncertainty of the volume measurements. You must initially have enough water in the cylinder to completely cover the metal slug, but be careful that the displaced water does not exceed the 50 mL mark.
2. Tip the graduated cylinder at a sharp angle to the vertical and carefully slide the metal slug into the graduated cylinder. Do not drop the metal slug into the graduated cylinder. Take care to avoid splashing water up the sides of the graduated cylinder, or break the cylinder. Place the graduated cylinder back on your bench and record the new volume. Don't forget to include the uncertainty of the measurement and take the temperature of your water.

Results and Calculations

Vernier Calipers

1. Use your length, diameter and mass measurements and their uncertainty values to calculate the relative error and percent relative error in your length, diameter and mass measurements. As illustrated in example 13.5.

2. Determine the volume and density of the cylinder.
3. Calculate the uncertainty in each measurement.
4. Then calculate the relative error and percent relative error in your measurements.
5. Calculate the percent error in your density determination.

Volume by Water Displacement

1. Use your volume and mass measurements and their uncertainty values to calculate the relative error and percent error in your volume and mass measurements.
2. Determine the density of the cylinder and its uncertainty value. Then calculate the relative error and percent relative error in your measurements.
3. Calculate the percent error in your density determination.

Create a table summarizing your major data.

Which method is more accurate when determining the volume of the metal slug the calipers or the water displacement? Be sure to use your data to support your answer.

Which method is more precise when determining the volume of the metal slug the calipers or the water displacement? Be sure to use your data to support you answer.

Identification of an Unknown Acid

Objective

The objective in this experiment is to prepare and standardize a sodium hydroxide solution and use it to determine the **equivalent weight**, **pK_a**, and **melting point** of an unknown acid. Using this information the identify of an unknown acid will be determined. The techniques required for this lab include the preparation of a standard acid solution, standardization of a base solution, titration measurement of pK_a and the melting point of a crystalline solid.

Introduction

Up to now, you have done a number of labs which could be classified as quantitative analysis. Quantitative analysis is the analysis of a sample to determine the concentration of a solute in a mixture. Now you will begin to do what is known as qualitative analysis. Qualitative analysis can be defined as the process of using the properties of an unknown substance in order to identify the substance. It is a common occurrence for a chemist to be given a sample and asked to identify the substances in a mixture. A forensic chemist might be asked to identify the toxin which killed a victim. A chemist working for the IOC might be asked to identify illicit substances in the urine sample from an athlete.

In this experiment, you will be given a sample of an unknown acid. Your job will be to identify this acid from measuring a number of physical properties of the compound. First, quantitative analysis will be used to determine the equivalent weight or gram molar mass (GMM) of an unknown acid.

Titration

The term **titration** refers to the addition of a solution of one reagent, usually from a burette, to a known amount of the other reagent, and then determining the volume of solution added when the reaction is complete. If the titration is done by addition of a base to an acid, typically there is a relatively large and sudden increase in pH as the equivalence point is reached. This point may be

detected visually when a color change occurs by using an appropriate indicator, or by measuring the change in pH with a pH meter.

As mentioned, sodium hydroxide will be used in the titration. However, sodium hydroxide solutions cannot be prepared with adequate precision simply by weighing out solid NaOH, since the commercial material is not sufficiently pure and absorbs water and CO₂ quickly from the air. In order for a titration to be accurate, the base solution must first be standardized. **Standardization** refers to the preparation of a solution of accurately known concentration. To standardize NaOH, **oxalic acid** is used since it can be obtained in a high state of purity and does not absorb moisture readily. Thus, to standardize a sodium hydroxide solution, we first prepare the solution noting the approximate concentration of NaOH and then titrate this solution with an oxalic acid solution of known concentration. The oxalic acid solution is referred to as a **standard solution** since it can be prepared such that its exact concentration is known. This solution is also called a **primary standard solution** and the student should be familiar with both terms. Phenolphthalein will be used as the indicator in this acid/base system.

The **equivalent weight** of an acid is defined as the weight of acid that provides one mole of H⁺ in the reaction. The units are grams per equivalent. For a monoprotic acid like HCl, the equivalent weight and the molecular weight are the same. For a diprotic acid like oxalic acid, if both hydrogens are consumed in the reaction, the equivalent weight is one-half the molecular weight. In this experiment, since the formula of the unknown acid is not available, the equivalent weight must be determined by the following relationship:

grams of acid/moles of H⁺ reacted. The number of moles of H⁺ is equal to the number of moles of OH⁻ from the base

Some compounds exist as hydrates. A **hydrate** is a compound in which the solid contains one or more molecules of water locked within the ions or molecules that make up the solid. The water molecules are part of the formula unit and are included when writing the formula for the hydrate. Oxalic acid exists as the dihydrate; this means that there are two molecules of water for every molecule of oxalic acid. Thus, the complete formula is written as:



Notice the “dot” inserted between the formula and water.

Melting Point

The problem with this is that there are many thousands of weak acids. Knowing the gram molar mass of an acid will certainly eliminate the great majority of possible compounds. However, simply knowing the gram molar mass of an acid does not provide sufficient information to identify the substance unambiguously. More properties of the substance must be measured in order to reach a unique identification.

There are a number of methods used by chemists to do qualitative analysis. These would include measuring the boiling or melting point of the substance, measuring the density of the substance, or the solubility of the substance. Also included are a number of more high tech methods such as various types of spectroscopy. These methods would include infrared spectroscopy, UV/vis spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy. Perhaps the qualitative tool of greatest preference to chemists is the gas chromatograph (GC) in tandem with a mass spectrometer (MS) (a GCMS). Your instructor may explain some of these tools. These methods are all fairly expensive.

We will limit ourselves to more classical and less expensive qualitative measurements to identify your unknown.

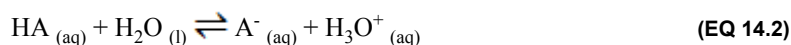
Specifically, two additional measurements beyond the gram molar mass will be used to identify the unknown acid. First, the melting point of the substance will be found. This should greatly narrow down the list of possible acids. The **melting point** of a solid occurs when the solid and liquid phases are in equilibrium, which occurs at a specific temperature. However, the time required to determine a specific melting point can be impractical, so a melting point range of temperatures between the first sign of melting and the complete melting of a solid is found. A *narrow range* of one to two degrees Celsius implies a high degree of purity, while a *broad range* usually implies an impure sample. As the thermal energy imparted by the melting point apparatus to the sample become large enough to overcome the intermolecular forces that hold the sample together the sample melts. The temperature recorded is when the first solid begins to melt until the last bit of solid disappears.

Solids often decompose or undergo unusual behavior before melting including changes in appearance such as loss of luster or darkening, softening, shrinking, or appearing moist before melting. These changes are not melting but, sintering; the actual melting point occurs when the first drop of liquid is seen until the last solid liquefies. When a substance melts with decomposition the substance will bubble or form a dark char. In these instances, to observe the melting point or decomposition point is dependent on the rate of heating.

In fact, it might be sufficient, in tandem with the GMM to make a sure identification from the given list of possible acids, which will be provided by your instructor. However, to make the identification more definite, the strength of the unknown acid will also be found.

