EXPERIMENT 8

STOICHIOMETRY- A SPECTROPHOTOMETRIC STUDY

Objectives:

The stoichiometry for the reaction between a metal cation and a ligand to form a coordination complex in solution will be determined. Spectrophotometry will be used to analyze the formation of the highly colored complex.

Background:

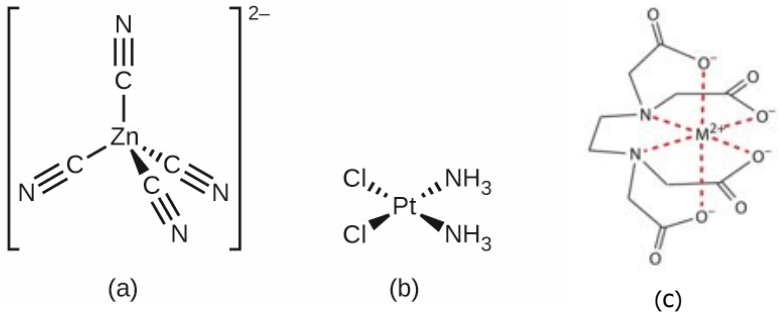
In a chemical reaction, reactants react in specific mole ratios. The mole ratio of the substances in the reaction is known as the **stoichiometry** of the reaction and is represented by the coefficients in the balanced chemical equation. For example, the stoichiometric ratio of the reactants A and B in the reaction shown below are represented by the mole ratios (a) 1:1 (b) 1:2 and (c) 1:3.

(a)	$A + B \rightarrow AB$	1 mole of reactant A reacts with 1 mole of reactant B
(b)	$A + 2B \rightarrow AB_2$	1 mole of reactant A reacts with 2 moles of reactant B
(c)	$A + 3B \rightarrow AB_3$	1 mole of reactant A reacts with 3 moles of reactant B

When the products of a reaction are known, the stoichiometry of the reaction can be determined by balancing the chemical equation. When the products of a reaction are not known the stoichiometry of the reaction must be determined experimentally.

In this experiment, the stoichiometry of the reaction between a metal cation and a ligand will be determined by finding the ratio of ligand molecules to metal atom. A **ligand** is a small ion or compound that acts as a Lewis base, donating two electrons to form a bond with the metal cation. If the reaction yields a solid product then a coordination compound has been formed. If the product of the reaction remains in solution the compound is a charged metal-organic **coordination complex** is known as a **complex ion**. The charge on the complex ion allows for high solubility in aqueous solutions and the intense color of the coordination complex in solution allows for the investigation of the stoichiometry using spectrophotometry. The general form of coordination complexes and complex ions are shown in Figure 1. Note that when a ligand has more than one sets of lone pair of electrons, two or more

bonds can be formed with the metal ion. This type of ligand is referred to as a **bidentate ligand** or a **chelating ligand** and the product is known as a **chelate**.



(a) (b) (c)

Figure 1. (a) The reaction between Zn^{2+} cation and four CN^- ligands forms the complex ion $[Zn(CN)_4]^{-2}$. The charged complex will remain in solution. (b) The coordination complex $PtCl_2(NH_3)_2$ will precipitate from solution as a neutral compound. (c) Chelate formed when six bonds are made between the ligand and metal cation.

During this experiment, copper (II) sulfate pentahydrate is dissolved in water to produce the metal cation reactant, Cu^{2+}. The copper cation is then reacted with a ligand solution to produce a coordination complex in the form of a complex ion as shown below.

$$Cu^{2+}_{(aq)} + n\ Ligand_{(aq)} \rightarrow [Cu(Ligand)_n]^{2+}_{(aq)} \qquad \text{Equation 1}$$

Students will be assigned one of two ligands, ethylenediamine (EDA) or tetraethylenepentamine (TEPA) to investigate the stoichiometry of the reactants. Results of the experiment will determine the number of ligand molecules, n, bound to Cu^{2+}.

