Chemistry 102

Lab Manual

Experiment 1: Statistical Analysis of Experimental Data

Background

Every measurement involves some measurement uncertainty. There are two sources of uncertainty in any measurements. The main source of uncertainty in any measurement is the measuring device that was used. The last number of a reading (not for digital readings) has to be estimated, as it is always uncertain. For example, if we were to measure the length of a key on a ruler at the point shown in Fig. 1, we could say it is between 2.3 cm 2.4 cm with certainty. However, we could estimate it to be 2.32 cm or 2.33 cm with some degree of uncertainty. We know for sure that the length is 2.3, but the last digit has to be estimated. The numbers recorded in a measurement are usually all the certain numbers plus the first uncertain number. These are called significant figures. Thus the number of significant figures in a measurement is dependent on the inherent uncertainty of the measuring device. We would thus say that the length measured on the ruler is 2.35 ± 0.05 cm, where 0.05 cm is the uncertainty in the measurement. The uncertainties for the typical instruments that we use in chemistry are shown in the Table 1.

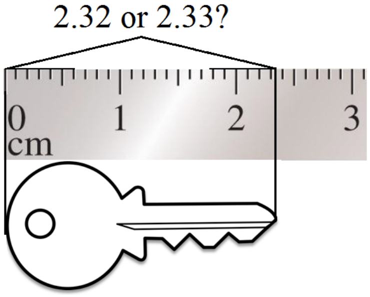


Figure 1- Uncertainty in measuring the length of a key

Table 1- Uncertainties for certain chemical Instruments

Instrument	Typical Uncertainty
Platform balance	0.50 g
Top-loading (centigram) balance	0.01 g
Top-loading semi-micro balance	0.001 g
Analytical balance	0.0001 g
100-mL graduated cylinder	0.2 mL
10-mL graduated cylinder	0.1 mL
50-mL buret	0.02 mL
25-mL pipet	0.02 mL
10-mL pipet	0.01 mL
Thermometer (graduated to1 ^{0}C)	0.2 ^{0}C
Barometer (mercury)	0.5 torr

Another source of uncertainty is what we refer to as “error”. Because many of our conclusions are drawn based on the experimental observations involving quantitative measurements, it is important for us to take into account any limitations for the reliability of those data that was used. In the following section, we will discuss and define different kinds of errors; systematic, random, and personal errors. Then we assess the quality of a measurement by considering its accuracy and precision. Because the limitations of both accuracy and precision could contribute greatly to the uncertainty in the measurement, we first start by defining these two terms.

1. Accuracy: Accuracy is how close the measurement or experimental result agrees with the "accepted" or "true" value. The smaller the error, the closer the measured value is to the true value and the more accurate is the result. The true value is sometimes difficult to establish. We either may calculate the accepted value through theoretical calculation or we rely on others (NIST, National Institute of Standards and Technology) to experimentally applying the same measurement technique to an unknown sample and to a carefully prepared or analyzed standard sample that resembles the unknown of our interest as much as possible. Therefore we could determine the accuracy by comparison with those standards. If we have the true value the accuracy of a measurement can be estimated by calculating the percent error involved in that measurement. The smaller the percent error in the measurement, the more accurate is the result. This would be like shooting arrows on a target and seeing how close you get to the center.

$$\%\,error = \left|\frac{Experimetally\ measured\ value - True\ Value}{True\ value}\right| \times 100\%$$

2. Precision: Precision is a measure of reproducibility of a measurement, or how closely individual measurements agree with one another. This is like shooting arrows on a target and seeing how closely grouped your shots were to one another, regardless of how far you missed the center of target. Typically, when we make a series of several measurements on the same sample or replicate samples, we do not get exactly the same value for each measurement. There will be a dispersion or spread of the measured values. The smaller the spread of values, the more precise will be the average (or mean) value of the measurements. If the accepted value **is not known** (as in the case of present experiment), then we can only evaluate the precision of our measurements by first calculating the mean or average value. Then we can determine the spread or dispersion of measurements by calculating the deviations. Deviation is a measure of the spread of individual values from the mean value. The deviations in results from the average value indicate the precision of that measurement. For example, if we measure the length of the key in figure 1, it is likely to give 3 different lengths (more or less close to each other). The precision (or reproducibility) of the 3 lengths can be expressed as percent deviation.

$$\%\,deviation = \frac{Average\ deviation}{Average\ value\ (\ or\ mean)} \times 100\%$$

Average or mean value can be calculated using the following formulas:

$$\bar{x} = \frac{x_1+x_2+x_3+x_4+\cdots}{N} \quad \text{Or} \quad \bar{x} = \frac{\sum x_i}{N}$$

Where $\bar{x}$ is arithmetic mean or average, and x_i is the value of each measurement, $\sum x_i$ is sum of all the measurements and N is the total number of measurements. The different between the average value, $\bar{x}$ and each measured value defined as deviation, $\delta = x_i - \bar{x}$. The Average deviation , $\bar{\delta}$ is the absolute value of the sum of all the deviation over the number of measurements:

$$\bar{\delta} = \frac{\sum|x_i-\bar{x}|}{N} \quad \text{Or} \quad \bar{\delta} = \frac{\sum|\delta_i|}{N}$$

We can rewrite the percent deviation as follow:

$$\%\,\delta = \frac{\bar{\delta}}{\bar{x}} \times 100\%$$

<u>3. Personal error, Systematic error, and Random error:</u> Laboratory errors can be classified into three categories. (These categories may overlap in some circumstances.) The first category is **personal error,** which can arise from not following instructions, using the wrong samples or equipment, using the wrong chemicals, and calculation errors. This type of error should produce obvious erroneous results after careful analysis. There is no recovery for this type of errors (except the calculation errors) after the measurement has been done other than repeating the experiment (but this time *without* making the personal error!). These errors are all preventable by paying attention to details.

A second type of error is termed a **systematic (or determinate) error**. These errors result in data that is consistently "off" from the true value in the same way. For example, if you were to use a wooden ruler as a tool to measure length, but it was a ruler that had *expanded* due humidity, your measurements would be consistently (systematically) too short.

These systematic errors are reproducible, and sometimes a correction factor can be used to fix the error if the extent of the error is known. Systematic errors have three sources: instrumental error, personal error, and method error. To detect and correct instrumental errors, calibrations can be made using standards sample. To minimize personal errors, most scientists develop the habit of systematically double-checking instrument readings, their own actions, notebook entries, and calculations, or use automated systems to collect data. To minimize method errors, the methods have to be validated using other known methods. All of these errors arise from a lack of systematic practices in the laboratory.

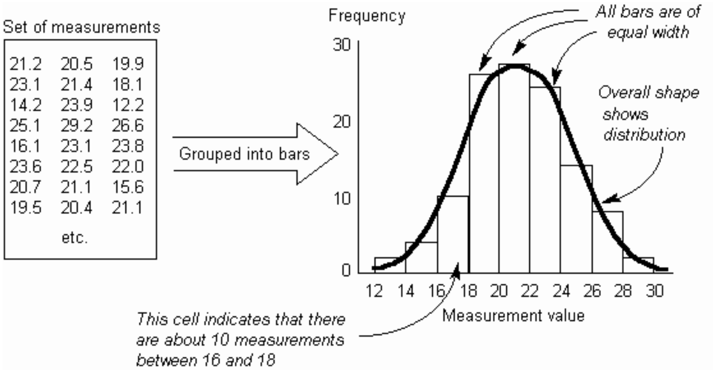
A final category of error is called a **random (or indeterminate) error**. These errors are usually uncontrollable arising from making measurements at the limit of the sensitivity of the measuring device. For example, analytical balances in the laboratory measure mass to the nearest 0.1 mg (which has a ±0.00005 g uncertainty) or a 50 mL buret is normally read to the nearest ±0.01 mL. With indeterminate errors, an error in one direction away from the true value is just as likely to happen as an error in the other direction. Random errors may be minimized by using a more sensitive instrument or by making multiple measurements and then choosing the average value. If enough multiple measurements are made, the random errors may cancel out to some extent.

A mathematical expression that shows the relationship between what a scientist observes and the possible errors (assuming gross errors are absent) is given below:

$$\boldsymbol{Observed\ measurement\ =\ true\ value\ +\ systematic\ error\ +\ random\ error}$$

Scientists attempt to determine a true value for something by making multiple measurements while eliminating gross errors, eliminating or correcting for systematic errors, and finally by using **statistics** to account for random errors. Let's examine how statistics are used to analyze multiple measurements that exhibit random errors.

<u>4. Statistical treatment of Random Errors:</u> Because there are random errors, a set of repeated measurements will not give identical values. In fact, if enough measurements were made, it is assumed that the values would lead to a Normal distribution of values (shown below). The resulting distribution of the measured value is displayed as a bar graph called a *histogram.* The best estimate of the true value of what you are trying to measure is the sample mean (sample average), or $\bar{x}$.



The **mean** value of the set of measurements is the most probable value, corresponding to the center of the Gaussian distribution curve.

The sample mean ($\bar{x}$), is calculated using the formula...

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n}$$

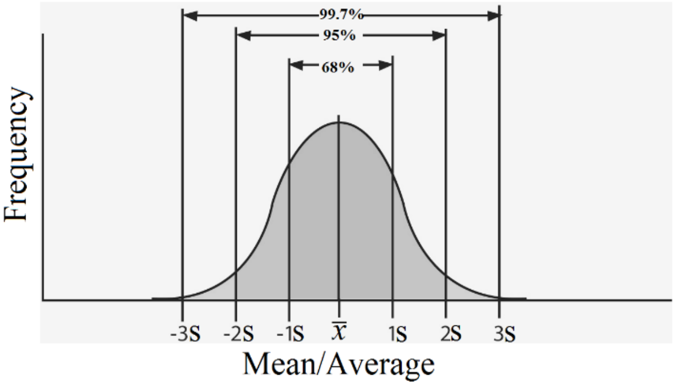
Where, 'n' is the total number of observations.

The spread, or dispersion, of the results is expressed by the **standard deviation**, s. The reproducibility or precision of a set of measurements is given by the sample standard deviation, s, and is calculated by adding up the squares of the deviations of each measurement (x_i) from the sample mean ($\bar{x}$), dividing by the number of measurements minus 1, (N-1), and taking the square root of the result:

$$s = \sqrt{\frac{\sum(x_i - \bar{x})^2}{N-1}} \qquad \text{Or} \qquad s = \left(\frac{\sum(x_i - \bar{x})^2}{N-1}\right)^{1/2} \qquad \text{Or} \qquad s = \left(\frac{\sum(\delta_i)^2}{N-1}\right)^{1/2}$$

We must recognize that when we repeat a measurement only two or three times, 3 we are not obtaining a very large sample of measurements, and the confidence that we can place in the mean value of a small number of measurements is correspondingly reduced. Therefore if only two or three measurements are made, the standard deviation may be approximated by the average deviation, $\bar{\delta}$, which is the mean value of the absolute values of the deviations, δ_i.

Assuming a Normal distribution curve for errors as it is shown below, the sample standard deviation, s, relates the probability that repeated measurements under the same conditions will produce expected results. We see that the probability of measurements occurring close to the mean will be greater than the probability of a measurement occurring far away from the mean. That is, you are reasonably certain that there is 68%, probability that a given measurement will fall within plus or minus one standard deviation of the mean value. There is also a 95% probability that a measurement will fall within plus or minus two standard deviations of the mean value.



However, the value of *s* by itself does not convey all the information needed to understand the measurements. For example, is a standard deviation of ±0.10 mL good or bad? If the sample average value (sample mean), $\bar{x}$, was 50.00 mL, then *s* = ±0.10 mL represents an excellent standard deviation. If, on the other hand, the sample average value (sample mean) was 0.50 mL, then ±0.10 mL represents a large degree of random error.

A better way to represent the significance of the magnitude of random error is called the **relative standard deviation** (RSD), or **coefficient of variation**, which is the standard deviation divided by the mean times hundred.

$$relative\ standard\ deviation\ (RSD)\ = \frac{standard\ deviation}{Average\ value\ (\ or\ mean)} \times 100$$

$$RSD\ = \frac{s}{\bar{x}} \times 100$$

4. How to calculate the standard deviation (s):

The steps for calculating the standard deviation are outlined below and the example of such a calculation is the tabulated in the table 2.