Acid Strength, pK_a

As a measure of the relative strength of an acid, chemists use a measurement known as the **acid dissociation constant**, which usually has the symbol K_a . The acid strength of acids, HA, is a property that can be used to explore the relationship between structure and chemical properties. This can be described using Brønsted-Lowry theory, where an acid has the ability to donate a proton to a base:



$$K_a = \frac{[\text{H}_3\text{O}^{+}][\text{A}^{-}]}{[\text{HA}]} \quad (\text{EQ 14.3})$$

Actually, because K_a values tend to vary over such a wide range, chemists usually report the pK_a of an acid, which is defined, similar to pH as follows:

$$pH = pK_a + \log\left(\frac{[\text{A}^{-}]}{[\text{HA}]}\right) \quad (\text{EQ 14.4})$$

when the anion and the acid are at the same concentration (that is, the acid is half-neutralized) the value of the pK_a of an acid is the pH.

When titrating your weak acid, for every mole of hydroxide added, one mole of HA is turned into the conjugate base A^{-} . While titrating your weak acid, you will create a buffer. A **buffer** is a mixture of a weak acid and a conjugate base in roughly equal molar proportions. One property of a buf-

fer is that its pH is changed only slightly by adding strong acid or strong base to it. For this reason, as you titrate your unknown acid, the pH will only change very slowly. Something very interesting happens to the equation for K_a at what is known as the half-titration point. By definition, the **half-titration point** is the point in the titration where exactly half the original weak acid has been converted to the conjugate base. In a titration, the half-titration point will occur at exactly half the volume of titrant as that required to reach the endpoint. At the half-titration point,

$$[\text{HA}] = [\text{A}^-] \quad (\text{EQ 14.5})$$

In this case, at the half-titration point the K_a equation above simplifies to:

$$K_a = [\text{H}^+] \quad \text{or} \quad \text{p}K_a = \text{pH} \quad (\text{EQ 14.6})$$

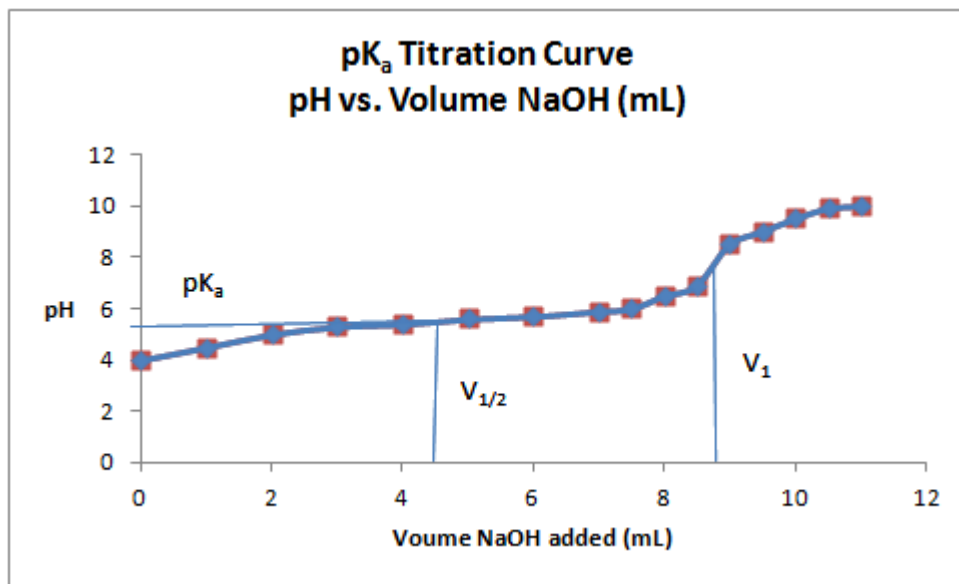
In other words, for example, if a titration of a weak acid required 9.00 mL to reach endpoint, then if one could measure the pH when the volume of base was 4.50 mL, then the pH at that point would equal $\text{p}K_a$ of the acid. Put even more simply, **$\text{p}K_a = \text{pH}$ at half-titration point.**

Your job, then, is to simply measure the pH of a solution of your unknown acid which has been half-titrated! When you half-titrate a weak acid, you are creating a pH buffer. This solution will be fairly resistant to pH change. For this reason, if you add water to the half-titrated solution, it will not affect the pH significantly.

$$\text{pH} = \text{p}K_a \quad (\text{EQ 14.7})$$

The pH is measured with a pH meter. A graph of pH versus mL of sodium hydroxide added.

FIGURE 14.1



The equivalence point (V_1), which is the point where the curve is the steepest, and the half-equivalence point ($V_{1/2}$) of the titration are shown on Figure 14.1. Using the half-equivalence point to determine the $\text{p}K_a$ of the unknown acid, and from the volume of base added at the equivalence point, the equivalent weight of the acid can be calculated. A list of all the possible acids for you to consider along with the $\text{p}K_a$ value for each of the acids will be provided by your instructor.

Once you have successfully measured the GMM, the melting point, and the pK_a of your unknown acid, you should be able to make an unambiguous identification of your acid from the list of possible acids which will be provided by your instructor.

Procedure

Read through the entire procedure first and determine what type of data and observations that you will be collecting. In the data and observations section of your notebook, construct an appropriate data table that facilitates efficient data recording.



NOTE: Record volumes to 0.01 mL and masses to 0.0001 g

Preparation of the Standard Oxalic Acid Solution

1. Calculate the mass of oxalic acid dihydrate, $H_2C_2O_4 \cdot 2 H_2O$, needed to make 250 mL of 0.050 *M* solution. Do not waste time trying to weigh out the exact amount that you calculated since you will know the final concentration once the solution is prepared.
2. Weigh a sample of the hydrate that is within 20 percent of the calculated amount. Tare a clean, dry beaker on the analytical balance, add an appropriate amount (within 20 percent of calculated) of oxalic acid, and weigh the beaker containing the acid. Do not transfer chemicals inside the analytical balance.
3. Transfer all of the acid to a 250.0 mL volumetric flask, fill the volumetric flask half-full with water and swirl contents until the acid is all dissolved. When you are certain that all of the solid has dissolved, add water to the mark, stopper the flask and invert several times to mix thoroughly. Return the volumetric flask at the end of the lab today!

Standardization of NaOH

1. Prepare one liter of approximately 0.10 *M* NaOH by dilution of the stock solution provided. Mix it thoroughly and store in a properly labeled plastic bottle. Be sure to record the original concentration of the stock solution, the amount of water that you used to dilute the stock solution and the final concentration of your NaOH solution.



Remember that all of these concentrations of NaOH are approximate; the first goal is to determine the exact concentration of NaOH by standardization

2. Using a volumetric pipet, transfer 25.00 mL of your oxalic acid solution into a 125 or 250 mL Erlenmeyer flask. Add two drops of phenolphthalein indicator to the acid solution. Fill the burette with your NaOH solution and titrate the acid in the flask with the NaOH from the burette. The titration is complete when the first pink color persists in the flask. Swirl the flask during the addition of base to ensure complete mixing.
3. Be sure to rinse the pipet with the acid solution and the burette with base before use, to remove any traces of water. The inside of the titration flask should be washed down with water just before reaching the end point to remove any drops of acid or base stuck on the side of the flask.
4. Try to add no more than one drop in the last addition as you approach the end point.

5. Perform titrations until you get three that differ in only the second decimal place for the mL of base used. Calculate the concentration of the base for each trial, and obtain a mean and standard deviation. The average concentration that you calculate is the concentration of your now standardized NaOH. Your standardized base will be used to titrate your unknown acid so be sure to cover the solution to prevent loss of water (which changes the concentration) and save it for use later in the experiment.