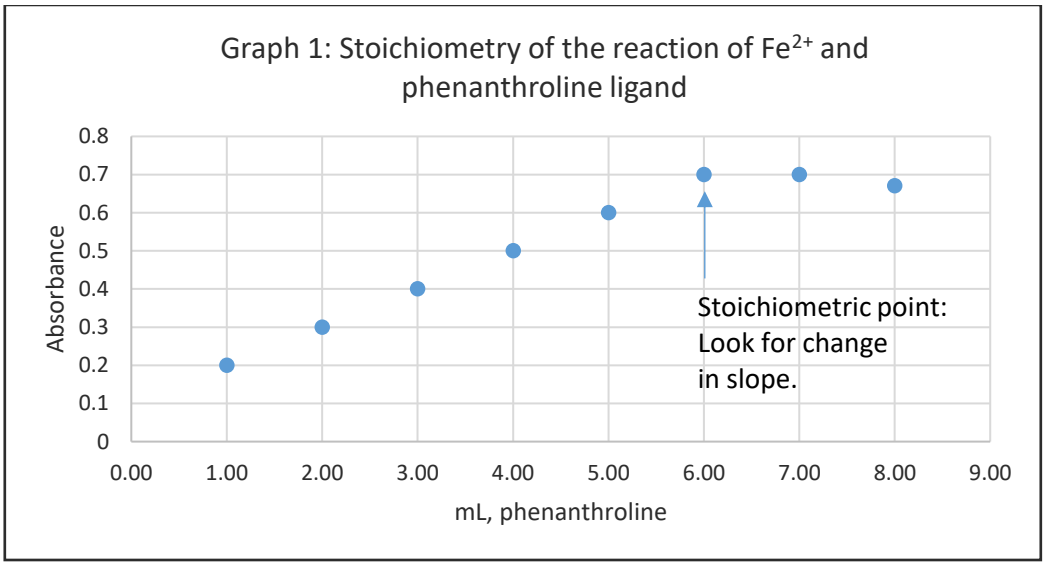
$CuSO_4.5H_2O$ ***Copper sulfate pentahydrate*** Molar Mass = 249.69 g/mol	$NH_2\text{-}CH_2CH_2\text{-}NH_2$ ***Ethylenediamine (EDA)*** $C_2H_8N_2$ Molar Mass = 60.10 g/mol	$NH_2\text{-}(CH_2CH_2NH)_3\text{-}CH_2CH_2\text{-}NH_2$ ***Tetraethylenepentamine (TEPA)*** $C_8H_{23}N_5$ Molar Mass = 189.30 g/mol

Reactant stoichiometry will be determined by running a series of trials using 5 mL of the copper (II) sulfate pentahydrate solution and varying volume of the ligand solution. The complex produces highly colored solutions therefore spectrophotometry can be used to monitor its concentration. As the concentration of the complex increases the absorbance of the solution will increase proportionally as described by the **Beer-Lambert Law,** Equation 2.

$A = \varepsilon bc$ Equation 2

A=absorbance
ε = molar absorptivity, liter/(mole cm) (characteristic of the analyte)
b = path length, cm (distance through the substance)
c = concentration, mole/liter

A plot of absorbance verses volume of ligand solution, similar to Graph 1, will be constructed to determine the maximum amount of ligand needed to react with a fixed amount of metal cation. Graph 1 shows the formation of an iron (II)-phenanthroline complex ion. The stoichiometric point was determined by locating the point on the plot where the absorbance stopped increasing. In this case, after 6.00 mL of the ligand solution was added to 5.00 mL of an Fe^{2+} solution. A ratio of three phenanthroline ligands to one Fe^{2+} cation was calculated by comparing the number of moles phenanthroline in 6.00 mL ligand solution to the number of moles of Fe^{2+} in 5.00 mL of the cation solution. The 3:1 ratio (or 3 moles ligand / 1 mole metal cation) represents the complex ion $[Fe(phen)_3]^{2+}$.