- ✓ First calculate the arithmetic mean or average value, $\bar{x}$, of the measurements.
- ✓ Then subtract the mean value, $\bar{x}$, from each one of the individual values, x_i, to obtain the deviation, δ_i. There will be both positive and negative deviations.
- ✓ Square each deviation, and add all of the squares.
- ✓ Divide the total by N-1, where N is the total number of measurements.
- ✓ Finally, take the square root of the result to obtain the estimate of the standard deviation.

Table 2- The Procedure for Calculating the Standard Deviation

Measured Value (x_i)	**Deviation** $(x_i - \bar{x})$	**Square of Deviation** $(x_i - \bar{x})^2$
4.28	−0.01	0.0001
4.21	−0.08	0.0064
4.30	0.01	0.0001
4.36	0.07	0.0049
4.26	−0.03	0.0009
4.33	0.04	0.0016

$\sum = 25.74 \qquad \sum = 0.00 \qquad \sum = 0.0140$

First we calculate the mean, $\bar{x} = \frac{\sum x_i}{N} = \frac{25.74}{6} = 4.29\ g$

Then we calculate the standard deviation (SD), $s = \left(\frac{\sum(\delta_i)^2}{N}\right)^{1/2} = \left(\frac{0.0140}{6-1}\right)^{1/2} = 0.053$
Therefore, the best value of the measurement is written as 4.29 $\pm$ 0.05 g

5. Median and Range:

When the number of measurements available N are few, the **median** is often more appropriate than the mean. In addition to the standard deviation, the **range** is also used to describe the scatter in a set of measurements or observations. The **range** is simply the difference between the largest and the smallest values or observations in a data set. Range = $x_{max} - x_{min}$, where x_{max} and x_{min} are the largest and smallest observations in a data set, respectively. The **median** is defined as the value that bisects the set of 'n' ordered observations, i.e., it is the central point in an ordered data set. If the 'n' is odd, then (N-1)/2 measurements are smaller than the median, and the next higher value is reported as the median (i.e., the median is the central point of that set). If the data set contains an even number of points, the median will be the average of the two central points.

Example: For N = 6 and x() = 2, 3, 3, 5, 6, 7; **median = (3+5)/2 = 4**; the **mean= (2 + 3 + 3 + 5 + 6 + 7)/6 = 4.33**; and the **range = (7 – 2) = 5.**

6. Grubbs Test

The Grubb's test is used to detect a single outlier in a data set of N values that are nearly normally distributed. This test is essentially based on the criterion of "distance of the suspected value from the mean of the data set compared with the standard deviation".
The test is performed by computing the Grubbs G which is defined as:

$$G_{exp} = |x_{outlier} - \bar{x}| / s \qquad (1)$$

Where:
$x_{outlier}$ is the suspected outlier
$\bar{x}$ is the mean of the N values
s is the standard deviation of N values

If the calculated G_{exp} is found to be:
$G_{exp} < G_{critical}$ then the point in question must be retained
Gexp > $G_{critical}$ then the point in question must be discarded and the mean and standard deviation must be recalculated.

Where $G_{critical}$ is found from statistical tables (see Table below)

$G_{critical}$ values at the 95% confidence level.

N	$G_{critical}$ (95%)**
3	1.15
4	1.46
5	1.67
6	1.82
7	1.94
8	2.03
9	2.11
10	2.18
11	2.23
12	2.29
13	2.33
14	2.37
15	2.41
16	2.44
17	2.47
18	2.50
19	2.53
20	2.56
21	2.58
22	2.60
23	2.62
24	2.64
25	2.66

A **typical example** with a possible outlier value: If our data set contains the following values...0.5993, 0.5997, 0.6400, 0.5980, and 0.601

First, arrange the data under examination in increasing order:

0.5980 0.5993 0.5995 0.5997 0.601 0.6400

Can we reject the 0.6400 value ? Calculate the mean of the data values and the standard deviation:

$$\overline{x} = 0.6062, \quad s = 0.0166$$

Calculate G_{exp} using equation (1):

$$G_{exp} = |0.6400 - 0.6062| / 0.0166 = 2.04$$

Compare with the critical value of $G_{critical}$ found in table I.1 at the 95% confidence level and for N = 6 observations. This value is equal to $G_{critical} = 1.82$

$G_{exp} = 2.04 > G_{critical} = 1.82$ and therefore we can reject 0.6400 at the 95% confidence level being certain that there is a probability $a < 0.05$ that our decision is false.

Procedure

1. **Circumference of a 150 mL Beaker**
    a. Tightly wrap a string around the circumference of a 150-mL beaker.
    b. Use a pencil to mark the two points of the string and measure the distance between the two points in centimeters.
    c. Repeat the above procedure for nine other 150-mL beakers.
    d. Calculate the mean, median, range and standard deviation for the data set.
    e. Explain why we cannot measure the %error for this data set?

2. **Mass, Volume and Density of Marbles**
    a. Make sure the marbles are clean by rinsing with soap and water before the experiment.
    b. Measure the mass of a marble on the balance, using a weighing boat. Weigh by difference.
    c. Measure the volume of the marble by using the water displacement method. Take a 25 mL or 50 mL graduated cylinder and fill it half way with tap water. Correctly measure the volume to 1/10 the last decimal place of the readings. So, if you find the measured volume to be 24.5 mL, then your data should be recorded to two decimal places...for example, 24.51 mL.
    d. Carefully add the marble to the graduated cylinder. The level of water in the cylinder will rise proportionally to the volume of the marble. Record the new level of water and calculate the volume of the marble.
    e. Repeat the above procedure for nine more marbles.
    f. Calculate the density of the each marble using the mass and volume measurements.
    g. Calculate the mean, median, range and standard deviation for the data set.
    h. If the density of a marble is 2.5 g/cm^3, calculate the error for each marble and then calculate and report the average error.
    (error = measured value – actual value) and average error is the sum of the absolute values of the errors divided by the total number of measurements.
    i. Are the errors observed in this experiment random or systematic?

3. **Volume of a test tube**
    a. Obtain a 13 x 100-mm test tube.
    b. Completely fill each test tube completely with water all the way to the top.
    c. Carefully pour the water into a graduated cylinder to measure the volume.
    d. Repeat these steps for nine more test tubes of similar size.
    e. Calculate the mean, standard deviation and % relative standard deviation for the data set.

4. **Temperature of boiling water**
    1. Obtain a 600 mL or 400 mL beaker and fill it three fourths with water.
    2. Place the beaker on a hot plate and turn on the heat dial to boil the water.
    3. Place a thermometer in the beaker and measure the temperature of the boiling water only after the water has been boiling for 5-10 minutes.
    4. Enter your data for the temperature of the boiling water on the board.
    5. Every student will enter their data on the board and once everyone has entered their data copy all the class in your lab notebook.
    6. Calculate the mean and standard deviation for the data set.
    7. Use the Grubb’s test to check if the lowest and highest values are outliers. Show your calculations.

Experiment 2: Determining the Rate of the Reaction of Potassium Permanganate and Oxalic Acid

Background:

The reaction between Potassium Permanganate and Oxalic Acid is as follows.

$$\underset{\text{(purple)}}{KMnO_4(aq)} + H_2C_2O_4(aq) \rightarrow \underset{\text{(colorless)}}{Mn^{2+}(aq)} + CO_2(g) + H_2O(l)$$

Reaction (1)

The balanced chemical reaction is.

$2\ MnO_4^-\ (aq) + 5\ H_2C_2O_4\ (aq) + 6H^+\ (aq) \rightarrow 2Mn^{2+}\ (aq) + 10\ CO_2\ (g) + 8\ H_2O\ (l)$ Reaction (2)

We can calculate the rate of the reaction by monitoring the disappearance of Potassium Permanganate ($KMnO_4$) once it completely reacts with Oxalic Acid ($H_2C_2O_4$). This color changes from purple to red to yellow once $KMnO_4$ is completely reacted.

The Rate of the reaction can be calculated as follows.

$$\text{Rate of reaction} = -\Delta[KMnO_4]/\Delta T = -\Delta[\ H_2C_2O_4]/\Delta T = \Delta[\ Mn^{2+}]/\Delta T$$

Equation (1)

The rate law is given by the following equation.

$\mathbf{R = k\ [KMnO_4]^x\ [H_2C_2O_4]^y}$ Equation (2)

To calculate the rate (R) we will use the change in the concentration for $KMnO_4$ over the time it takes for the color change.

Rate = Initial concentration of $KMnO_4$/ elapsed time

$\mathbf{Rate = -\Delta KMnO_4/\Delta t = -\ (\ 0 - [KMnO_4]_{initial})\ /\ (t_{\ sec} - 0)}$ Equation (3)

We can then use the method of initial rates to find the exponents x & y. This method involves measuring and comparing the initial rates of a reaction when different initial concentrations are used.

Procedure:

Effect of Concentration:

We will run three reactions keeping the changing the concentrations of $KMnO_4$ and $H_2C_2O_4$. We will use micropipettes to dispense the correct volumes of each solution as shown in the table below.

Table 1- Vary Concentration

	Test Tube A		Test Tube B
Trial	$H_2C_2O_4$, μL	D.I. H_2O, μL	$KMnO_4$, μL
1	500	600	100
2	1000	100	100
3	500	500	200

Once you prepare the solutions, mix the contents of test tube A with that of test tube B for each trial and record the time (in seconds) when the solution turns from purple to yellow. Record your observations in your lab notebook.

Repeat the experiments (trial 1-3) and calculate the average time for each trial.

Effect of Temperature:
We will also check the effect of temperature on the reaction rate by carrying out the experiment at three different temperatures. Room Temperature (RT), RT + 10 °C, and RT + 20 °C. In these experiments will keep the concentrations of the reactants constant and only change the temperature. Record the time (in seconds) when the solution turns from purple to yellow. If time permits, repeat the experiments (trial 4-6) to calculate the average time for each trial.

Table 2- Vary Temperature

		Test Tube A		Test Tube B
Trial (Temperature)	Measured Temperature °C	$H_2C_2O_4$, µL	D.I. H_2O, µL	$KMnO_4$, µL
4 (RT)		500	600	100
5 (RT + 10)		500	600	100
6 (RT + 20)		500	600	100

Data Analysis:

1. Calculate the rate for each trial (1-6) using Equation (3).
2. Use the method of initial rates to find the order with respect to each reactant. For example, if we compare trial 1 and trial 2, we double the concentration of $H_2C_2O_4$ while keeping the concentration of $KMnO_4$ constant in the two trials. So the ratio of the rates (using Equation 2) are proportional to the concentrations of $H_2C_2O_4$ only and we can find the order ('y') with respect to $H_2C_2O_4$. Similarly, we can solve for 'x' by comparing trials 1 and 3.
3. Once you have found the rate law for the reaction you can then calculate the rate constant for each trial (1-6) by inserting the rate and the molar concentrations of each reactant in the rate law.

Post Lab Questions:

(1) Suppose a student prepares the solution from trial 2 in Table 1. When the contents of the reaction test tube A and B are mixed together, it takes 160 seconds for the color change. What is the rate for this reaction?

(2) Compare the reaction rate at the three different temperatures. Divide the rate at room temperature by the rate at 10˚C above room temperature. How much does increasing the temperature affect the rate of the reaction?

(3) Calculate the rate of reaction using the rate law equation you derived for your data at room temperature if you start with an oxalic acid concentration of 0.25M and a potassium permanganate concentration of 0.30M. Include units in your answer.

(4) What variable in the rate law equation changes as a result of the changing temperature? If you were to perform your experiment at 100°C above room temperature, would this variable be expected to increase or decrease? Briefly explain your answer.

Experiment 3: The Iodine Clock Experiment to Study the Kinetics of a Chemical Reaction

Refer to the following link to understand the Theory, Background, Description of the Experiment, Rate Equation, Reaction Orders, Activation Energy (Ea).

https://chem.libretexts.org/Ancillary_Materials/Laboratory_Experiments/Wet_Lab_Experiments/MIT_Labs/Lab_3%3A_Chemical_Kinetics/1_-_The_Iodine_Clock_Reaction

Procedure:
In this experiment we will calculate the time it takes for the generation of I_2 in the reaction between $S_2O_8^{2-}$ and I^- (Equation 5). This is done in the presence of $S_2O_3^{2-}$, KNO_3 and $(NH_4)_2SO_4$. The KNO_3 and $(NH_4)_2SO_4$ are just added to maintain a constant number of ions (ionic strength) in the reaction mixture.

