Experiment 12: Reaction Stoichiometry and the Formation of a Metal Ion Complex
(This experiment was adapted from Santa Monica College, Chemistry 11 and from https://chem.libretexts.org/Ancillary_Materials/Laboratory_Experiments/Wet_Lab_Experiments/General_Chemistry_Labs/Online_Chemistry_Lab_Manual/Chem_11_Experiments/08%3A_Reaction_Stoichiometry_and_the_Formation_of_a_Metal_Ion_Complex_(Experiment).)

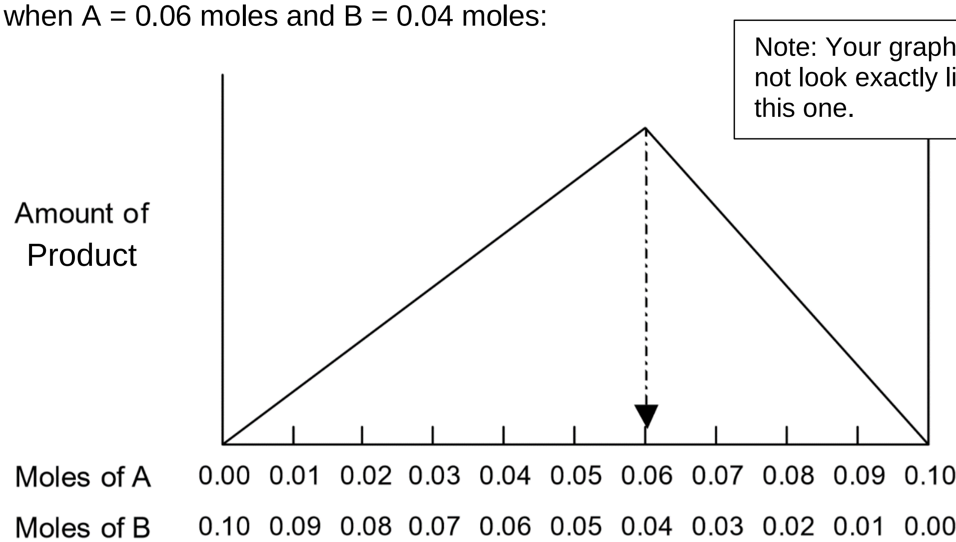
Purpose
To determine the reaction stoichiometry for the formation of a metal ion complex between iron(II) cations and 1,10-phenanthroline.

Background
The Method of Continuous Variation
Consider the study of a reaction where solutions of reactants A and B are mixed and product Q is formed:

$$x\,A + y\,B \rightarrow z\,Q$$

The reactant mixtures are carefully chosen so that sum of the moles of A and B are constant, and the amount of product that forms for each mixture is measured. This is known as the method of continuous variation. If either A or B is in excess, the excess will remain in solution rather than be used to form product. The maximum amount of Q is formed when A and B are mixed in the correct stoichiometric amounts, when there is just enough of each to react with nothing left over.

Suppose for example that x = 3 and y = 2, and that total number of moles of A and B is kept fixed at 0.10 moles. The amount of product formed will be at a maximum when the ratio A:B is 3:2, that is when A = 0.06 moles and B = 0.04 moles:

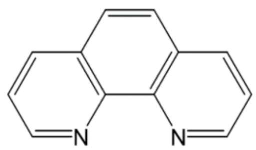


Note that to the left of the maximum on the plot (A<0.06 moles), there is not enough of A to react with all the B present. Thus, less than the maximum amount of product will be generated. To the right of the maximum (B<0.04 moles), there is not enough of B to react with all the A present. So once again, less than the maximum amount of product will be generated. As long as the total amount of A+B is constant, the maximum amount of product forms when the A:B ratio is the stoichiometric ratio for that reaction.