Tasks to be completed:

1. Prepare 100.00 mL of a copper (II) sulfate pentahydrate solution.
2. Prepare nine complex ion solutions containing 5.00 mL copper (II) sulfate pentahydrate solution and varying volume of ligand solution.
3. Measure absorbance of all nine solutions using a Spectro-Vis Spectrophotometer.
4. A plot in Excel will be created to determine the stoichiometry of the reaction by analyzing the mole ratio of reactants in the product (coordination complex).

Experimental Procedure: To be completed in groups of two students.

One partner will prepare the copper sulfate pentahydrate solution, the other partner will prepare the buret with the supplied ligand solution. Partners will work together to prepare and analyze the complex ion reaction solutions.

I. Preparation of Copper (II) Sulfate Pentahydrate Solution

1. Record Assigned ligand on the Data Sheet.

2. Carefully mass the appropriate amount of copper (II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) as shown in the table below into a weigh dish. Be as accurate as possible. Record the mass on the Data Sheet.

Assigned Ligand	Approximate mass of $CuSO_4 \cdot 5H_2O$
Ethylenediamine (EDA)	0.44 grams
Tetraethylenepentamine (TEPA)	0.20 grams

3. Using a glass funnel, transfer the copper (II) sulfate pentahydrate to a 100 mL volumetric flask. Use deionized water in a wash bottle to rinse the inside of the weigh dish into the flask to completely transfer all massed material. **100% transfer copper salt from the weigh dish to the volumetric flask is REQUIRED**.

4. Remove the funnel and fill the volumetric flask to about half the volume with deionized. Swirl the solution gently to dissolve the salt. When there is no sign of solid particles in solution, add additional deionized water to the calibration mark using a medicine dropper near the end to avoid over filling. Be very careful not to add water past the calibration mark or the solution should be re-made.

5. To mix, place a cap on the volumetric flask, invert flask, holding the cap tightly, and shake gently. Re-invert and shake gently again. Repeat this procedure at least 10 times until a homogeneous solution is achieved.

6. Prepare a buret with the copper (II) sulfate pentahydrate solution.

   a. Transfer a portion of the newly prepared copper (II) sulfate pentahydrate solution into a 100 mL beaker. Make sure the stopcock is closed and add about 5 mL of the solution to a buret. Hold the buret horizontally and turn to completely coat the inside of the buret. Drain the rinse into a waste beaker.

   b. Close the stopcock and fill the buret with the copper (II) sulfate pentahydrate solution above the 10.00 mL marking using a supplied plastic funnel. Open the stopcock briefly to allow the solution to rapidly run through the stopcock region to eliminate air trapped in the stopcock and stem. **Re-fill the buret to begin at 0.00 mL**.

II. Preparation of Ligand Solution

1. Prepare a buret with the ligand solution. *Students should wear gloves while working with the ligand solution.*

   a. In a clean, dry 50 mL beaker obtain 40 mL of your assigned ligand solution. Record the molarity of the solution.

   b. Rinse and fill a second buret with the ligand solution. Remember to drain the rinse into a waste beaker. Re-fill the buret to the 20.00 mL marking.

III. Preparation of Complex-ion Solutions

Following the table found on page 8-9 prepare the nine trial solutions.

Ethylenediamine (EDA) ligand	Tetraethylenepentamine (TEPA) ligand
a. For each trial, dispense 5.00 mL of copper (II) sulfate pentahydrate solution into a clean, dry test tube. b. Add the required amount of EDA ligand solution. c. Continue sample preparation until all 9 solutions are prepared. d. Cover the test tube opening with Parafilm and mix by placing a thumb over the Parafilm cap and inverting 10 times e. Allow the solutions to rest for 10 minutes to complete the formation of the complex ion.	a. For each trial, dispense 5 drops of buffer solution into a clean dry test tube. b. Dispense 5.00 mL of copper (II) sulfate pentahydrate solution into the test tube. c. Add the required amount of TEPA ligand solution. d. Continue sample preparation until all 9 solutions are prepared. e. Cover the test tube opening with Parafilm and mix by placing a thumb over the Parafilm cap and inverting 10 times. f. Allow the solutions to rest for 10 minutes to complete the formation of the complex ion.