In **part I**, we will run four reactions keeping the same concentration of $Na_2S_2O_3$, KI, KNO_3 in test tube A, and varying the concentration of $Na_2S_2O_8$ in test tube B. So, $[I^-]$ is constant, while $[S_2O_8^{2-}]$ is varied. We will use micropipettes to dispense the correct volumes of each solution as shown in the table below.

Table 1- Vary $[S_2O_8^{2-}]$

	Test Tube A				Test Tube B	
Trial	Starch μL	1.2 x 10^{-2} M $Na_2S_2O_3$, μL	0.20 M KI, μL	0.20 M KNO_3, μL	0.20 M $(NH_4)_2S_2O_8$, μL	0.20 M $(NH_4)_2SO_4$, μL
1	100	200	400	400	800	0
2	100	200	400	400	400	400
3	100	200	400	400	200	600
4	100	200	400	400	100	700

Once you prepare the solutions, mix the contents of test tube A with that of test tube B for each trial and record the time (in seconds) when the solution turns blue which indicates the presence of excess I_2 once all the $Na_2S_2O_3$ has been consumed. Record your observations in your lab notebook.

In **part 2**, we will run four reactions keeping $[S_2O_8^{2-}]$ the same but $[I^-]$ is varied. We will once again measure the time it takes (in seconds) for the mixture to turn blue when test tubes A and B are mixed respectively.

Table 2- Vary $[I^-]$

	Test Tube A				Test Tube B	
Trial	Starch μL	1.2 x 10^{-2} M $Na_2S_2O_3$, μL	0.20 M KI, μL	0.20 M KNO_3, μL	0.20 M $(NH_4)_2S_2O_8$, μL	0.20 M $(NH_4)_2SO_4$, μL
5	100	200	800	0	400	400
6	100	200	400	400	400	400
7	100	200	200	600	400	400
8	100	200	100	700	400	400

In **part 3,** we will observe the effect of temperature on reactions rates. In this set of experiments, we will essentially keep the $[S_2O_8^{2-}]$ and [I-] the same but vary the temperature. This will be done by using a water bath to keep the temperature of the two test-tubes constant. We will then use a thermometer to measure the room temperature (RT) and once the solutions in the two test-tubes have equilibrated, you can then proceed to mix the contents and record the time for the blue color to appear, just as the case for part 1 and 2. We will carry out four experiments, RT-10 (room temperature -10°C), RT (room temperature), RT + 10 (room temperature +10°C), and RT +20 (room temperature +20°C) as shown in table 3. You will need to add ice to get the data for trial 9.

Table 3- Vary Temperature

		Test Tube A				Test Tube B	
Trial (Temperature)	Measured Temperature °C	Starch µL	1.2 x 10^{-2} M $Na_2S_2O_3$, µL	0.20 M KI, µL	0.20 M KNO_3, µL	0.20 M $(NH_4)_2S_2O_8$, µL	0.20 M $(NH_4)_2SO_4$, µL
9 (RT - 10)		100	200	400	400	200	600
10 (RT)		100	200	400	400	200	600
11 (RT + 10)		100	200	400	400	200	600
12 (RT + 20)		100	200	400	400	200	600

Finally in **Part 4,** we will observe the effect of a catalyst, Cu $(NO_3)_2$ on reaction rate. For these series of experiments, prepare the two test tubes as described in Table 4 (Note: this is the same setup as Table 2 except that we are adding one drop of 2.0 x 10^{-2} M Cu $(NO_3)_2$ in test tube A). Carry out the same steps by measuring the time it takes for the mixture to turn blue when test tubes A and B are mixed respectively.

Table 4 – Effect of Catalyst

	Test Tube A					Test Tube B	
Trial	Starch µL	1.2 x 10^{-2} M $Na_2S_2O_3$, µL	0.20 M KI, µL	0.20 M KNO_3, µL	0.02 M $Cu(NO_3)_2$	0.20 M $(NH_4)_2S_2O_8$, µL	0.20 M $(NH_4)_2SO_4$, µL
13	100	200	800	0	1 drop	400	400
14	100	200	400	400	1 drop	400	400
15	100	200	200	600	1 drop	400	400
16	100	200	100	700	1 drop	400	400

Data Analysis:

We need to carry out the following analysis as our goal for this experiment.

1. **<u>Establish the Rate Law for the reaction.</u>**

$$\underset{\text{persulfate}}{S_2O_8^{2-}} + \underset{\text{iodide}}{2I^-} \rightarrow \underset{\text{sulfate}}{2SO_4^{2-}} + \underset{\text{iodine}}{I_2}$$

Reaction [1]

This is done by using the data of Part 1 and Part 2 to find the order with respect to $[S_2O_8^{2-}]$ and $[I^-]$, calculate the Rate Law , and finally calculate the 'k' for each reaction.

The Rate law for this reaction is given by: $\mathbf{R = k\,[S_2O_8^{2-}]^x\ [I^-]^y}$ where, x and y are the orders with respect to $S_2O_8^{2-}$ and I^- respectively.

The rate of the reaction at constant temperature and ionic strength can be expressed as the change in concentration of a reagent or product over the change in time and can be equated to the rate law expression:

$$rate = -\frac{\Delta[S_2O_8^{2-}]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t}$$

The amount of I_2 produced first reacts with the thiosulfate ion as seen in the reaction below.

$$\underset{\text{thiosulfate}}{2S_2O_3^{2-}} + \underset{\text{iodine}}{I_2} \rightarrow \underset{\text{tetrathionate}}{S_4O_6^{2-}} + \underset{\text{iodide}}{2I^-}$$

Reaction [2]

The iodine (I_2) produced in reaction [1] is absorbed immediately by reaction with thiosulfate ion as shown in reaction [2]. As long as any $S_2O_3^{2-}$ remains in solution, the concentration of I_2 is effectively zero. When all of the $S_2O_3^{2-}$ is used up, any additional I_2 that is made via reaction [1] will react with a starch indicator, which will then turn blue.

The combination of reactions [1] and [2] together with the starch indicator constitutes one type of Iodine Clock Reaction. The "clock" or color change indicated when enough iodine has been produced by reaction [1] to use up all of the $S_2O_3^{2-}$. A knowledge of the original $S_2O_8^{2-}$ concentration and the stoichiometric ratio between I_2 and $S_2O_8^{2-}$ leads to the quantity of $S_2O_8^{2-}$ that has reacted when the blue color appears. Because one mole of I_2 reacts with 2 moles of $S_2O_3^{2-}$ during reaction [2], the quantity of I_2 produced at the time the blue color first appears (= t) is equal to one-half the initial quantity of $S_2O_3^{2-}$ (which is known). Also, from reaction [1], one mole of I_2 is produced from one mole of $S_2O_8^{2-}$. So, to calculate $\Delta\ S_2O_8^{2-}$, we can use the mole relationships between $S_2O_3^{2-}$, I_2 and $S_2O_8^{2-}$.

mol $S_2O_3^{2-}$ (1 mol I_2/2 mol $S_2O_3^{2-}$) (1mol $S_2O_8^{2-}$/ 1 mol I_2) = mol $S_2O_8^{2-}$

for example in Table 1: mol $S_2O_3^{2-}$ = 1.2×10^{-2} M $S_2O_3^{2-}$ x 0.0002 L = **2.4×10^{-6} mol $S_2O_3^{2-}$**

so, 2.4×10^{-6} mol $S_2O_3^{2-}$ (1 mol I_2/2 mol $S_2O_3^{2-}$) (1mol $S_2O_8^{2-}$/ 1 mol I_2) = **1.2×10^{-6} mol $S_2O_8^{2-}$**

M $S_2O_8^{2-}$ = mol $S_2O_8^{2-}$ / total volume = 1.2×10^{-6} mol $S_2O_3^{2-}$ / 0.0019 L = **6.3×10^{-4} M $S_2O_8^{2-}$**

So, **$\Delta\ S_2O_8^{2-} = 6.3 \times 10^{-4}$ M**

and **Rate = $\Delta\ S_2O_8^{2-}/\Delta t = 6.3 \times 10^{-4}$ M/ Δt** Equation [1]

where 't' is the time elapsed for the color of the solution to turn blue in each experiment.
Since the amount of $S_2O_3^{2-}$ never changes for each reaction, we can use Equation [1] to calculate the rates for all the experiments, 1-16 in this lab.

To calculate the order with respect to I^- and $S_2O_8^{2-}$, first we need to calculate the molarity of I^- and $S_2O_8^{2-}$.
Using the data from trial 1 in Table 1 as an example...

$[I^-]$ = 0.20 M I^- x 0.0004L / 0.0019 L = **0.042 M**

$[S_2O_8^{2-}]$ = 0.20 M $S_2O_8^{2-}$ x 0.0008L / 0.0019 L = **0.084 M**

Now that we know how to calculate the rate, $[I^-]$, and $[S_2O_8^{2-}]$ we can use the following example below to calculate 'x' and 'y' to find the rate law.

Effect of Concentration on the Reaction Rate: Finding the Rate Law

The rate law is determined using the method of initial rates. The following example will illustrate how to find a reaction order using the method of initial rates.

Example: The following data was obtained for the reaction: $A + B \rightarrow C$

Experiment	[A], M	[B], M	Rate (M/s)
1	0.020	0.10	1.20
2	0.030	0.10	1.80
3	0.030	0.25	11.25

The general rate law for this example is

$$\text{Rate} = k[A]^x[B]^y$$

Since [A] changes between Experiment 1 and 2, while [B] remains constant, the order for A is obtained by taking the ratio of the rates from these two experiments:

$$\frac{1.80\ \text{M/s}}{1.20\ \text{M/s}} = \frac{k[0.030]^x[0.10]^y}{k[0.020]^x[0.10]^y}$$

Since k is constant at a given temperature and $[B]^y$ is constant for Experiments 1 and 2, the equation simplifies to:

$$\frac{1.80\ \text{M/s}}{1.20\ \text{M/s}} = \left(\frac{[0.030]}{[0.020]}\right)^x \quad \text{or} \quad 1.50 = 1.5^x$$

Thus, x = 1 for this example.

Experiments 2 and 3 may then be used to find the order for B, as shown below

$$\frac{11.25\ \text{M/s}}{1.80\ \text{M/s}} = \frac{k[0.030]^x[0.25]^y}{k[0.030]^x[0.10]^y}$$

By cancelling out the common terms and dividing the rate and concentration values, we obtain

$$6.25 = 2.5^y$$

Taking the log of both sides and rearranging to solve for y gives

$$y = \frac{\log(6.25)}{\log(2.5)} = 2.0 \approx 2$$

2. Find the activation energy (Ea) and frequency factor (A).

Use data from Part 3 to find 'k' for each reaction.

Activation energy (E_a)

Recall the Arrhenius equation:

$$k - Ae^{-E_a/RT}$$

Taking natural logarithm of both sides of this equation we obtain:

$$\ln k = -\frac{E_a}{R}\frac{1}{T} + \ln A$$

A plot of ln *k* versus 1/*T* yields a straight line whose slope is -*E*a/*R* and whose y-intercept is ln A, the natural logarithm of the Arrhenius constant.

3. Effect of Catalyst on Reaction Rates:

Calculate the Rate for each of the reactions in Part 3 (13-16) to observe the effect of a catalyst in reaction rates. Discuss your observations and results.

For your lab report.

1. Calculate the Rate of the reaction for each of the 16 trials using Equation [1] which is **Rate = Δ $S_2O_8^{2-}$/ Δt = 6.3×10^{-4} M/ Δt = 6.3×10^{-4} M/ t (seconds)**

2. Next, find the order with respect to $S_2O_8^{2-}$, and I^-, using Table 1 and Table 2 respectively.

3. For Table 3, we need to calculate the rate constant for each temperature. So once we know the order of the reactions for $S_2O_8^{2-}$, and I^-, we can then calculate the rate constant using the Rate Law equation. **$R = k\,[S_2O_8^{2-}]^x\ [I^-]^y$** by substituting the rate, and concentrations of $S_2O_8^{2-}$, and I^-, in trials 9-12.

   Once you have calculated the k for each trial in Table 3, plot a graph of Ln k vs 1/T to find the activation energy Ea from the slope, and the frequency factor (A) from the Y-intercept. Attach your excel sheet in your report.

4. Compare the rates from Table 2 and Table 4. You will notice that trials 5 and 13 have similar concentrations of $S_2O_8^{2-}$ and I^-. Similarly, trials 6 &14, 7 &15 and 8 &16 have similar concentrations? Compare the rates and comment on their differences.