Molar Mass of a Monoprotic Unknown Acid

Using standardized sodium hydroxide titrate the unknown monoprotic acid to determine the equivalent weight of the acid. Since the unknown acid is a monoprotic acid, you will not need to worry about the distinction between equivalent weight and gram molar mass.

1. On the analytical balance, measure out approximately 0.50 g of your unknown acid. **Be sure to record your unknown number in your lab book.** Being very careful not to lose any of the acid, transfer to a 250 mL Erlenmeyer flask which has been cleaned but not necessarily dried. Add 50-100 mL of water as well as two drops of phenolphthalein indicator to the flask.
2. If the acid does not dissolve easily, you may need to heat the mixture gently. If most, but not all the acid dissolves, you may proceed with the titration, as the conjugate base of the acid created during the titration will be quite soluble in water.
3. Clean, rinse and condition a 50-mL buret with standardized approximately 0.10 *M* sodium hydroxide solution. **Be sure to record the concentration of the NaOH in your lab book.** Fill the buret to somewhere near the top and titrate your sample to phenolphthalein endpoint.
4. Repeat the procedure three times. To be sure your results are good, calculate the ratio of grams of unknown used to volume of titrant used. The ratios should agree within 1%. At this point, you may want to calculate the GMM of your unknown acid from the three titrations and calculate the average of your values.

The Melting Point

First, you will be measuring the melting point of your acid. (If the melting point apparatus is crowded, you can go on and do the experiment to measure pK_a first if you like). The melting point of a substance is the temperature at which the solid crystals of that compound turn to a liquid. This will be a fairly simple measurement.

1. Place just a few small crystals of your unknown acid in the center of the top of your melting point apparatus. Only a very small amount of solid is required to determine a melting point. Insert a thermometer in the appropriate channel in the apparatus.
2. Allow the temperature to increase fairly slowly and record the temperature at which it melts. You should not bother to be extremely careful in this first attempt, as you are just trying to get an approximate melting point the first time around.
3. Once you have an approximate melting point, now you will measure the melting point much more carefully by approaching the melting point very gradually. Clean off the surface of the melting point apparatus and put more crystals on top as before. This time, when you are a few degrees below the melting point, begin to raise the temperature quite slowly. This can be done by turning down the hot plate or by putting a few layers of paper between the hot plate and the melting point apparatus. You may have to use your imagination a bit at this point! The temperature should rise at no more than two degrees per minute at the melting point to measure an accurate melting point.

4. If you have any doubt at all about the melting point, perform the procedure one additional time. If you have two fairly good values which are slightly different, you can take the melting point to be the average of those two values. Record your results in the data section.

Measuring pK_a

Your job, then, is to simply measure the pH of a solution of your unknown acid which has been half-titrated! When you half-titrate a weak acid, you are creating a pH buffer. This solution will be fairly resistant to pH change. For this reason, if you add water to the half-titrated solution, it will not affect the pH significantly.

1. Measure out another sample of the unknown acid on the analytical balance.

Using the Vernier Interface

1. Calibrate the pH electrode using two buffer solutions of known pH. Once the reading stabilizes, follow the directions on the screen.
2. Using the known GMM of the unknown acid obtained from your earlier titration, calculate the volume needs to titrate it.
3. Divide the volume by two and add this volume to your sample.
4. Measure the pH using the calibrated pH meter. This will be the pK_a of your unknown.
5. Repeat the process to get an average pK_a .

Determining the Identity of Your Unknown Acid

At this point, you should use the pK_a you measured to begin to eliminate possible weak acids from the list provided. Once you have narrowed the list down a bit, you should narrow it further, either by determining the GMM of your candidates from their formulas and comparing the result to your measurements, or by looking up the melting points of the candidates in the Handbook of Chemistry and Physics (known as the CRC).

With any luck, the pK_a in combination with either the melting point or the GMM should reduce your possibilities down to just a couple of acids. Now, use the third measurement (MP or GMM) to narrow your choice to one. This is your proposed choice of the identity of your unknown acid.

If you like, you may use the template provided below for recording your experimental values for your unknown acid, as well as the values you find in the literature for your best guess as to the actual acid, as well as your second best guess.

Sample Data Sheet

Do not use this data sheet for your records. This is provided as an example of what should be in your lab notebook before you begin the experiment.

TABLE 14.1 Preparation of Standard Oxalic Acid Solution

mass of oxalic acid _____
 volumetric flask _____

TABLE 14.2 Standard Solution Preparation

Initial concentration of stock solution _____
 Pipet size _____
 Amount of water used for dilution _____
 Approximate concentration of your standard solution _____

TABLE 14.3 Standardization of NaOH Solution

	Trial #1	Trial #2	Trial #3	Trial #4
Initial buret reading				
Final buret reading				
Volume of base used				

TABLE 14.4 Melting Point of Unknown Solid Acid

	Trial #1	Trial #2	Trial #3	Average
Melting Point Range				

TABLE 14.5 Titration of Unknown Solid Acid

	Trial #1	Trial #2	Trial #3	Trial #4
Initial buret reading				
Final buret reading				
Volume of base used				
Mass of unknown				

Sample Calculation Sheet

Do not use this sheet for your records. This is provided as an example of what should be in your lab notebook before you begin the experiment.

TABLE 14.6 Standard Oxalic Acid Solution

Mass of oxalic acid	
Moles of oxalic acid	
Volumetric flask	
Molarity of oxalic acid	
Molarity of H ⁺ ions in oxalic acid	

TABLE 14.7 Standardization of NaOH Solution

	Trial #1	Trial #2	Trial #3	Trial #4
Moles of oxalic acid				
Volume of NaOH				
Molarity of NaOH				
Average molarity				

TABLE 14.8 Determination of Equivalent Weight

	Trial #1	Trial #2	Trial #3	Trial #4
Mass of unknown				
Volume of NaOH				
Moles of NaOH				
Moles H ⁺ reacted				
Equivalent weight				
Average equivalent weight				

TABLE 14.9 Identification of Unknown Acid

	Average Measured Values	Identity of Acid	Literature Values	Second Best Guess	Literature Values
Gram Molar Mass					
Melting Point					
pK _a					

Post Lab Questions

1. What mass of oxalic acid dihydrate, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$, is needed to prepare 250.0 mL of 0.050 *M* solution?
2. If 0.750 grams of oxalic acid dihydrate required 31.0 mL of NaOH solution in a titration, what was the concentration of the base?
3. What was the equivalent weight of an acid if 0.250 grams of it just neutralized 41.0 mL of 0.161 *M* NaOH solution?

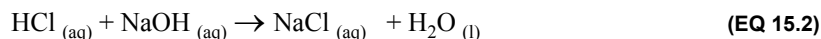
Determining the Effectiveness of an Antacid

Objective

In this lab you will gain further experience with titrations by observing reactions with hydrochloric acid and commercial antacids, calculate the amount of acid neutralized by commercial antacids, and tabulate and compare results to determine most cost-effective antacid.

Introduction

Double displacement reactions that involve acids and bases are **neutralization reactions**, combining to form salts and water.