IV. Analyze solutions using Spectrophotometry:

1. Obtain the SpectroVis spectrophotometer and connect it to a computer equipped with LoggerPro software. Open LoggerPro.

2. Blank the spectrophotometer by filling an empty cuvet ¾ full with deionized water. Verify that the cuvet is free of fingerprints, scratches, and air bubbles. Dry the outside of the cuvet.
   a. Open the *Experiment* menu and select *Calibrate → (Spectrometer*). The following message appears in the Calibrate dialog box: "*Waiting … seconds for the device to warm up*." After 60 seconds, the message changes to: "*Warmup complete*."

   b. Place the blank in the cuvet holder of the spectrophotometer. If using a cuvet with frosted sides, align the cuvet so that the clear sides are in line with the light source of the spectrophotometer. Click "*Finish Calibration*", and then click OK.

3. Collect absorbance spectra for each complex-ion solution.
   a. Using the same cuvet, empty the water and rinse with a small portion of Trial 1 solution. Empty the rinse into a waste beaker. Refill the cuvet ¾ full with Trial 1 solution and dry the outside of the cuvet. Place it in the spectrophotometer. Select Collect to obtain an absorption spectrum of the solution. After the spectrum appears select Stop. To save the spectrum, open the *Experiment* menu and select "*Store Latest Run*".

   b. Empty the cuvet into a waste beaker. Rinse the cuvet with deionized water from a wash bottle then a small portion of solution from Trial 2. Refill the cuvet ¾ full with Trial 2 solution and collect an absorbance spectrum, remembering to dry the outside of the cuvet before placing it back into the spectrophotometer. Save the spectrum by opening the *Experiment* menu and selecting "*Store Latest Run*". Repeat these steps for the remaining Trial solutions.

   c. Once all solutions have been analyzed, scroll through the absorbance data and record the absorbance reading for each solution for the wavelength representing the complex ion, see table below. This may not be the wavelength of maximum absorbance.

Assigned Ligand	Analysis wavelength
Cu^{2+}-EDA complex ion	555 nm
Cu^{2+}-TEPA complex ion	620 nm

   d. Enter an appropriate title for the plot of the spectra by right clicking on the graph and selecting *Graph Options*. Enter the title in the appropriate box- don't forget to include the name of the metal cation and ligand use to form the complex ion! Orient the graph by selecting *File → Page Setup* and select landscape orientation.

2. Submit the LoggerPro graph for grading.
   a. Screenshot the LoggerPro plot and paste it into the Word. OR
   b. If the screenshot is saved as a .pdf or .jpg file, this can be directly uploaded for grading.

Waste Handling and Clean Up:

- Dispose of all liquid and solid waste in the appropriately-marked waste container.
- Dispose of emptied cuvets in the trash receptacle.
- Wash the 100 mL volumetric flask and cap with soap and water followed by deionized water rinse. Leave cap off to dry.
- Empty test tubes into a waste beaker and rinse with a small portion of water from a wash bottle. Empty beaker in waste.
- Rinse buret with deionized water and dry outside. Wash plastic funnels and caps with soapy water followed by a deionized water rinse.
- Unplug cord from the Vernier spectrophotometer and leave at the bench.
- Verify that balances and area around balances are clean and that balance doors are shut. Zero balance.
- Wipe down benchtop area, including sink area, with a damp sponge.

Data Analysis:

Create an Excel plot to determine the volume of ligand needed to reach the stoichiometric point.

1. Open an Excel worksheet.
2. In Column A enter volume of ligand in mL. Enter values only, DO NOT include units. In Column B enter the absorbance values.
3. Create a scatter plot by highlight data in both Columns A and B. From the top menu, choose Insert, Scatter plot with markers only.
4. To add Titles and Axis Labels: From the top menu, under Chart Tools choose the Layout tab. Alternatively, click on Add Chart Element. Select Chart Title and chose a location for the title. Enter an appropriate title. (Remember- DO NOT restate the axis label as an appropriate title!). Select Axis Titles to enter axis labels. Do not forget to include units.
5. Select Legend and choose none.
6. Determine the volume of ligand at the stoichiometric point. This is the point where there is a distinct change in slope of the plotted points occur. Refer to Graph 1 on page 8-3 to help identify the stoichiometric point. Record the volume of ligand on the data sheet.
7. MARK the stoichiometric point on the Excel graph then submit for on-line for grading.
   a. Each student MUST submit their own graphs for credit.