Experiment 4: Determining an Equilibrium Constant Using Spectroscopy

Background: In this experiment, we will study the equilibrium between iron (III) ion, Fe^{3+} and the thiocyanate anion, SCN^-. When the two solutions are mixed a complex is formed $FeSCN^{2+}$, the thiocyanatoiron(III) ion. This complex is red-orange in color. The simplified reaction between Fe^{3+} and SCN^- is given as

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq)$$

The equilibrium constant for this reaction is given as

$$K_{eq} = \frac{[FeSCN^{2+}]_{eq}}{[Fe^{3+}]_{eq}\,[SCN^-]_{eq}}$$

In order to determine Keq, it is necessary to determine the equilibrium concentrations of the reactants and products in solutions, which are prepared by mixing carefully measured volumes of Fe^{3+} and SCN^- solutions of known initial concentrations. The equilibrium concentration of the $FeSCN^{2+}$ ion, $[FeSCN^{2+}]$eq, formed in such a solution can be determined from the measured absorbance of the solution using a spectrophotometer. This is possible because $FeSCN^{2+}$ absorbs blue and green light (447 nm), producing a solution that is reddish orange in color while the Fe^{3+} and SCN^- ions do not absorb visible light. The amount of light absorbed is thus proportional to $[FeSCN^{2+}]$ in accordance with Beers Law. It is therefore necessary to first prepare solutions of known $[FeSCN^{2+}]$ (called standard solutions) and obtain a calibration plot of absorbance vs. $[FeSCN^{2+}]$.

To understand the theory and procedure for this experiment, please read the following link.
It is very important that you read this material before you begin your experiment.

https://chem.libretexts.org/Ancillary_Materials/Laboratory_Experiments/Wet_Lab_Experiments/General_Chemistry_Labs/Online_Chemistry_Lab_Manual/Chem_12_Experiments/02%3A_Determination_of_Kc_for_a_Complex_Ion_Formation_(Experiment)#mjx-eqn-3

You will perform Part A- unknown mixtures, Part B-stock solution and Part D-calibration curve using the stock solution. Note: Use test tubes for Part A and D, and a 50 mL beaker for Part B to prepare your stock solution.

Preparation of Stock (standard) solution (Part B): Collect 15 mL of 0.2 M $Fe(NO_3)_3$ in a 50 mL beaker. Take another 50 mL beaker and label it as Stock Solution. Pipet out 10 mL of the 0.2 M $Fe(NO_3)_3$ solution into this beaker + 8 mL D.I. water + 2 mL 2.00×10^{-3} M KSCN. Using a stirring rod to mix this solution. You will use this solution for Table 2.

1. Prepare tables in your lab notebook as described below.
2. Answer the Pre-Laboratory Assignment till Step 5.

Data Tables:

Table 1- Part A Initial concentrations of Fe^{3+} and SCN^- in Unknown Mixtures

Tube	2.00×10^{-3} M $Fe(NO_3)_3$ mL	2.00×10^{-3} M KSCN mL	H_2O mL	$[Fe^{3+}]_{initial}$	$[SCN^-]_{initial}$	Abs	$[FeSCN^{2+}]_{eq}$ (From graph)
1	5.00	5.00	0				
2	5.00	4.00	1.00				
3	5.00	3.00	2.00				
4	5.00	2.00	3.00				
5	5.00	1.00	4.00				

Table 2- Part D Spectroscopic Method (Using the Calibration Curve)

Tube	Composition	Abs	$[FeSCN^{2+}]$
Blank	0.200 M $Fe(NO_3)_3$		0
1	Stock Solution (Part B)		2.0×10^{-4} M
2	4.00 mL Stock + 1.00 mL H_2O		
3	4.00 mL Stock + 2.00 mL H_2O		
4	4.00 mL Stock + 3.00 mL H_2O		

Plot a graph of Abs vs $[FeSCN^{2+}]$ and use this graph to calculate $[FeSCN^{2+}]_{eq}$ for part A (Table 1).

Calculate Keq values for the solutions in Table 1, by preparing an I.C.E. table using $[Fe^{3+}]_{initial}$, $[SCN^-]_{initial}$, and $[FeSCN^{2+}]_{eq}$ values.

An example of the calculations for this lab is found in the video below.

https://www.youtube.com/watch?v=z7d9K-unMy4

Experiment 5: Equilibrium and Le Châtelier's Principle

Purpose: In this experiment, we will examine how the equilibrium systems shifts when a stress is applied.

Background: Equilibrium systems occur when the rate of the forward and reverse reactions are equal for a reversible reaction. When a system at equilibrium is subjected to a change in temperature, pressure, or concentration, the system responds by attaining a new equilibrium that minimizes the impact of that change. Henri Le Châtelier's, a French chemist, studied equilibrium systems and this lead him to conclude, when a stress is applied to a system at equilibrium, it will shift to minimize the effect of the applied stress, which is known as Le Châtelier's principle. If a system at equilibrium is disturbed, one of the rates (forward or reverse) will temporarily increase, and when the system reaches a new equilibrium state, the concentration of each substance will be different than the original, yet the equilibrium constant remains unchanged. For example, increasing the concentration of a reactant will cause a change that decreases the concentration of the reactant(s) and thus increase the concentration of the product(s) or a shift to the right, according to Le Châtelier's principle.

A detailed explanation of the experimental background and procedure is available on the following link below.

https://chem.libretexts.org/Ancillary_Materials/Laboratory_Experiments/Wet_Lab_Experiments/General_Chemistry_Labs/Online_Chemistry_Lab_Manual/Chem_10_Experiments/12%3A_Equilibrium_and_Le_Chatelier%27s_Principle_(Experiment)

Procedure: Follow the directions of the procedure in the above link. Follow the complete experimental procedure. Write down all your observations in your lab report using the sample data tables.

Sample data tables:

Part 1- Saturated Sodium Chloride Solution.

Test Tube	Change Introduced	Observations	Reaction
1			

Part 2- Acidified Chromate Solution

Test Tube	Change Introduced	Observations	Reaction
1			
1			

Part 3- Aqueous Ammonia Solution

Test Tube	Change Introduced	Observations	Reaction
1			

Part 4- Cobalt (II) Chloride Solution

Test Tube	Change Introduced	Observations	Reaction
1			
2			
3			

Part 5- Iron (III) Thiocyanate Solution

Test Tube	Change Introduced	Observations	Reaction
1			
2			
3			
4			

Lab Report: For your informal lab report, attach your data/observation sheet, answer the pre-lab and lab report sections in the experimental link.

Experiment 6: Determining the Equivalent Mass and Dissociation Constant of an Unknown Weak Acid by Titrimetry

Background: In this experiment, we will determine the equivalent mass (molar mass) and the Ka of a weak acid by titrating it with sodium hydroxide

To understand the theory and procedure for this experiment, please read the following links.

It is very important that you read this material before you begin your experiment.

https://chem.libretexts.org/Courses/Saint_Marys_College_Notre_Dame_IN/Chem_122L%3A_Principles_of_Chemistry_II_Laboratory_(Under_Construction__)/06%3A_Titration_of_an_Unknown_Acid

https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_A_Molecular_Approach_(Tro)/17%3A_Aqueous_Ionic_Equilibrium/17.04%3A_Titrations_and_pH_Curves

Procedure: There are two parts to the experiment.

In Part A we will standardize 0.1 M NaOH using potassium hydrogen phthalate (KHP) which is a weak monoprotic acid with a molar mass of 204.2 g/mol. The reaction is as follows

KHP (aq) + NaOH (aq → NaKP (aq) + H_2O (l) ....where NaKP is the sodium salt of KHP.

This part of the titration will be carried out using an acid base indicator (phenolphthalein). Below is a brief description of the procedure.

1. Clean and label three 125- mL (or 250- mL) Erlenmeyer flasks.
2. Add 0.5 g to 0.6 g of KHP into each flask. The exact mass of KHP should be recorded in your lab notebook.
3. Add approximately 50-60 mL of D.I. water to each flask and dissolve the KPH solution by gently swirling the flasks.
4. Add 2-3 drops of phenolphthalein indicator to each flask.
5. Prepare a buret by rinsing with D.I. water and then with the NaOH solution of 0.1 M approximate concentration.
6. Titrate each solution of KHP with the NaOH solution till the color changes from colorless to pale pink.
7. Record your end point etc. in Table 1 and calculate the molarity of NaOH. We will use this standardized solution of NaOH to analyze the equivalent mass and Ka of the unknown weak acid.

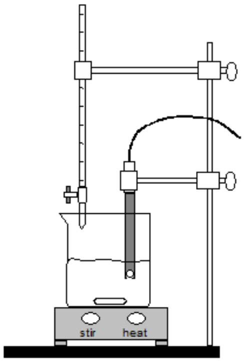
In Part B we will use the standardized NaOH solution to determine the equivalent mass and Ka of the unknown weak acid using a pH meter.

1. Weigh 0.2 g to 0.25 g of your unknown acid in a 250 mL beaker, place a magnetic stir bar and add 40-50 mL D.I. water to dissolve it.
2. Setup the pH electrode and buret as shown in the figure below.
3. We will first conduct a pilot titration by adding 0.5 mL of NaOH and measuring the pH.
4. Record your data using Table 2 as an example.
5. Continue this titration till you see a sizeable jump in the pH.
6. Continue adding 0.5 mL of NaOH at least 3 mL passed the equivalence point.
7. Now repeat the same procedure by following steps 1 and 2 for another sample of your unknown using a clean 250 mL beaker. Try to weigh close to the mass of unknown in your first trial.

8. This time, since you know the approximate equivalence point of your titration, you will collect more data at the half equivalence point and the equivalence point by adding NaOH dropwise instead of 0.5 mL increments. This is in order to get more points for our graph.
9. Once you have reached the equivalence point continue to add NaOH in 0.5 mL increments till you have passed 5 mL of the equivalence point.
10. **Plotting the pH (Y-axis) vs volume of NaOH (X-axis) after each volume increment of titrant has been added can yield a titration curve as detailed as desired, but there are better ways of locating the equivalence point. The most common of these is to take the first or second derivatives of the plot: $\Delta(pH)/\Delta V$ and $\Delta^2(pH)/\Delta V^2$. You will need to plot all three curves and use the 2nd derivative plot to find the equivalence point.**
11. Please look at the tutorial video which has been posted on YouTube to understand how to plot these graphs. **https://www.youtube.com/watch?v=Q2sF56OpNAY&t=2s**
12. Determine the equivalent mass of the unknown acid from the equivalence point and the Ka from the half equivalence point. The pH at half the equivalence point is the pKa of the unknown acid.

An example of the calculation is given in this link...

http://classes.colgate.edu/jchanatry/chem102/exp19_calcs.htm



Data Tables:

Table 1- Part A Standardization of NaOH

	Trial 1	Trial 2	Trial 3
Mass of KHP			
Initial Volume of NaOH			
Final Volume of NaOH at end point			
Volume of NaOH used			
Molarity of NaOH			
Average Molarity of NaOH			

Table 2- Part B pH titration of unknown acid for pilot titration

Mass of Unknown Acid = _____________ g

Volume of NaOH	pH
0.00 mL	
0.50 mL	
1.00 mL	

Using Excel, plot the following graph: (watch the video posted on step 11 of the procedure).

1. pH (Y-Axis) vs V_{NaOH} (X-Axis)
2. $\Delta(\mathrm{pH})/\Delta V$ (Y-Axis) vs V_{NaOH} (X-Axis) (1st derivative plot)
3. $\Delta^2(\mathrm{pH})/\Delta V^2$ (Y-Axis) vs V_{NaOH} (X-Axis) (2nd derivative plot)

Post Lab Questions:

1. Explain the difference between the terms endpoint and equivalence point.

2. Calculate Ka for an acid whose pKa is 4.87.

3. A student does a monoprotic weak acid-strong base titration using 0.4774 g. of an unknown acid, and finds that 26.98 mL of 0.1157 M NaOH are required to reach the equivalence point.

   a) How many moles of base were needed to reach the equivalence point?
   b) How many moles of acid were neutralized?
   c) Calculate the molar mass of the unknown acid.