The determination of unknown concentrations of acids or bases can be done using the method known as **titration**. Titrations involve adding one solution whose concentration (of acid or base) is known, the **titrant**, usually from a buret to a specific volume of another solution of unknown concentration (acid or base), the **analyte**. One mole of H^+ ion neutralizes one mole of OH^- . As the reaction proceeds, the pH of the solution changes. When all H^+ ions have been neutralized, this is the titration's **equivalence point**. At this point the addition of the basic solution will have a dramatic effect on pH. This point may be detected visually when a color change occurs by using an appropriate indicator, or by measuring the change in pH with a pH meter. A chemical **indicator** which changes color at various pHs, can be used to find the **end point**, which should be near the equivalence point. For example, the indicator phenolphthalein is a pinkish-red in basic solutions between pH 8.2-10.0 and colorless in acidic solutions changes colors. There is often a slight difference between the change in the indicator color and the actual equivalence point of the titration. This is an indeterminate error (i.e. systematic error). To minimize this error an indicator with an end point very close to the equivalence point of the reaction should be used.

Back titration is a method of indirect titration, where the concentration of the analyte is determined by reacting it with a known number of moles of excess reagent. The excess reagent is then neutralized by titrating it against a second reagent of known concentration. The concentration of the analyte in the original solution can be found based on the amount of reagent consumed.

EXAMPLE 15.1

A student places 100.00 mL of 0.1000 M HCl solution in a flask with a crushed antacid tablet and phenolphthalein indicator. After the reaction has gone to completion, he titrates the excess acid with 0.1000 M NaOH solution. The initial reading of the buret is 0.40 mL. At the end point, the final reading of the buret is 27.15 mL. The student wants to determine the number of H⁺ moles that were neutralized by the antacid.

First, calculate the volume of base required to neutralize the acid.

$$\begin{aligned} \text{final volume} - \text{initial volume} &= \text{volume of base required to neutralize acid} \\ 27.15 \text{ mL} - 0.40 \text{ mL} &= 26.75 \text{ mL required to neutralize acid} \end{aligned} \quad (\text{EQ 15.3})$$

Second, calculate how many moles of base were used to neutralize the acid.

$$\begin{aligned} \text{molarity of base} \times \text{L of base used to neutralize acid} &= \text{moles of base used} \\ 0.02675 \text{ L} \times \frac{0.1000 \text{ mol NaOH}}{1 \text{ L NaOH soln}} &= 0.002675 \text{ mol NaOH} \end{aligned} \quad (\text{EQ 15.4})$$

Third, calculate the number of moles of acid neutralized by the added NaOH. Since this is a monoprotic acid it is a one-to-one reaction. Therefore, one mole of base neutralizes one mole of acid.

$$0.002675 \text{ mol NaOH} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}} = 0.002675 \text{ mol HCl} \quad (\text{EQ 15.5})$$

Fourth, determine how many moles of acid were in the flask prior to titration.

$$0.10000 \text{ L HCl} \times \frac{0.1000 \text{ mol HCl}}{1 \text{ L HCl soln}} = 0.01000 \text{ mol HCl} \quad (\text{EQ 15.6})$$

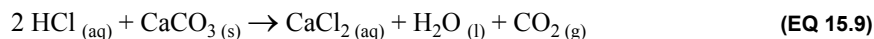
Fifth, calculate number of moles of acid that the antacid tablet neutralized. The number neutralized is the difference between the number that was added initially and that left over.

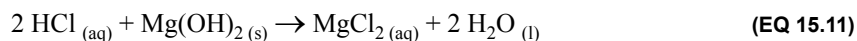
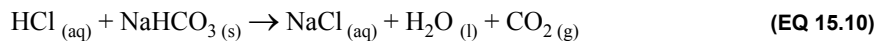
$$\text{mol HCl before neutralization} - \text{mol HCl neutralized by titration} = \text{mol HCl neutralized by antacid} \quad (\text{EQ 15.7})$$

$$0.01000 \text{ mol HCl} - 0.002675 \text{ mol HCl} = 0.007325 \text{ mol HCl} = 0.00733 \text{ mol HCl neutralized} \quad (\text{EQ 15.8})$$

A back titration is useful if the end point of the reverse titration is easier to identify than the end point of the normal titration. They are also useful if the reaction between the analyte and the titrate is very slow.

Hydrochloric acid is the acid present in our stomachs. Many of us are plagued with a condition called heartburn. Heartburn is a result of acid reflux into the esophagus. Commercial **antacids** are effective in neutralizing stomach acid. How effective an antacid may be is determined by the amount of acid neutralized. In this experiment you will make this determination. The mixing of hydrochloric acid and a commercial antacid in an Erlenmeyer flask mimics what goes on in the stomach. The antacid is made up of active and inactive ingredients. The base component of the antacid is the active ingredient, calcium carbonate, sodium bicarbonate, and magnesium hydroxide are common examples:





Once the antacid has exhausted its neutralizing capabilities there will be acid left in the flask. You will determine and compare the neutralizing capabilities of several commercial antacids. The more effective the antacid, the more moles of acid it can neutralize. You will titrate the solution with a known concentration of base to figure out how many moles of acid are left in the flask after the antacid has been used up. This is an example of a back titration.

After gathering and analyzing your data, you will be able to do determine mass effectiveness:

$$\text{mass effectiveness} = \frac{\text{mol HCl neutralized by antacid}}{\text{g antacid tablet}} \quad \text{(EQ 15.12)}$$

and cost effectiveness of each antacid:

$$\text{cost effectiveness} = \frac{\text{mol HCl neutralized by antacid}}{\text{cost of tablet}} \quad \text{(EQ 15.13)}$$

You will also determine the mass of base per tablet and compare it to the manufacturer's values. Using this information you will determine the "best" antacid from the ones supplied.

Procedure

Part A: Sodium Hydroxide Standardization

1. In a beaker prepare about 400 mL of a 0.1 M sodium hydroxide solution from the pellets provided. Record the mass of the sodium hydroxide to as many decimal places as you can. Be sure to stir well.



NOTE: Notice how the numbers on the balance are increasing! Sodium hydroxide is hygroscopic.

2. Obtain a volumetric pipet and buret from the stockroom. Be sure to thoroughly clean and condition them.
3. Carefully pipet 10.00 mL of the 1.00 M HCl into the Erlenmeyer flask.
4. Add an appropriate indicator, such as bromothymol blue, to your solution.
5. Fill the buret with the NaOH solution. Record the initial volume to 2 decimal places.
6. Titrate the HCl solution by adding the NaOH solution drop-wise to the flask that contains your acid and the indicator. Gently swirl the flask while titrating. As you approach the end point, be sure to rinse off the tip of the buret and the sides of the flask with deionized water. When you see the indicator permanently change color that lasts at least 60 seconds, you have reached the end point.
7. Record the final volume of the base solution.
8. Repeat the procedure four more times. Your volume of base added should be within 0.05 mL of each other.

Part B: Antacid Titration

1. Obtain one tablet of antacid. Weigh the tablet and record the weight to the nearest 0.001 g.
2. Crush the tablet with the mortar and pestle.
3. Add the crushed tablet quantitatively to an Erlenmeyer flask. Use a powder funnel or weigh paper to transfer the powdered tablet to the flask and rinse the mortar, pestle, and funnel with several aliquots of DI water to be sure that all of the antacid has been transferred to the Erlenmeyer flask.
4. Obtain a volumetric pipet and buret from the stockroom. Be sure to thoroughly clean and condition them. If you have not already done so.
5. Carefully pipet 10.00 mL of the 1.00 M HCl into the Erlenmeyer flask with the crushed tablet and swirl. Gently heat the mixture to help dissolve the tablet and any inert ingredients, which may be in the antacid.
6. If the tablet does not dissolve add an additional 10.00 mL of acid.
7. Test with litmus paper. If still basic continue to add aliquots of HCl until the solution is acidic to litmus.
8. Add an appropriate indicator, such as phenolphthalein, to your now acidic solution.
9. Obtain about 150 mL of NaOH in a beaker. Fill the buret with the NaOH solution. Record the initial volume to 2 decimal places.
10. Titrate the antacid solution by adding the NaOH solution drop-wise to the flask that contains your antacid and the indicator. Gently swirl the flask while titrating. As you approach the end point, be sure to rinse off the tip of the buret and the sides of the flask with deionized water.