Determine the stoichiometry of the reaction.

1. Calculate the molarity of the prepared 100.00 mL copper (II) sulfate pentahydrate solution.

$$Molarity, CuSO_4 \cdot 5H_2O = \left(\frac{mass\ CuSO_4 \cdot 5H_2O, g}{molar\ mass\ CuSO_4 \cdot 5H_2O, g/mol}\right)\left(\frac{1}{100.00\ mL}\right)\left(\frac{1000\ mL}{1\ L}\right)$$

2. Calculate the number of moles of Cu^{2+} ion in 5.00 mL of the copper (II) sulfate pentahydrate solution.

$$mol\ Cu^{2+} = \left(Molarity\ CuSO_4 \cdot 5H_2O, \frac{mol}{L}\right)\left(\frac{5.00\ mL}{1}\right)\left(\frac{1\ L}{1000\ mL}\right)\left(\frac{1\ mol\ Cu^{2+}}{1\ mol\ CuSO_4 \cdot 5H_2O}\right)$$

3. Calculate the number of moles of ligand (EDA or TEPA) at the stoichiometric point. **NOTE:** The *volume of ligand solution* needed to reach the stoichiometric point was determined from results of the Excel plot.

$$mol\ ligand = (Volume\ of\ ligand\ solution, mL)\left(\frac{1\ L}{1000\ mL}\right)\left(Molarity\ ligand\ solution, \frac{mol}{L}\right)$$

4. Determine the mole ratio of reactants.

$$\left(\frac{mol\ ligand}{mol\ Cu^{2+}}\right) = mol\ ratio = n\ in\ complex\ ion\ formula$$

Round the mole ratio to a whole number. This ratio represents n, the number of ligands bound to the Cu^{2+} metal center in the coordination complex.

5. Write the formula for the coordination complex ion.

Using the mole ratio, write the formula for the product coordination complex. The formula should be written where n is the mole ratio.

$[Cu(ligand)_n]^{2+}$

Data Sheet Name:_____

Date: _____ CHM123L section ____ Instructor_____

Partner _____

Mass of copper (II) sulfate pentahydrate _____

Assigned ligand (circle one) : **Ethylenediamine (EDA)** or **Tetraethylenepentamine (TEPA)**

Molarity of assigned ligand solution (from bottle): _____

Wavelength at which absorbance values were evaluated _____

Trial #	Buffer, # drops **TEPA Ligand ONLY! Not used with EDA ligand!**	Volume $CuSO_4$ solution, mL	Volume Ligand solution, mL	Absorbance
1	5	5.00	1.00	
2	5	5.00	1.50	
3	5	5.00	2.00	
4	5	5.00	2.50	
5	5	5.00	3.00	
6	5	5.00	3.50	
7	5	5.00	4.00	
8	5	5.00	4.50	
9	5	5.00	5.00	

Report Sheet Name:_____

Date: _____ CHM123L section ____ Instructor_____

Name of assigned Ligand: _____

Molarity of copper (II) sulfate pentahydrate solution	
Number of moles of Cu^{2+} in 5.00 mL of the copper (II) sulfate pentahydrate solution	
Volume of ligand at the stoichiometric point (From Excel plot)	
Number of moles of ligand at the stoichiometric point	
Mole ratio of reactants, n	
Formula of coordination complex	

Report Sheet (cont.)

Answer the questions fully.

1. Using the experimentally determined stoichiometry and the formula of the assigned ligand, write the *balanced reaction equation* for the formation of the complex ion. See Equation 1 for help.

2. Identify regions of absorbance and transmittance in terms of wavelength and associated colors in the absorbance spectrum of the product coordination complex. Does the visual color of the solution predict the absorbance spectrum?