4. Suppose that a student performing this experiment mistakenly calibrated the pH meter using pH 8 buffer instead of pH 7 buffer. As a result of this error, all of the student's pH readings were too low.

   a) Would this error have affected the calculated molar mass of the unknown acid? Briefly explain.

   b) Would this error have affected the experimentally determined pKa of the unknown acid? Briefly explain.

5. Identify your unknown acid from the list of possible unknowns from the table provided in the first experimental link. Calculate the percent error for the equivalent mass determination in your experiment. Explain briefly the possible sources of error in your experiment.

Experiment 7: pH of Strong Acids, Weak Acids, Salts and Buffer Effects

Background: In this experiment we will..

1. Compare and calculate the pH of a series of hydrochloric acid and acetic acid dilutions.
2. Measure the pH of various salt solutions.
3. Compare the pH of acidic and basic solutions in the presence of a buffer and D.I. water.

Use the following links to understand the theory and calculations for this lab.

https://chem.libretexts.org/Bookshelves/General_Chemistry/Book%3A_Chem1_(Lower)/13%3A_Acid-Base_Equilibria/13.03%3A_Finding_the_pH_of_weak_Acids_Bases_and_Salts

https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Acids_and_Bases/Ionization_Constants/Calculating_A_Ka_Value_From_A_Measured_Ph

https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Acids_and_Bases/Buffers/How_Does_A_Buffer_Maintain_Ph

Procedure:

Part 1: pH of a Strong Acid

1. Obtain exactly 5.0mL of 0.10M HCl in a 25 mL (or 50 mL) graduated cylinder.
2. Fill your wash bottle with distilled water and use your wash bottle to fill the graduated cylinder to exactly 25.0 mL. Pour the solution into a 50 mL beaker.
3. Use your wash bottle to rinse out the graduated cylinder into the 400 mL beaker used as a temporary waste container and set the graduated cylinder aside until the next dilution is made.
4. Calibrate your pH meter with the pH 7 buffer according to the instructions given to you in the equipment procedures section.
5. Once calibrated, rinse off the bulb of the pH meter with distilled water and insert the pH meter into the beaker containing the diluted acid.
6. Gently stir the solution with the pH meter and watch the reading. When the reading has stabilized on the pH meter, record the value in your lab notebook. Record all decimal places on the pH meter.
7. Rinse the pH meter with distilled water and return it to the buffer solution.
8. Transfer exactly 5.0 mL of the diluted solution from your 50 mL beaker to your 25mL graduated cylinder.
9. Pour the remaining solution in the 50 mL beaker into a 400 mL waste beaker. Rinse out the 50 mL beaker with distilled water from your wash bottle and set aside for the next pH reading.

10. Use your wash bottle to fill the graduated cylinder containing the acid solution to exactly 25.0 mL.

11. Pour the solution from your graduated cylinder into the 50 mL beaker and record the pH.

12. Rinse your pH meter with distilled water and return it to the buffer solution.

13. Repeat steps 8-13 two more times for a total of 4 different dilutions and pH measurements.

14. When finished, pour remaining solution into waste beaker and rinse all equipment with distilled water.

Part 2: pH of a Weak Acid

1. Repeat the steps in part 1 using 0.10 M acetic acid instead of the HCl.

Part 3: Determine the pH of various salt solutions (This part can be prepared and shared by 4 persons)

1. Clean six 50 mL beakers. Label them with each of the following: 0.10 M NaCl, 0.10 M $NaC_2H_3O_2$, 0.10 M $NaHCO_3$, 0.10 M Na_2CO_3, 0.10 M NH_4Cl, and 0.10 M $NH_4C_2H_3O_2$.

2. Add 20 mL of each solution to the appropriately labeled beaker.

3. Measure the pH of each solution using your pH electrode. Make sure you properly rinse with D.I. water between each measurement.

Part 4: Preparation of sodium acetate buffer solution.

1. Weigh a clean and dry 150 mL beaker.

2. Add 2.0 g of solid anhydrous sodium acetate ($NaC_2H_3O_2$) to the beaker.

3. Carefully add 4.0 mL of **6 M acetic acid** to the beaker.

4. Using your 50 mL graduated cylinder, add 46.0 mL of D.I. water to the beaker.

5. Stir the solution using a stirring rod until the sodium acetate has completely dissolved.

6. This buffer solution now contains, 2.4×10^{-2} mol each of sodium acetate and acetic acid and will be used in part 5 of the experiment.

Part 5: Buffer Effects

1. Obtain your buffer solution which was prepared in Part 4.

2. Pour 25 mL of your buffer solution in another 50 mL beaker.

3. Check the calibration on the pH meter. Once calibrated, rinse off the bulb of the pH meter with distilled water and insert the pH meter into the beaker containing the buffer solution.

4.Gently stir the solution with the pH meter and watch the reading. When the reading has stabilized on the pH meter, record the value in your lab notebook. Record all decimal places on the pH meter.

5. Rinse the pH meter with distilled water and return it to the buffer solution.

6. Obtain exactly 1 mL 0.10M HCl in a 10 mL graduated cylinder. Pour the 1 mL of HCl into the buffer solution.

7. Rinse the pH meter with distilled water and insert it into the buffer solution. Use it to stir the solution gently before recording the pH of the buffer solution containing the HCl.
8. Pour the solution into the waste beaker when finished and rinse the beaker with distilled water before continuing.
9. Repeat steps 1-8 substituting 0.10M NaOH for the 0.10M HCl.
10. Repeat the entire procedure for part 5 substituting 25 mL of water for the buffer solution.
11. When finished, pour the solution from the waste beaker into the waste container and rinse all equipment with distilled water before returning it to your drawer.

Tables 1: pH of Strong Acid Solutions

Dilution Number	Concentration of HCl, M	Measured pH	Theoretical pH
1			
2			
3			
4			

Tables 2: pH of Weak Acid Solutions

Dilution Number	Concentration of Acetic Acid, M	Measured pH	Ka based on Measured pH	Theoretical Ka from literature
1				
2				
3				
4				

Tables 3: pH of Salts

Salt	pH	Salt type
NaCl		
$NaC_2H_3O_2$		
$NaHCO_3$		
Na_2CO_3		
NH_4Cl		
$NH_4C_2H_3O_2$		

Tables 4: Buffer effects

Salt	Measured pH	Theoretical pH
Original Buffer		
Water		
Buffer with HCl		
Water with HCl		
Buffer with NaOH		
Water with NaOH		

Discussion Questions

You must use your data to answer these questions. If the answer you give does not reflect YOUR data and results, you will receive no credit for the question.

1. Note the large pH change that resulted when a dilution was made to the strong acid solution. Why was a large pH change not noticed when a weak acid was used?

2. Calculate the percent error in your experimentally determined Ka values in Table 2 as compared to the literature Ka values. Are you confident that your pH measurements are accurate? Briefly explain why or why not. If not, explain where error could have resulted in your experiment.

% error in Ka = (|calculated Ka – literature Ka| / literature Ka) x 100%

3. When you measure the pH of salt solutions does the measured pH agree with the type of salt measured? Include any deviations from your observations.

4. What would be the pH of a 0.500 M ammonium chloride solution? K_b of $NH_3 = 1.8 \times 10^{-5}$.

5. Compare the change in pH due to the addition of HCl to the buffer solution to the pH change seen when HCl was directly added to water. Briefly explain why there is such as large pH change in the water, but little pH change in the buffer solution.

6. What would be the result if you added an amount of HCl that exceeded the amount of acetate ion in the buffer solution? Explain how you would calculate the pH of the solution under these conditions.

Experiment 8: Determination of the solubility of Potassium Hydrogen Tartrate

Purpose: In this experiment, we will determine the solubility of a sparingly soluble organic salt in water. We will also examine the solubility of the salt in the presence of ionic solutions, one of which has a common ion with the salt.

Potassium hydrogen tartrate is a sparingly soluble organic salt. It is a weak monoprotic acid and is prepared by treating tartaric acid (a diprotic acid) with enough potassium hydroxide to neutralize half the moles of tartaric acid. This leads to the formation of potassium acid tartrate or potassium hydrogen tartrate (KHTar). This compound is also referred to as potassium bitartrate or cream of tartar. KHTar being a weak acid dissolves sparingly in water as follows.

$$\mathbf{KHTar(s) \rightleftarrows K^{+}(aq) + HTar^{-}(aq)} \qquad \text{Equation (1)}$$

The solubility product is given as

$$\mathbf{Ksp = [K^{+}]\,[HTar^{-}]} \qquad \text{Equation (2)}$$

where $[K^{+}] = [HTar^{-}]$ = molar solubility

$HTar^{-}$ (aq) is a weak acid and can be titrated using a strong base like standardized NaOH to determine its concentration and subsequently the solubility. The reaction is as follows.

$$\mathbf{HTar^{-}(aq) + OH^{-}(aq) \longrightarrow Tar^{2-}(aq) + H_2O(l)} \qquad \text{Equation (3)}$$

At the equivalence point, the moles of NaOH = moles of $HTar^{-}$. So, by carrying out an acid-base titration we can determine the molar solubility of KHTar.

In this experiment, we will also study the effect of a common ion on solubility by measuring the solubility of KHTar in water (part 1) and then in a known concentration of potassium nitrate (part 2) which has a common ion (K^{+}) with the salt (KHTar). In addition, in part 3, we will also investigate how the addition of an ionic compound which does not have a common ion with sparingly soluble salt effects the solubility.

Procedure:

Part 1: Solubility of KHTar in water

1. Weigh about 1 g of KHTar on a centigram balance and transfer it to a clean 150 mL beaker.
2. Add 75 mL of deionized water to the beaker.
3. Agitate the solution for about 15 minutes by placing a magnetic stir bar in the flask and using a stir plate.
4. After 15 minutes, stop stirring the mixture and let the solid settle down while measuring the temperature of the supernatant solution. Note down the temperature in your lab notebook.
5. Remove the stir bar, clean it with deionized water and return it back.

6. Filter the supernatant solution using a long stem funnel, stirring rod and filter paper apparatus which your instructor will help you set up.
7. Collect the filtrate into another 150 mL beaker. The filtrate should be clear.
8. Pipet out 25 mL of the filtrate into a clean 125 mL Erlenmeyer flask.
9. Add one to two drops of phenolphthalein indicator.
10. Titrate with standardized NaOH till the color of the solution turns from colorless to pale pink.
11. You will repeat step 8 and 9 for another trial using 25 mL of the filtrate.
12. Record your data on Table 1.

Part 2: Solubility of KHTar in 0.10 M KNO_3.

In part 2 of the experiment, we will carry out the same procedure as in part 1, except that we will substitute deionized water in step 2 with 0.10 M KNO_3. So, you will add 75 mL of 0.10 M KNO_3 instead of D.I. water to 1 g of KHTar.

Record your results in Table 2.

Part 3: Solubility of KHTar in 0.10 M NaCl.

In part 3 of the experiment, we will carry out the same procedure as in part 1, except that we will substitute deionized water in step 2 with 0.10 M NaCl. So, you will add 75 mL of 0.10 M NaCl instead of D.I. water to 1 g of KHTar.

Record your results in Table 3.

Table 1: Solubility of KHTar in water

Molarity of Standard NaOH solution = _____________M

Temperature of KHTar solution = _____________ ºC

	Trial 1	Trial 2
Initial buret reading (mL)		
Final buret reading (mL)		
Volume of titrant (mL)		
Moles of NaOH used		
Moles of KHtar$^-$		
Volume of saturated solution of KHTar (L)		
Molar solubilty of KHTar (M)		
Average Molar Solubility of KHTar (M)		▨

Table 2: Solubility of KHTar in 0.10 M KNO_3

Molarity of Standard NaOH solution = _____________M

Temperature of KHTar solution = _____________ ºC

	Trial 1	Trial 2
Initial buret reading (mL)		
Final buret reading (mL)		
Volume of titrant (mL)		

Moles of NaOH used		
Moles of KHtar$^-$		
Volume of saturated solution of KHTar (L)		
Molar solubilty of KHTar (M)		
Average Molar Solubility of KHTar (M)		

Table 3: Solubility of KHTar in 0.10 M NaCl

Molarity of Standard NaOH solution = _____________M

Temperature of KHTar solution = _____________ °C

	Trial 1	Trial 2
Initial buret reading (mL)		
Final buret reading (mL)		
Volume of titrant (mL)		
Moles of NaOH used		
Moles of KHtar$^-$		
Volume of saturated solution of KHTar (L)		
Molar solubilty of KHTar (M)		
Average Molar Solubility of KHTar (M)		

Discussion Questions

1. From your calculations of the solubility of KHTar in water, KNO_3 and NaCl solutions, do you see any difference in the three solutions? Why?