When you see the indicator permanently change color that lasts at least 60 seconds, you have reached the end point.

11. Record the final volume of the base solution.
12. Repeat the procedure four more times, remembering to use the same brand of antacid.
13. Titrate with at least one other antacid or the number specified by your instructor.

Partner Variation

1. Work with a partner and as a group titrate four different antacids and compare the antacids in terms of effectiveness.

Results and Calculations

1. Complete Table 15.2 to determine the concentration of the NaOH solution and the standard deviation.
2. Complete Table 15.4 and Table 15.5 to analyze the antacid tablets. Be sure to show one calculation of each type.
3. What does your standard deviation tell you about your results?
4. What does the percent deviation tell you about your results?
5. Identify the best antacid based on your analysis of your data.

Report

Copy Table 15.3 , Table 15.3 , and Table 15.4 into your lab notebook to use during the experiment. Complete Table 15.2 , Table 15.4 , and use Table 15.5 to analyze your data.

TABLE 15.2 Standardization of NaOH Solution

	Trial #1	Trial #2	Trial #3	Trial #4
Molarity of HCl solution				
Volume of analyte				
Initial buret reading				
Final buret reading				
Volume of titrant				
Molarity of NaOH solution				
Average Molarity of NaOH solution				
Standard Deviation				

TABLE 15.3 Reagent Data

Brand of antacid	
Cost of antacid	per tablets
Amount of base per tablet	
Concentration of HCl solution	
Concentration of NaOH solution	

TABLE 15.4 Antacid Back-Titration Data using Standardized NaOH Solution

	Trial #1	Trial #2	Trial #3	Trial #4
Mass of flask				
Mass of flask and tablet				
Mass of tablet				
Volume HCl added				
Initial buret reading				
Final buret reading				
Volume of titrant				

TABLE 15.5 Antacid Analysis

	Trial #1	Trial #2	Trial #3	Trial #4
Number of moles of HCl initially added				
Number of mol NaOH from buret				
Number of moles of base from tablet (i.e. moles of HCl neutralized by antacid tablet)				
Number of moles HCl neutralized per gram tablet				
Average number moles of acid neutralized per tablet				
Standard deviation				
Average number of moles neutralized per gram tablet				
Standard deviation				
Cost of antacid per tablet				
$\frac{\text{average number of moles HCl neutralized}}{\text{cost of tablet}}$				
average moles of base/tablet				
average mass of base/tablet				
% deviation				

Post Lab Questions

1. Which of the antacid tablets analyzed by your lab section is the most cost effective?

2. Calcium dietary supplements are composed primarily of calcium carbonate which is also the main component of marble.
 - a. Briefly explain why calcium carbonate would be a good calcium ion source for those suffering from chronic heartburn.

 - b. Marble statues erode when exposed to acid rain. Give a brief explanation for this erosion; include a chemical equation.

3. How does the dye affect your titration? Propose some modifications that might be made to the procedure if you are trying to analyze a pink colored tablet.

4. Carbonate functions as a buffer. **Buffers** are weak acids or bases, which are capable of minimizing pH changes. How might this affect the results of your titrations?

Determination of Molar Mass by Freezing Point Depression

Objective

To determine the molar mass of an unknown that is a nonelectrolyte and nonvolatile using freezing point depression of a known solvent and the freezing point depression, K_f , from experimental data.

Introduction

When a non-volatile substance is dissolved in a solvent, the vapor pressure of the solvent is lowered. This affects the boiling and freezing temperatures of the solution by lowering the freezing point and elevating the boiling point relative to the pure solvent. Those properties that depend solely on the number of solute particles (ions or molecules) and are not dependent on the properties of those particles are called **colligative properties**.

Can this freezing point depression or boiling point elevation be put to any practical use? Certainly! In this experiment you will use the freezing point depression to determine the molar mass of an unknown substance. You can also use this phenomena to raise the boiling point of the water that cools your car. It is called **antifreeze**, but in San Diego there is little reason to be concerned about your coolant freezing. Antifreeze depresses the freezing point and elevates the boiling point of the coolant water in your radiator. This is important because as soon as the water in your radiator boils it no longer is useful as a coolant.

Molality, m , is used to express the concentration of the solute. Remember, molality is the number of moles of a solute dissolved in kilograms of solvent.

$$\text{molality} = m = \frac{\text{moles of solute}}{\text{kg of solvent}} \quad (\text{EQ 16.1})$$

Freezing point depression is found by finding the difference in the freezing point of the pure solvent from that of the solution.

$$\Delta T_f = T_{f \text{ pure solvent}}^{\circ} - T_{f \text{ solution}}^{\circ} \quad (\text{EQ 16.2})$$

The relationship between the freezing point of solution and the freezing point of the pure solvent is:

$$\Delta T_f = K_f m \quad (\text{EQ 16.3})$$

It is important to note that this equation is for non-dissociating substances. You need to account for the number of ions in solution for those substances that dissociate. For these compounds the total number of ions must be accounted for.

$$\Delta T_f = i K_f m \quad (\text{EQ 16.4})$$

In Equation 16.4, the van't Hoff factor, i , represents the total number of ions produced in solution per formula unit of salt. For example, i for CaCl_2 is three; for each formula unit there are three ions present upon dissociation.

EXAMPLE 16.1

Analysis of β -carotene, a dietary source of vitamin A, shows that it contains 10.51% H and 89.49% C. Dissolving 0.0250 g of β -carotene in 1.50 g of camphor ($K_f = 37.7^\circ\text{C}/m$) gives a freezing point depression of 1.17°C .

- a. What is the molecular weight of β -carotene?

Use Equation 16.3 to solve for the number of molality of solution.

$$m = \frac{\Delta T}{iK_f} = \frac{1.17^\circ\text{C}}{1(37.7^\circ\text{C}/m)} = 0.0310 \frac{\text{mol } \beta\text{-carotene}}{1000 \text{ g camphor}} \quad (\text{EQ 16.5})$$

Now, use the calculated molality to determine the number of moles of solute.

$$1.50 \text{ g camphor} \times \frac{0.0310 \text{ mol } \beta\text{-carotene}}{1000 \text{ g camphor}} = 4.66 \times 10^{-5} \text{ mol } \beta\text{-carotene} \quad (\text{EQ 16.6})$$

Remember, molar mass has units of g/mol. You know the number of moles of solute and the mass of the solute. The molar mass can now be calculated.

$$\frac{0.0250 \text{ g } \beta\text{-carotene}}{4.66 \times 10^{-5} \text{ mol } \beta\text{-carotene}} = 537 \text{ g/mol} \quad (\text{EQ 16.7})$$

- b. What is the molecular formula of β -carotene?

$$\left(537 \frac{\text{g}}{\text{mol}}\right) \left(\frac{89.49}{100}\right) = \frac{480.5613 \frac{\text{g}}{\text{mol}}}{12.011 \frac{\text{g}}{\text{mol}}} = 40.01009908 \approx 40C \quad (\text{EQ 16.8})$$

$$\left(537 \frac{\text{g}}{\text{mol}}\right) \left(\frac{10.51}{100}\right) = \frac{56.4387 \frac{\text{g}}{\text{mol}}}{1.008 \frac{\text{g}}{\text{mol}}} = 55.99077381 \approx 56H \quad (\text{EQ 16.9})$$

Therefore, the molecular formula of β -carotene is $\text{C}_{40}\text{H}_{56}$.

Procedure

Part I: Determining the Freezing Point of Pure Lauric Acid

In order to calculate the molar mass of the unknown solute in Part III, you will need to measure the freezing point of the pure solvent.

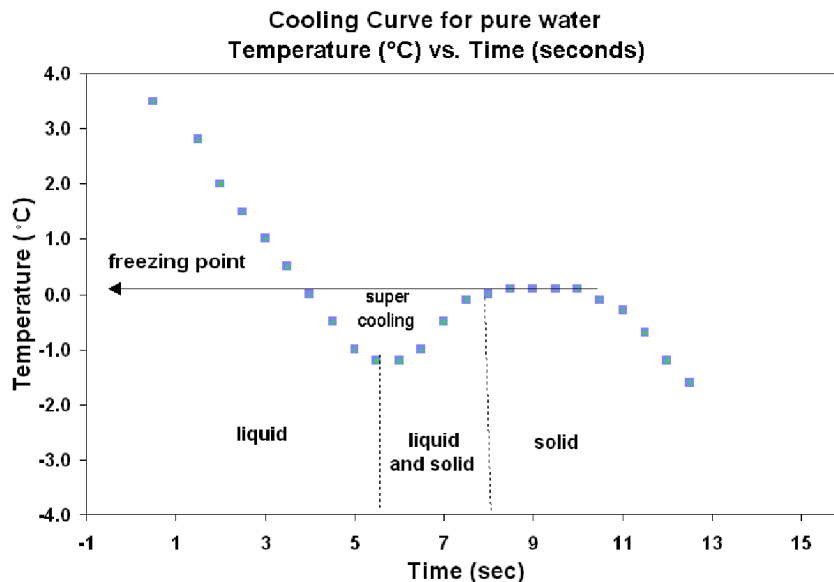
1. Weigh a large test tube and add approximately 8 g of lauric acid. Re-weigh the test tube and its contents.
2. Prepare a water bath by filling a 400 mL beaker with tap water and support the beaker on a ring clamp furnished with wire gauze. Heat the beaker of water with a Bunsen burner or hot plate to between 70-80 °C. Make sure that the water level remains above 200 mL in this beaker.



While the sample is melting prepare the electronic interface to run an experiment collecting the temperature. Sample the temperature about once every two seconds.

3. Fill a second beaker with room temperature tap water on your bench (20-25 °C).
4. Clamp the test tube containing the lauric acid to the ring stand and immerse it in the hot water. After all the lauric acid has been liquefied wait an additional 2-3 minutes. The lauric acid will begin to melt as soon as the water temperature is above its melting point. **Be Cautious! Do not spill hot lauric acid on yourself or touch the bottom of the test tube.**
5. Lower the test tube into the room temperature bath, add a stir bar and the thermistor. **Make sure that the thermistor does not touch or become too close to the stir bar.** Run the thermistor program until the liquid is solid and the stir bar stops moving. Your sample will begin to freeze and the stirrer will no longer spin. Your curve may look something like that illustrated in Figure 16.1. **Make sure that you save your data to a flash drive.**

FIGURE 16.1



6. **Do not attempt to pull the probe out of the solidified sample (even a little) - this might damage it.** Use the hot water bath to re-melt the acid and gently remove the probe when the sample liquefies. Repeat the experiment a second time.
7. Once finished re-melt the sample and remove the probe. Carefully wipe any excess sample from the probe with a tissue. Clean up any drips or spills in the hood and balance area. Save your data to a flash drive. **Do not put the reagents down the sink! Be sure to remove the magnetic stir bar before disposing of your chemicals. Dispose of chemicals as instructed.**

Part II: Measuring the Freezing Point for Lauric Acid/Water Solution

In order to determine K_f for lauric acid, you need to also determine the freezing point for a solution with known concentration. You will use DI water as your known solute.

1. Add 1-2 drops of DI water to your test tube containing the lauric acid. Re-weigh the test tube and contents.
2. Repeat steps 2-7 in Part I to determine the freezing point of this solution. **Make sure that you save your data to a flash drive.**

Part III: Measuring the Freezing Point for Lauric Acid/Unknown Solute Solution

In order to determine the molar mass of the unknown solute, the freezing point of the solution must be determined. In this manner the molar mass can be determined using the value for K_f and ΔT_f . An example of this calculation is found in Example 16.1.

1. Discard the contents of the previous steps in the labeled waste container under the hood. Weigh about 1 gram of an unknown solute to the nearest 0.001 g.
2. Add this to a known amount of lauric acid. Once again, use approximately 8 grams of the solvent weighed to the nearest 0.001 g. Mix the solute and solvent using a mortar and pestle. If the two solids are not well mixed, the unknown acid will form a layer at the bottom of the test tube and will not melt.
3. Repeat steps 2-7 in Part I to determine the freezing point of this solution. **Make sure that you save your data to a flash drive.**
4. Dispose of your solution appropriately and make sure the balance area, reagent area and hoods are clean.

Data Treatment

1. Determine the freezing point for each run using the graphs. Make sure that you use appropriate techniques to account for any supercooling (Your instructor will help you with this). There should be a total of six experimental runs: 2 for the pure solvent, 2 for the known solute (optional), and 2 for the unknown solute. Average the two runs for each determination and use those in subsequent calculations. Compare your freezing point for the pure solvent to that found in the *CRC Handbook*. Calculate a percent error.
2. If Part II was completed, calculate K_f for lauric acid and compare it to the literature value by calculating a percentage error. If Part II was not completed use the literature value of lauric acid ($K_f = 3.90 \text{ }^\circ\text{C}/m$) in your molar mass determination.
3. Calculate the molar mass of your unknown solute. Compare your molar mass to that of benzoic acid by calculating a percent error.
4. Create a table summarizing your major data.

Post Lab Questions

1. A solution is prepared by dissolving 4.9 g sucrose ($C_{12}H_{22}O_{11}$) in 175 g water. Calculate the freezing point of this solution.
2. Is the freezing point of 0.01 *m* KF_(aq) higher or lower than that of 0.01 M glucose_(aq)? Explain.
3. The freezing point of t-butanol is 25.50 °C and K_f is 9.1 °C/*m*. Usually t-butanol absorbs water on exposure to air. If the freezing point of a 10.0 g sample of t-butanol is 24.59 °C, how many grams of water are present in the sample?
4. A 0.350 g sample of a large biomolecule was dissolved in 15.0 g of chloroform, and the freezing point depression was determined to be 0.240 °C. Calculate the molar mass of the biomolecule (K_f for chloroform is 4.70 °C/*m*).
5. In the winter of 1994, record low temperatures were registered throughout the United States. For example, in Champaign, Illinois, a record low of -29 °F was recorded. At this temperature can the salting of icy roads with calcium chloride be effective in melting the ice? Assume that the solubility of calcium chloride in cold water is 74.5 g per 100.0 grams of water.