2. A student observed the molar solubility of $Ca(OH)_2$ under a variety of conditions. In each of the following scenarios, explain briefly what would be the effect of molar solubility of $Ca(OH)_2$

   a. $Ca(OH)_2$ dissolved in a solution of 0.10 M $Ca(NO_3)_2$.

   b. $Ca(OH)_2$ dissolved in a solution of 0.10 M KOH.

   c. $Ca(OH)_2$ dissolved in a solution of 0.10 M NaCl.

3. Briefly explain why we took temperature readings for part 1 and part 2 of the experiment?

4. Calculate the Ksp for KHTar, in water based on your experimentally determined molar solubility of KHtar.

5. Calculate the % error of your experimentally determined Ksp in question 4 as compared to the literature value of Ksp for KHtar.

6. The Ksp for AgI is 8.3×10^{-17}

   (a) Calculate the molar solubility of AgI in water.
   (b) Calculate the molar solubility of AgI in 0.031 M $AgNO_3$ solution.
   (c) Calculate the molar solubility of AgI in 0.10 M KI solution.

Experiment 8: Qualitative Analysis of Cations.

Purpose: In this experiment, we will develop a general scheme to separate the following cations: Ag^+, Pb^{2+}, Fe^{3+}, Ca^{2+} and K^+.

Background: Cations are classified based on their solubility into various groups. For this experiment, Ag^+, Pb^{2+} are classified as Group I cations, Fe^{3+} is a group III cation, Ca^{2+} is a Group IV cation, and K^+ is a Group V cation. A brief overview of the selective precipitation of cations in found in the following link.

https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_General_Chemistry_(Petrucci_et_al.)/18%3A_Solubility_and_Complex-Ion_Equilibria/18.9%3A_Qualitative_Cation_Analysis

Group I cations can be separated from Group III and Group IV cations because they form insoluble chlorides. The Group III cations form insoluble sulfides and hydroxides. Group IV cations form insoluble carbonates. Various reagents are used to selectively precipitate these cations and then follow up by confirming the presence of a particular cation. Some examples of procedures for the selective precipitation of Grp I, Grp III, Grp IV and Grp V cations are given below.

https://chem.libretexts.org/Ancillary_Materials/Laboratory_Experiments/Wet_Lab_Experiments/General_Chemistry_Labs/Online_Chemistry_Lab_Manual/Chem_12_Experiments/06%3A_Qualitative_Analysis_of_Group_I_Ions_(Experiment)

https://chem.libretexts.org/Ancillary_Materials/Laboratory_Experiments/Wet_Lab_Experiments/General_Chemistry_Labs/Online_Chemistry_Lab_Manual/Chem_12_Experiments/07%3A_Qualitative_Analysis_of_Group_III_Ions_(Experiment)

https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Qualitative_Analysis_of_Common_Cations_in_Water_(Malik)/6%3A_Group_IV_and_Group_V_cations/6.2%3A_Separation_and_confirmation_of_individual_ions_in_group_IV_precipitates_and_group_V_mixture

Please use to following link to understand the techniques which will be used in this experiment and the next (qualitative analysis of anions)

http://www.public.asu.edu/~jpbirk/qual/qualanal/semimicr.html

Procedure: Prepare a test tube with approximately 15 drops of the know mixture containing Ag^+, Pb^{2+}, Fe^{3+}, Ca^{2+} and K^+

Part 1: Precipitation of Grp I cations

1. Add 2 drops of 6 M HCl.
2. Centrifuge the solution being careful to place a test tube containing water of the same level as your test solution for balancing the centrifuge. A good speed to begin centrifuging is 3000 rpm.
3. Add one more drop of 6 M HCl to test for completeness of the precipitation of Grp I cations. Centrifuge if necessary.
4. Your precipitate contains Grp I cations and the supernatant contains Grp III, Grp IV and Grp V cations.
5. Decant the supernatant solution into another test tube.

A. Separation and confirmation of Pb^{2+}

1. Wash the precipitate from Part 1- Step 4 with 1 or 2 mL of D.I. water. Centrifuge and decant the supernatant.
2. Add 2 mL of D.I water to the test tube containing the precipitate and place in a 250 mL beaker half full of boiling water for 5-10 mins.
3. Centrifuge and decant the supernatant solution which contains $PbCl_2$.
4. The remaining precipitate contains Ag^+ ions.
5. Acidify the supernatant from step 3 with 3 drops 6 M acetic acid and a few drops of 0.1M K_2CrO_4.
6. A yellow precipitate of $PbCr_2O_4$ confirms the presence of Pb^{2+} ions.

B. Confirmation of Ag^+

1. To the precipitate from Step 3 in part A, add 10 drops 6 M NH_3 (NH_4OH) and stir thoroughly.
2. Ag^+ forms a complex with ammonia $[Ag(NH_3)_2]^+{}_{(aq)}$.
3. Add 6 M HNO_3 to make the solution acidic using blue litmus paper.
4. The presence of a white precipitate of AgCl confirms the presence of Ag^+ ions.

Part 2: Precipitation of Grp III cations

1. To the supernatant solution from Part 1- Step 4, add 6 M NH_3 (NH_4OH) to make the solution alkaline and then add 5 drops NH_3 (NH_4OH) in excess.
2. This will lead to the formation of $Fe(OH)_3$ precipitate. The remaining supernatant solution contains Grp IV and Grp V cations.
3. Next, we will proceed to separate and confirm the Grp III cation Fe^{3+}.

C: Confirmation of Fe^{3+}

1. To the precipitate from Part 2- step 2, add 5 drops of 6M HCl to dissolve it.
2. Dilute the solution by adding an equal volume of D.I. H_2O.
3. Add 5 drops of 0.1 M KSCN and stir.
4. The presence of a deep red color of $FeSCN^{2+}$ confirms the presence of Fe^{3+} ions.

Part 3: Precipitation of Grp IV cations.

1. To the supernatant from Part 2- step 2 add 15 drops of $(NH_4)_2CO_3$.
2. Stir the contents with a stirring rod, centrifuge and decant the supernatant into another test tube. The supernatant contains Grp V cations.
3. Add 15 drops of D.I. water to the precipitate and repeat step 2, but this time you can discard the supernatant.
4. The precipitate contains calcium carbonate.

D: Confirmation of Ca^{2+}

1. Add 5 drops of 6 M acetic acid to dissolve the ppt.
2. Heat the test tube in a boiling water bath for 2 minutes.
3. Add more drops of 6 M acetic acid if needed to completely dissolve the precipitate.
4. To the solution add 10 drops of 0.2 M ammonium oxalate $(NH_4)_2C_2O_4$.
5. Stir the contents of the test tube and centrifuge.
6. Decant the supernatant.
7. The formation of white precipitate of CaC_2O_4 is a strong indication that Ca^{2+} is present in the test sample.

8. The presence of Ca^{2+} is further verified by a flame test where Ca^{2+} gives a characteristic orange-red color confirming its presence.
9. Carry out the flame test using a clean nichrome wire by dipping the loop into the solution to be tested and observe the color of the flame when the wire-loop is heated in the edge of the burner flame.
10. Once you have completed the test, clean the wire-loop with acid, by dipping it into a test tube containing 6M HCl and then burning it in the flame till it is red hot.

Part 4: Confirmation of Grp V cations.

1. The supernatant from Part 3- step 2 contains Grp V cations.
2. We will use the flame test to confirm the presence of K^+

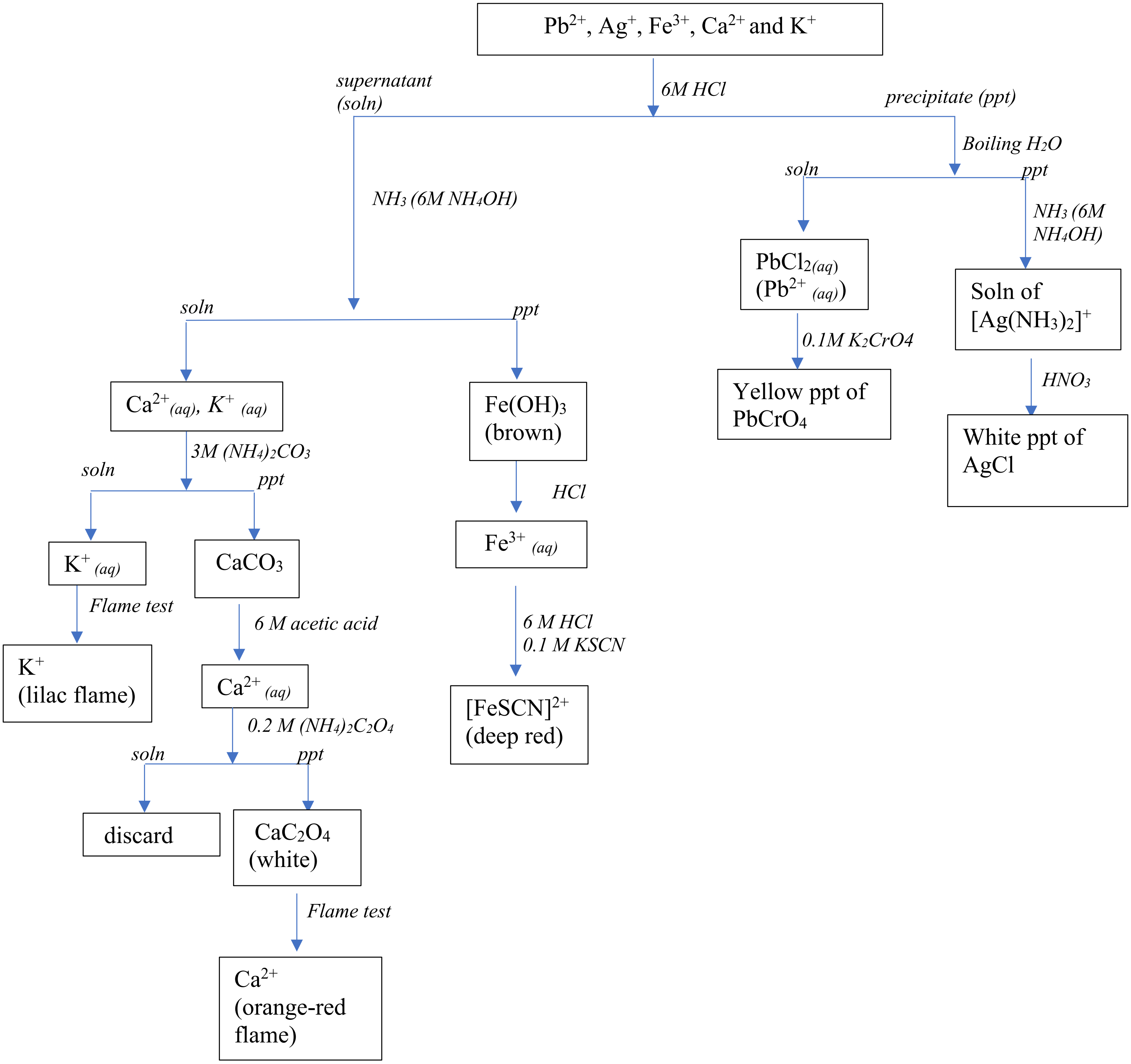
D: Confirmation of K^+

1. Concentrate your supernatant from Part 3- Step 2 to a moist slurry. This can be accomplished by pouring the contents of your test tube into a 50 mL beaker and evaporating the solvent by heating the solution.
2. Carry out the flame test just like in Part 3- Step 9.
3. Observe the flame against a dark background with and without a cobalt glass (filters out color of Na^+).
4. A violet or lilac flame is confirmatory for the presence of K^+ in your test-solution.
5. Once you have completed the test, clean the wire-loop with acid, by dipping it into a test tube containing 6M HCl and then burning it in the flame till it is red hot.

Repeat all the above steps with your unknown sample to identify the presence of Grp I, Grp III Grp IV, and Grp V cations in your unknown mixture.

The following flow chart outlines the experimental procedure.

Flow chart for separating Group I, Group III, Group IV and Group V cations



Informal Lab report:

Unknown Code : ___________________

Identity of Cations in Unknown: ___________________

Post Lab Questions:

1. Briefly explain how we prepare a ammonium buffer solution in part 2. Will the pH of this solution be acidic, basic or neutral?