6. The freezing point depression constants of the solvents cyclohexane and naphthalene are $20.1\text{ }^{\circ}\text{C}/\text{m}$ and $6.94\text{ }^{\circ}\text{C}/\text{m}$ respectively. Which would give a more accurate determination by freezing point depression of the molar mass of a substance that is soluble in either solvent? Why?
7. A forensic chemist is given a white solid that is suspected of being pure cocaine ($\text{C}_{17}\text{H}_{21}\text{NO}_4$, molar mass = 303.35 g/mol). She dissolves $1.22 \pm 0.01\text{ g}$ of the solid in $15.60 \pm 0.01\text{ g}$ benzene. The freezing point is lowered by $1.32 \pm 0.04\text{ }^{\circ}\text{C}$.
- What is the molar mass of the substance?
 - Assuming that the percent uncertainty in the calculated molar mass is the percent uncertainty in the temperature change, calculate the uncertainty in the molar mass.
 - Could the chemist unequivocally state that the substance is cocaine? For example, is the uncertainty small enough to distinguish cocaine from codeine ($\text{C}_{18}\text{H}_{21}\text{NO}_3$, molar mass = 299.36 g/mol)?
 - Assuming that the absolute uncertainties in the measurements of temperature and mass remain unchanged, how could the chemist improve the precision of her results?

Chemical Equilibrium and Le Châtelier's Principle

Objective

In this experiment, you will study the equilibrium conditions of six different reactions. You will first establish the equilibrium by mixing the solutions provided for each reaction and then add reagents in order to perturb the established equilibrium. Each time that you cause a change in the equilibrium, you will observe the changes (look for evidence of reaction), write a net ionic equation illustrating the changes and then comment on how the reaction rate is affected, either the forward or reverse reaction rate. The goal is to learn how equilibria respond to changes in concentrations and changes in temperature.

Introduction

Many chemical reactions are considered to be reversible, meaning that the reactants are not completely converted into the products due to a competing reverse reaction. Consider the reaction:



The forward reaction is $A + B \rightarrow C + D$ and the reverse reaction is $C + D \rightarrow A + B$. Both of these reactions occur simultaneously as indicated by the double-headed arrow in the original reaction. The forward reaction occurs at some characteristic rate dependent upon the concentrations of the reactants and the temperature. The reverse reaction also occurs at some particular rate that is also dependent upon concentrations and temperature. When the rate of the forward reaction is equal to the rate of the reverse reaction, the system is said to be at equilibrium. At equilibrium, the products react at the same rate they are produced; thus the concentrations of the substances do not change.

Equilibrium Effects from Changes in Concentration

Le Châtelier's Principle states that, for a system at equilibrium, if the conditions are changed, the system responds in such a manner to counteract the change. For example, in the reaction above, the rate of forward reaction is increased when component A is added to the system. This results in a

decrease in the concentration of component B and an increase in the concentrations of C and D. This shows that the equilibrium has been shifted to the right.

Looking at the effect of changing the concentrations of any of the reactants or products we see that:

- An increase in the concentration of A or B will increase the rate of the forward reaction and shift the equilibrium to the right.
- An increase in the concentration of C or D will increase the rate of the reverse reaction and shift the equilibrium to the left.
- A decrease in the concentration of A or B will decrease the rate of the forward reaction and shift the equilibrium to the left.
- A decrease in the concentration of C or D will decrease the rate of the reverse reaction and shift the equilibrium to the right.

Equilibrium Effects from Changes in Temperature

Temperature changes can also affect the position of equilibrium. For the endothermic reaction shown here:



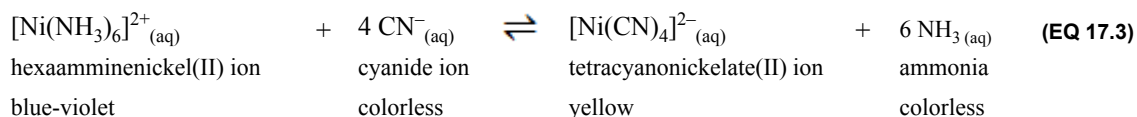
a temperature increase would increase the rate of both reactions. However, the forward reaction requires heat to proceed and an increase in temperature would provide this heat thereby increasing the rate significantly. The reverse reaction generates heat and more available heat in the form of increased temperature does not significantly affect the rate. Thus, in this case, a temperature increase will shift the equilibrium to the right.

Stated another way: an endothermic reaction shifts to the right if the temperature of reaction is increased. An exothermic reaction shifts to the left if the temperature of reaction is increased.

When studying chemical equilibria, one must observe a system, determine measurable indications of equilibrium shifts, and write chemical equations describing the shifts that are occurring. Following is a sample experiment.

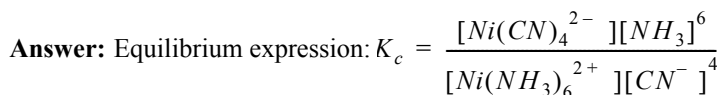
Sample Write-Up

The following equilibrium can be established:



Reagents available to establish this equilibrium: 0.1 M NiCl₂, 6 M NH₃, 1 M NaCN, 12 M HCl

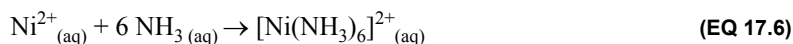
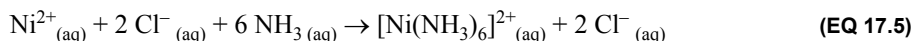
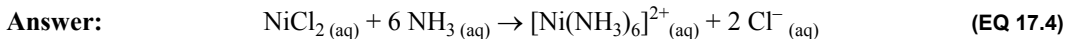
1. What is the equilibrium expression for Equation 17.3?



2. What reaction will produce hexaamminenickel(II) complex ion, $[\text{Ni}(\text{NH}_3)_6]^{2+}$?

Answer: Mixing nickel(II) chloride, NiCl_2 , with ammonia, NH_3 , will generate the complex:

a. Write the net ionic reaction taking place:



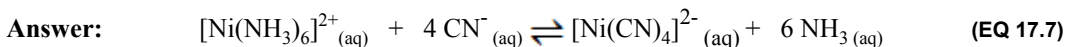
3. Addition of what reagent will shift the equilibrium to the right?

Answer: Add 1 M sodium cyanide, NaCN .

4. What do you observe?

Answer: Color changes from blue violet to yellow.

5. What is the net ionic equation?



6. What is the reason for the shift?

Answer: The rate of the forward reaction has increased.

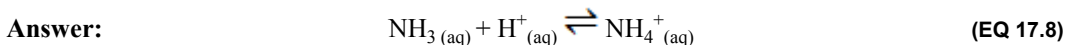
7. If the sodium cyanide, NaCN , is used up, how else could the reaction be shifted to the right?

Answer: Add 12 M hydrochloric acid, HCl .

8. What do you observe?

Answer: Color changes from blue violet to yellow.

9. What is the net ionic equation?



10. What is the reason for the shift?

Answer: The rate of the reverse reaction has decreased.

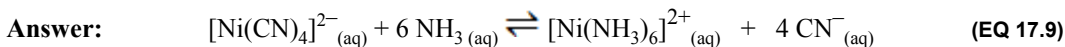
11. Addition of what reagent will shift the equilibrium to the left?

Answer: Add 6 M aqueous ammonia, NH_3 .