2. What is the biggest precaution we need to take when we centrifuge?

3. A solution contains Pb^{2+} ions in solution. Describe a reaction with a single reagent that will identify the presence of lead cations.

4. A student is carrying out the same qualitative analysis lab. After adding HCl in the first step, she adds NH_3 to the separated supernatant solution but does not see the formation of a precipitate. Which cation is absent from her unknown solution?

5. Draw a flow chart just to explain how you identified your unknown ion/s in this experiment.

Experiment 10: Qualitative Analysis of Anions

Purpose: In this experiment, we will develop a general scheme to confirm the presence of SO_4^{2-}, PO_4^{3-}, CO_3^{2-} , Cl^-, Br^-, I^- and NO_3^- ions.

Background: In this lab, you will identify anions in an unknown. However, unlike the last lab (Qualitative Analysis of Cations), you will not be using a flow chart in which you separate ions as supernatant solutions and precipitates. Instead, in this lab, you first will perform a series of preliminary tests to analyze and confirm the anions. You will then be handed unknown solutions from which you need to identify the corresponding anions. To get an idea of the theory and reactions for the analysis read the following links..

https://staff.buffalostate.edu/nazareay/che112/ex7.htm

http://www.public.asu.edu/~jpbirk/qual/qualanal/anprop.htm

Procedure: It is convenient to categorize the anions in terms of their reactivity.

Group A: The Barium Precipitate Group (SO_4^{2-} $CO_3^{2-}$and PO_4^{3-})

1. Dissolve a small amount (pea sized) of sodium sulfate (Na_2SO_4) in 10-15 drops of D.I. water in a small test tube.
2. Add 5-7 drops of 0.1 M barium chloride ($BaCl_2$).
3. Add 5 drops of 3 M HNO_3.
4. Note down your observations in your lab notebook
5. Repeat the same procedure (Step 1 to Step 4) for samples of sodium carbonate (Na_2CO_3), and sodium phosphate (Na_2HPO_4. $12H_2O$).

Confirmation of SO_4^{2-} : The presence of a white precipitate of $BaSO_4$ is the confirmation of the SO_4^{2-} ion.

$$Ba^{2+}{}_{(aq)} + SO_4^{2-}{}_{(aq)} \rightarrow BaSO_{4(s)}$$

Confirmation of PO_4^{3-} : Dissolve an amount of Na_2HPO_4. $12H_2O$ in 10 drops of D.I. H_2O. Add 15 drops of conc. HNO_3 (to be done in the hood). Next, add 4 drops of 0.5 M $(NH_4)_2MoO_4$ ammonium molybdate. A yellow precipitate of $(NH_4)_3PO_4$ $.12MoO_3$, indicates the presence of phosphate. If a precipitate does not form immediately, heat in a water bath for a few minutes.

$$PO_4^{3-} + 3H_3O^+ \rightarrow H_3PO_{4\,(aq)} + 3H_2O$$

$$3\ NH_4^+ + 12\ MoO_4^{2-} + H_3PO_4 + 21\ H^+ \rightarrow (NH_3)_3PO_4.12MoO_3\ (s) + 12\ H_2O$$

Note: The remaining ions are confirmed in other groups.

Group B: The Acid Volatile Group (CO_3^{2-})

1. Dissolve a small amount of sodium carbonate (Na_2CO_3) in 5-7 drops of D.I. water in a small test tube.
2. Add 5 drops of 3M H_2SO_4 to the tube.
3. Record your observations in your lab notebook.

Confirmation of CO_3^{2-} : The carbonate anion is the anion of carbonic acid (H_2CO_3) which is a weak acid. This acid is unstable in solution and decomposes to produce CO_2 gas. The observed effervescence indicates the presence of CO_3^{2-}.

$$CO_3^{2-} + 2\ H_3O^+ \rightarrow CO_2(g) + 3H_2O$$

Group C: The Silver Precipitate Group (Cl^-, Br^- and I^-)

1. Dissolve a small amount of NaCl in 5-7 drops of D.I. water in a small test tube.
2. Add 5 drops of 0.1 M $AgNO_3$ followed by 5 drops of 3M HNO_3.
3. Stir thoroughly and record your observations, especially the color of the precipitate.
4. Repeat the same procedure (Step 1 to Step 3) for samples of NaBr and NaI.

Confirmation of Cl^-, Br^-, and I^-: Silver salts of halides are insoluble. AgCl is a white precipitate, AgBr is creamish and AgI is yellow.

$$\mathbf{Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}\ (white)}$$

$$\mathbf{Ag^+_{(aq)} + Br^-_{(aq)} \rightarrow AgBr_{(s)}\ (cream)}$$

$$\mathbf{Ag^+_{(aq)} + I^-_{(aq)} \rightarrow AgI_{(s)}\ (yellow)}$$

The colors of these three halide precipitates are very similar so we need to confirm the presence of these anions further. All the halides (Cl^-, Br^-, I^-) function as reducing agents. We use the differences in their abilities to function as reducing agents as a way of differentiating between the three halides. Their oxidized forms, (Cl_2, Br_2, I_2) which are their elemental states decrease in their relative strengths as oxidizing agents in the following order. $Cl_2 > Br_2 > I_2$

Therefore, chlorine (Cl_2) will oxidize Br- to elemental bromine (Br_2) . Bromine dissolves in dicholoromethane a.k.a. as methylene chloride (CH_2Cl_2) to give a solution of red-amber color.

$$\mathbf{Cl_2\ (aq,\ colorless) + 2Br^- \longleftrightarrow Br_2\ (aq)\ yellow\text{-}brown + 2Cl^-\ (aq)}$$

$$\mathbf{Br_2\ in\ CH_2Cl_2 \rightarrow red\text{-}amber\ color}$$

Chlorine (Cl_2) will also oxidize I- to elemental iodine (I_2). Iodine dissolves in dicholoromethane a.k.a. as methylene chloride (CH_2Cl_2) to give a solution of violet color.

$$\mathbf{Cl_2\ (aq,\ colorless) + 2I^- \longleftrightarrow I_2\ (aq)\ yellow\text{-}brown + 2Cl^-\ (aq)}$$

$$\mathbf{I_2\ in\ CH_2Cl_2 \rightarrow violet\ color}$$

Procedure to confirm halides:

1. Dissolve an amount of NaCl in 5 drops of D.I. water.
2. Add 10 drops of chlorine water, stopper and shake thoroughly.
3. Add 5 drops of dichloromethane (methylene chloride, CH_2Cl_2) and observe the lower layer of the mixture.
4. Note the color of the CH_2Cl_2 (lower) layer and record your observations.
5. Repeat the same procedure (Step 1 to Step 3) for samples of NaBr and NaI.

Group D: The soluble group (NO_3^-)

Nitrate is reduced to nitric oxide in the presence of Fe^{2+} in an acidic medium.

$NO_3^-{}_{(aq)} + Fe^{2+}{}_{(aq)} + H^+{}_{(aq)} \rightarrow Fe^{3+}{}_{(aq)} + NO + H_2O_{(l)}$

$NO + Fe^{2+}{}_{(aq)} \rightarrow [FeNO]^{2+}$

The nitric oxide forms a complex with the excess Fe^{2+}. This appears as a brown ring at the interface of the concentrated acid layer and the aqueous medium containing Fe^{2+}.

Confirmation of NO_3^- (Brown Ring Test)

1. In a small test tube, dissolve an amount of $NaNO_3$ in 4 drops of the solution which contains a mixture of 1M $FeSO_4$ in 1M H_2SO_4.
2. Add 5-6 drops of 3 M H_2SO_4 to this solution until it is acidic (check with litmus paper).
3. Incline the test tube at a 45° angle.
4. Carefully add 5 drops of concentrated H_2SO_4 so the drops roll down the side of the test tube and slide gently onto the top of the solution. DO NOT MIX the solutions!
5. Allow the test tube to stand for a few minutes and look for the appearance of a brown ring at the interface of the sulfuric acid layer (the bottom) and the test solution layer.

Analysis of Unknowns: For each unknown sample, perform all the test from the categories and confirm the anions using their respective procedures.

Informal Lab Report:

Unknown Code: ____________________

Identity of Anions in Unknown: ____________________

Post Lab Questions:

1. Suppose you have the thiocyanate (SCN^-) ion as an unknown. How will you confirm its presence? Write down the appropriate reaction/s. (Hint: Look at your observations in the Qualitative Analysis of cations lab experiment).

2. The sulfide anion (S^{2-}) is another anion that produces a gas in the presence of acid. Which gas will be produced? Write down the reaction using Na_2S as an example.

3. To test the presence of halides, we need to add acid to the solution when we add $AgNO_3$. Explain why HCl cannot be used?

4. Suppose that a series of spot tests on an unknown solution yields the following results.
   A white precipitate upon the addition of $BaCl_2$ (aq)
   No yellow precipitate upon the addition of $(NH_4)_2MoO_4$.
   Bubbles form when acid is added to the solution.
   A white precipitate upon the addition of $AgNO_3$.

   What are the possible anions in this unknown solution?

Experiment 11: Thermodynamics of Solubility of Potassium Nitrate

Background: In this experiment we will study the solubility of KNO_3, in water at different temperatures to calculate Ksp and other thermodynamic functions. The reaction of the dissolution of KNO_3 is as follows.

$$KNO_3(s) \rightleftharpoons K^+(aq) + NO_3^-(aq)$$

Equation (1)

The Ksp for this reaction is found to be

$$K_{sp} = [K^+][NO_3^-]$$

Equation (2)

From the relationship between ΔG and Equilibrium constant

$$\Delta G = -RT\ lnK_{sp}$$

Equation (3)

ΔG is related to enthalpy and entropy by the following relationship

$$\Delta G = \Delta H - T\Delta S$$

Equation (4)

Substituting Equation (3) in Equation (4) leads to Equation (5). The plot of lnKsp vs 1/T is a straight line with a slope of - ΔH/R and the y-intercept of ΔS/R.

$$lnK_{sp} = -\frac{\Delta H}{R}\left(\frac{1}{T}\right) + \frac{\Delta S}{R}$$

$$\boldsymbol{y \quad = \quad m \quad x \quad + \quad b}$$

Equation (5)

Theory and Procedure

To understand the theory and procedure for this experiment, please read the following link.

https://chem.libretexts.org/Courses/Saint_Marys_College_Notre_Dame_IN/Chem_122L%3A_Principles_of_Chemistry_II_Laboratory_(Under_Construction__)/11%3A_Thermodynamics_of_Solubility

We will be following the exact procedure as the link above. Make sure you watch the prelab video. Take notes in your lab notebook to prepare yourself for the experiment.

Data Table:

Table 1- Experimental Data

Trial 1	Volume of Solution	T in ^{o}C
1		
2		
3		
4		
5		

Table 2- Calculation and Results

Trial 1	[K^+] in M	[NO_3^-]in M	Ksp	T in K	Ln Ksp	1/T
1						
2						
3						
4						
5						

Plot a graph of lnKsp vs 1/T and calculate ΔH and ΔS from the slope and y-intercept respectively.

Post Lab Questions:

1. From your calculations of Ksp, calculate the ΔG for each of the trials using equation 3.

2. Is the dissolution of KNO_3 spontaneous at all temperatures or only at high or low temperatures?

3. Is the dissolution of potassium nitrate in water an exothermic or endothermic process? What experimental evidence supports your answer?

4. If magnesium nitrate was used instead of potassium nitrate in this experiment, would the molar solubility of nitrate [$NO3^-$] be lower, higher or stay the same for each trail? Explain why?

Experiment 12: Preparation of a Galvanic Cell and Determination of Avogadro's Number by Electrochemistry

Background: In this experiment we will determine Avogadro's number by electrolysis.

In this experiment an understanding of galvanic and electrolytic cells is important. Please read the information in the following link to understand the differences of the two. For the measurement of current in this experiment, we will use a galvanic cell in part 1 and an electrolytic cell in part 2.

https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Supplemental_Modules_(Analytical_Chemistry)/Electrochemistry/Electrolytic_Cells

To calculate Avogadro's number, we use the equation for the measurement of charge (Q) which is in Coulombs. The relationship between charge and current is given by the following equation.

$$Q = I \times t \qquad \text{Equation (1)}$$

Where 'I' is the current on Amperes and 't' is time in seconds. One Ampere is the quantity of charge moving past a point in one second. Also, the charge of a single electron is 1.602×10^{-19} C.

$$Q = (C/s) \times t \qquad \text{Equation (2)}$$

By measuring the current over a period of time we can calculate the total charge of the electrons passing through the wire, which when divided by the charge of a single electron gives us the total number of electrons.