12. What do you observe?

Answer: Color changes from yellow to blue violet.

13. What is the net ionic equation?



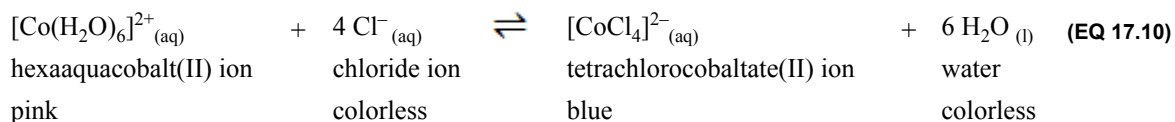
14. What is the reason for the shift?

Answer: The rate of the reverse reaction has increased.

Equilibrium Experiment Demonstration

Your instructor will demonstrate how to manipulate the following equilibrium. Complete the questions that follow.

Equilibrium established:



Reagents: 0.1 M CoCl₂, 2 M HCl, 0.1 M AgNO₃

1. Equilibrium expression:
2. Hexaaquacobalt(II) ion, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, is produced by:
3. The net ionic equation is:
4. The equilibrium will be shifted to the RIGHT by (Choose a reagent to add in order to shift equilibrium):
5. Observation that suggests the equilibrium is shifted to the right: (Color change, gas formation, temperature change, precipitate formation)
6. The net ionic equation is:
7. The reason for the shift: (Forward or reverse reaction speeds up or slows down)
8. The equilibrium will be shifted to the LEFT by: (Choose a reagent to add in order to shift equilibrium)
9. Observation that suggests the equilibrium is shifted to the left: (Color change, gas formation, temperature change, precipitate formation)
10. The net ionic equation is:
11. The reason for the shift: (Forward or reverse reaction speeds up or slows down)
12. Increasing the temperature will shift the equilibrium in which direction?
13. Observation that suggests the equilibrium is shifting: (Color change, gas formation, temperature change, precipitate formation)
14. The reasons for the shift: (Forward or reverse reaction speeds up or slows down)
15. Is the reaction exothermic or endothermic?
16. The net ionic equation is:

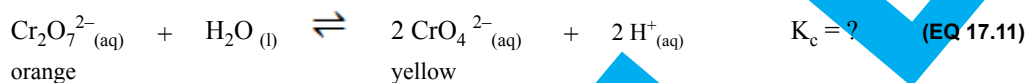
Procedure

There are six reactions to study in this part of the experiment. For each reaction, select solutions from the **list of reagents** to establish the equilibrium, that is, to produce ALL the species shown in the equilibrium equation.

Once you have established the equilibrium, manipulate the concentrations in order to shift the equilibrium first to the right and then to the left. Record your observations, verifying that the shift has occurred and write the ionic equations to illustrate what is happening on a molecular level. Indicate the change in reaction rate (for the forward or reverse reaction) after each change that you induce in the equilibrium.

Use small test tubes and minimal amounts of solutions; usually a few drops will suffice. Do not add more reagent than the minimum amount needed to change the equilibrium. If the concentration of a reagent becomes too great, you may not be able to shift the equilibrium back again, or, unexpected side reactions may occur. If you keep your solutions dilute, you should be able to shift the equilibrium back and forth with relative ease.

1. **Reagents:** 0.1 M $\text{K}_2\text{Cr}_2\text{O}_7$, 1 M HCl, 1 M NaOH



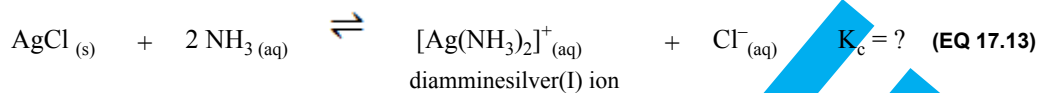
- a. Dichromate ion produced by
- b. Equilibrium shifted to the right by
- c. Observation
- d. Net Ionic Equation
- e. Reason for shift
- f. Equilibrium shifted to the left by
- g. Observation
- h. Net Ionic Equation
- i. Reason for shift

2. **Reagents:** 0.1 M BaCl_2 , 0.1 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$, 1 M HCl, 1 M NH_3



- a. Barium oxalate produced by
- b. Net Ionic Equation
- c. Equilibrium shifted to the right by
- d. Observation
- e. Net Ionic Equation
- f. Reason for shift
- g. Equilibrium shifted to the left by
- h. Observation
- i. Net Ionic Equation
- j. Reason for shift

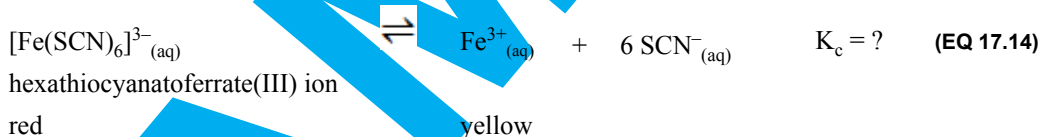
3. **Reagents:** 0.1 M AgNO₃, 6 M NaCl, 6 M NH₃



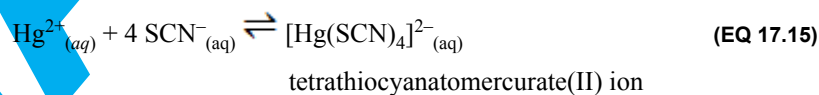
white

- Silver chloride produced by
- Net Ionic Equation
- Equilibrium shifted to the right by
- Observation
- Net Ionic Equation
- Reason for shift
- Equilibrium shifted to the left by
- Observation
- Net Ionic Equation
- Reason for shift

4. **Reagents:** 0.01 M FeCl₃, 0.01 M NH₄SCN, 0.01 M HgCl₂



Hint: A few drops of Hg²⁺_(aq) removes SCN⁻ ions from solution:



- Hexathiocyanatoferrate(III) ion, [Fe(SCN)₆]³⁻ produced by
- Net Ionic Equation
- Equilibrium shifted to the right by
- Observation
- Net Ionic Equation
- Reason for the shift
- Equilibrium shifted to the left by
- Observation
- Net Ionic Equation
- Reason for the shift

6. **Reagents:** $\text{NH}_4\text{Cl}_{(s)}$, DI water, saturated $\text{NH}_4\text{Cl}_{(aq)}$, 12 M $\text{HCl}_{(aq)}$



Hint: Be sure that the saturated ammonium chloride is saturated (i.e. has solid ppt at the bottom of the reagent container). If not add ammonium chloride to your beaker until saturated.

- a. Add about 0.5 g of ammonium chloride to a small test tube, which is about one-third full with DI water. After adding the solid stir and feel the bottom of the test tube to note any temperature change. Record your observations in your lab book.

Is the solution of ammonium chloride exothermic or endothermic?

Write the net ionic equation, putting heat as a reactant or product.

- b. To a second test tube add about 3.0 mL of saturated ammonium chloride.
 c. To this test tube, add 12 M hydrochloric acid (**CAUTION!**) drop wise until you see a definite change. Record your observations of this change in your lab book.

Is the reaction shifted to right or the left?

Reason for shift.

Write the net ionic equation.

- d. Put the resulting test tube into a hot water bath while stirring the mixture. Record your observations.

Is the reaction shifted to the right or the left?

Reason for shift.

Write the net ionic equation.

- e. Put the test tube in ice water. Record your observations.

Is the reaction shifted to the right or the left?

Reason for the shift.

Write the net ionic equation.