\# of electrons = Total charge passed/ charge of a single electron. So,

# of electrons = $I \times t / 1.602 \times 10^{-19}$ Equation (3)

We will use the oxidation of copper at the anode to calculate Avogadro's number. The reaction for the oxisation of copper at the anode is given by

$$Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^- \qquad \text{Equation (4)}$$

From the above reaction, for every atom of Cu lost, two electrons are transferred. From Equation (3) we can calculate the total number of electrons and thus the total number of atoms of Cu lost. We can correlate the change in mass of the copper anode to the mols of copper. We can then calculate Avogadro's number

 # Cu atoms/ mols of Cu = Avogadro's number Equation (5)

Part 1: Preparation of a Galvanic Cell.

For this part, we will prepare a galvanic cell of Zn and Cu by using the following procedure.
Since we are observing the spontaneous reaction of the oxidation of Zn and the reduction of Cu, this cell functions like a battery generating current.

1. Polish a **short** Zn strip and a **short** Cu strip with the sandpaper provided.
2. We will use a well plate for this part of the experiment.
3. Insert the Zn strip into a well containing 1M $ZnSO_4$.

4. Insert the Cu strip into another well containing 1M $CuSO_4$.
5. Dip the precut filter paper in a beaker containing 1 M KNO_3. This will be your salt bridge which will connect both wells.
6. On the multimeter **plug BLACK into BLACK (COM) and RED into RED (VΩmA).**
7. Clip the RED alligator clip to the Cu strip which is the cathode and the BLACK alligator clip to the Zn strip which is the Anode.
8. Turn on the multimeter to the DCV dial to measure the voltage of your galvanic cell for 2 mins.
9. Turn on the multimeter to 200 mA and check if you see any current generated.
10. Repeat the experiment for Trial 2 and note down your findings in Table 1.

Part 2: Determination of Avogadro's number by electrolysis.

For this part, we will once again use the Zn and Cu electrodes and an external current will be applied to by using the following procedure. We will measure the current over a period of time.

1. Make sure the power supply is powered off and unplugged.
2. Polish a **long** Zn strip and a **long** Cu strip with the sandpaper provided.
3. Measure the mass of both the strips on an analytical balance to the 0.0001 g.
4. Insert both strips into a 50 mL beaker which is placed on a stir pate. Position the electrodes so they are not touching.
5. Add 25 mL of 1.0 M H_2SO_4 and the magnetic stir bar to maintain a medium stirring rate.
6. Adjust the placement of the electrodes to ensure that they are in contact with the solution.
7. **On the multimeter plug BLACK into BLACK (COM) and RED into YELLOW (10ADC).**
8. **On the power supply, plug BLACK in BLACK (-) and RED into RED (+).**
9. **Clip the RED alligator clips to each other.**
10. **Clip the BLACK alligator clip from the power supply to the Zn electrode.**
11. **Clip the BLACK alligator clip from the multimeter to Cu electrode.**
12. Your setup should look like the figure in this link https://www.vernier.com/experiment/chem-a-31_determining-avogadros-number/
13. Set the dial of the power supply to 6 V.
14. Turn the multimeter dial to 10A (approx. the 4 o'clock position).
15. Use the stopwatch provided to keep time. You can also use the stopwatch on your phone.
16. One partner needs to keep time.
17. Plug in the power supply on the power source when you are ready to record your data.
18. Start your timer and record the current reading (in mA) every 15 seconds on your Data Table 2 till you reach 5 minutes (300 s).
19. When the experiment is complete, carefully remove the two electrodes and pat on a paper towel.
20. Measure the mass of both the electrodes on the analytical balance.
21. Repeat the experiment for Trial 2.

In order to understand the theory and procedure of this experiment first watch this prelab lecture by Dr. H on YouTube.

https://www.youtube.com/watch?v=zTKAe4S_6qs

https://www.youtube.com/watch?v=qLsL9vQJTpY&t=446s

Data Table:

Table 1- Experimental Data for Part 1

	Trial 1	Trial 2
Voltage reading of galvanic cell (V)		
Current reading of galvanic cell (mA)		
Theoretical voltage of galvanic cell (V)		
% error		

Table 2- Experimental Data for Part 2

	Trial 1	Trial 2
Initial Mass of Cu anode (g)		
Final Mass of Cu anode (g)		
Initial Mass of Zn cathode (g)		
Final Mass of Zn cathode (g)		

Time (s)	Trial 1 Current (A)	Trial 2 Current (A)
0		
15		
30		
45		
60		
Collect data till 300 s		

Table 3- Calculations for Part 2

	Trial 1	Trial 2
Mass lost by Cu anode		
Moles of Cu		
Current reading in 'A'		
Total time in 's'		
Coulombs used **(Equation 1)**		
# of electrons transferred. **(Equation 3)**		
# of Cu atoms oxidized at anode		
Avogadro's number **(Equation 5)**		

Post Lab Questions:

1. Write down the half-cell reactions (anode and cathode) for Part 1 and Part 2 of this experiment.

2. Calculate the percent error in the determination of Avogadro's number from part 2 (both trials) of the experiment.

3. Faraday's constant is defined as the charge in coulombs (C) of one mole of electrons. Calculate the Faraday's constant using the anode data from Part 2 of the experiment.

4. In part 2, which data gives a closer value for the determination Avogadro's number? anode or cathode? Explain briefly.

5. In this experiment, explain why we cannot calculate Avogadro's number using the data from part 1?

Experiment 13: Thermodynamics of Electrochemical Cells

Background: In this experiment we will study the temperature dependance of an electrochemical cell and determine the ΔG, ΔH and ΔS values.

For this experiment a good understanding of the relationship between thermodynamic functions and electrochemistry is important. Please use the following link to understand the theory.

https://chem.libretexts.org/Courses/Howard_University/General_Chemistry%3A_An_Atoms_First_Approach/Unit_7%3A_Thermodynamics_and_Electrochemistry/Chapter_19%3A_Electrochemistry/Chapter_19.4%3A_Electrochemical_Cells_and_Thermodynamics

https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Physical_Chemistry_(Fleming)/10%3A_Electrochemistry/10.04%3A_Entropy_of_Electrochemical_Cells

From the relationship of Gibbs free energy, we know that

$\Delta G = - nFE$ Equation (1)

From the definition of ΔG we also know that $\Delta G = \Delta H - T\Delta S$ Equation (2)

The temperature dependance of the Gibbs function is related to ΔS by the following equation which is derived by combining equations (1) and (2) and taking derivatives.

$$-\frac{\Delta(\Delta G)}{\Delta T} = n\,F\left(\frac{\Delta E}{\Delta T}\right) = \Delta S$$

Equation (3)

Substituting for ΔG and ΔS in equation (2), we get

$$-\frac{\Delta H}{nF} = E - T\left(\frac{\Delta E}{\Delta T}\right) \qquad \text{or} \qquad E = \frac{\Delta E}{\Delta T}T - \frac{\Delta H}{nF}$$

Equation (4)

A plot of E vs T gives a straight line with slope = ΔE/ΔT from which we can calculate the ΔS using equation(3) and the intercept = ΔH/nF

Procedure : Temperature dependance of a galvanic cell.

In this experiment, we will measure the voltage of a galvanic cell prepared from Cu and Zn. The cell reaction is as follows.

$Zn\,(s) + Cu^{2+}\,(aq) \longleftrightarrow Zn^{2+}\,(aq) + Cu\,(s)$ Ecell = 1.10 V (theoretical)

1. Polish a Zn strip and a Cu strip with the sandpaper provided.
2. Insert the Zn strip into a test tube containing ~20 mL of 1 M $ZnSO_4$.
3. Insert the Cu strip into a test tube containing ~20 mL of 1M $CuSO_4$.
4. Place both test tubes in a 400 mL beaker containing 200 mL of water which serves as a water bath.

5. Dip a strip of filter paper in 1 M KNO_3 and connect it to both test tubes to serve as a salt bridge just like in the previous experiment.
6. Place the beaker with the test tubes on a hot plate.
7. Place a thermometer into the water bath.
8. On the multimeter **plug BLACK into BLACK (COM) and RED into RED (VΩmA).**
9. Clip the RED alligator clip to the Cu strip which is the cathode and the BLACK alligator clip to the Zn strip which is the Anode.
10. Make sure the alligator clips are not in contact with the solutions or the water in the water bath.
11. Turn the dial on the multimeter to **DCV** 2 (approx.. the 10 o'clock position). Depending on the voltage you may need to adjust the dial.
12. The meter reading should be between ~ 0.9 V to ~1.2 V and should be positive.
13. Measure the initial temperature of the water bath and note down the voltage of the cell on Table 1. This is the room temperature (R.T.) reading.
14. Turn on the hot plate to about the middle heat setting.
15. You and your partner need to watch the cell potential and the temperature at all times. They will change slowly at first but then change more quickly as the bath heats up.
16. Begin recording temperature and voltage readings as you heat every 5°C between 30 °C and 65 °C on Data Table 1.
17. When the experiment is done. Turn off the hot plate and prepare the experiment again to do trial 2.

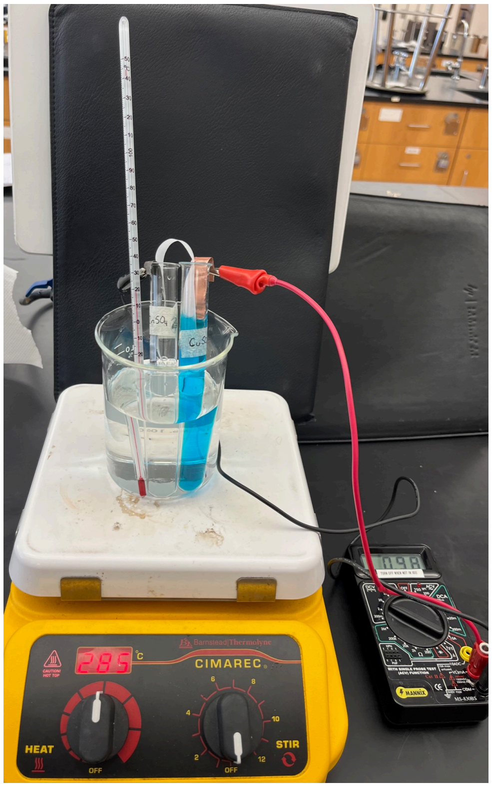


Figure 1: Experimental Setup

Data Table:

Table 1- Experimental Data for Heating the cell. (Trial 1 and Trial 2)

Temperature (^oC)	Temperature in Kelvin	Trial 1 Voltage (V)	Trial 2 Voltage (V)
Room Temperature (R.T.)			
30.0			
35.0			
40.0			
45.0			
Continue taking readings till 65 ^oC in 5 ^oC increments.			

Using excel plot a curve of E.M.F. (voltage) vs Temperature in Kelvin for each trial. Find the regression (R^2) and equation of the line. Calculate the ΔS from the slope and ΔH from the y-intercept using equation (4)

Post Lab Questions:

1. Calculate the ΔG at 50 ^oC for both trials in this experiment.

2. From the signs of Ecell, ΔG, ΔH and ΔS comment whether the reaction is spontaneous or not.

3. What is the maximum work done by the cell under standard conditions based on your data for Ecell at 313 K? (**Hint:** look at the first link for the equation)

4. The thermodynamic properties for the cell which we used in the lab is given below.

Species	**ΔHº (298 K), kJ/mol**	**Sº (298 K), J/mol.K**	**Δ Gº (298 K), kJ/mol**
Cu^{2+} (aq)	64.9	-98	65.5
Zn^{2+} (aq)	-153.39	-109.8	-147.1
Cu (s)	0	33.2	0
Zn (s)	0	41.6	0

Use the data to calculate the ΔGº, ΔHº and ΔSº for the reaction at 298 K

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

5. Compare your experimental ΔG values to the ΔGº value calculated above. What is the % difference? You may use the average ΔG values for both trials.

References: In addition to the above links, the following lab handout from the United States Naval Acadcemy was used as a reference.
https://www.usna.edu/ChemDept/_files/documents/151pdf/2017%20Labs/Exp%2042B%20thermo%20of%20echem%20cell%20FV%20f17.pdf