The reaction to be studied in this lab involves the formation of a metal ion complex. Metal ions, especially transition metal ions, possess the ability to form complexes with both organic and inorganic molecules called ligands. Here, iron(II) cations will be mixed with the ligand 1,10-phenanthroline to produce an iron(II)-phenanthroline complex:

$$m\ Fe^{2+} + n\ phen \longrightarrow Fe_m(phen)_n^{\ 2+}$$

Where phen is an abbreviation for 1,10-phenanthroline shown below:



Using the method of continuous variation as outlined earlier, several reactant solutions are prepared in which the mole quantities of the metal ion and the ligand are varied but the sum of the mole quantities is kept constant. The amount of complex produced will be measured, the maximum indicating when the correct stoichiometric ratio of Fe^{2+}:phen is used. (You will be determining the m and n in $Fe_m(phen)_n^{\ 2+}$)

In this experiment, both the Fe^{2+} and phenanthroline solutions will have the same molarity concentration. Mixtures prepared with the same total number of moles will therefore have the same total volume (recall that moles = M x L). As an additional consequence, in each prepared mixture the volume ratio of reactants used will be identical to the mole ratio of reactants used. Therefore, it will be more convenient to analyze the amount of complex product formed as a function of reactant volumes, rather than as a function of reactant moles.

The spectrophotometer will be used to measure the amount of complex formed, since the complex is a red-orange color. You will need to determine the wavelength that has the maximum absorbance of light for this complex ion, then you will be able to do the stoichiometry part of the experiment. Since the iron(II)-phenanthroline complex is a red-orange color, it is expected to absorb blue-green wavelengths, between 460 and 550 nm.

Chemicals
2.5×10^{-4} M Fe^{2+} solution ($FeSO_4$ and hydroxylamine hydrochloride)
2.5×10^{-4} M 1,10-phenanthroline solution
Deionized water

Equipment
50-mL buret, buret stand with buret clamp
spectrophotometer
Parafilm
13 small test tubes
Beakers, small
plastic droppers

Procedure

Part A: Determining λ_{max} for the Complex

1. Fill one test tube approximately 2/3 full with equal amounts of DI water and phenanthroline. This solution will be used as your calibration blank. Plastic droppers are fine for measuring the approximate volumes of each. Fill a second test tube approximately 2/3 full with a mixture of equal volumes of Fe^{+2} and phenanthroline. Since this mixture will be used to find the λ_{max}, it does not have to be prepared with exact measurements. You can use plastic droppers to approximate the volumes of each solution used. Let this solution sit for approximately 10 minutes, to allow for color development.
2. Adjust the absorbance reading on the spectrophotometer to zero using the blank. Then measure the absorbance by the complex ion solution between 480 nm and 530 nm at 10 nm intervals. Note that each time the wavelength is changed the instrument must be recalibrated to zero with the blank. Record this data in your notebook worksheet and identify the wavelength of maximum absorbance of the complex (λ_{max}).
3. Save your blank for the next part of the experiment. Dispose of this complex ion mixture after you have identified λ_{max}.

Part B: Preparing Mixtures of Reactant Solutions

1. Obtain approximately 40 mL of Fe^{2+} stock solution. Rinse a buret with DI water. Then, rinse it three times, each with 2 mL of Fe^{2+} solution. Then add the remaining iron solution to your buret. Use your buret to add the Fe^{2+} solution to each of the 11 test tubes. The volume of the Fe^{2+} solution for each tube is:

Test Tube #	**mL Fe^{2+}**		**Test Tube #**	**mL Fe^{2+}**
1	4.50		7	1.50
2	4.00		8	1.00
3	3.50		9	0.75
4	3.00		10	0.50
5	2.50		11	0.25
6	2.00			

2. Obtain approximately 40 mL of phenanthroline solution. Drain your buret, and then rinse it with DI water. Then, rinse it three times, each with 2 mL of phenanthroline solution. Then add the remaining phenanthroline solution to your buret. Use your buret to add the phenanthroline solution to each of the 11 test tubes. The volume of the phenanthroline solution for each tube is:

Test Tube #	**mL Phen**		**Test Tube #**	**mL Phen**
1	0.50		7	3.50
2	1.00		8	4.00
3	1.50		9	4.25
4	2.00		10	4.50
5	2.50		11	4.75
6	3.00			

3. Mix each solution well by covering the tube with Parafilm and inverting it

many times. The red-orange color of the iron(II)-phenanthroline complex should be fully developed after ten minutes. While you are waiting for the color to develop, rinse your buret with 10 mL DI water, four times. Let the DI water run through the tip of the buret. **Do not let your iron(II)-phen solutions sit for more than 15 minutes.**

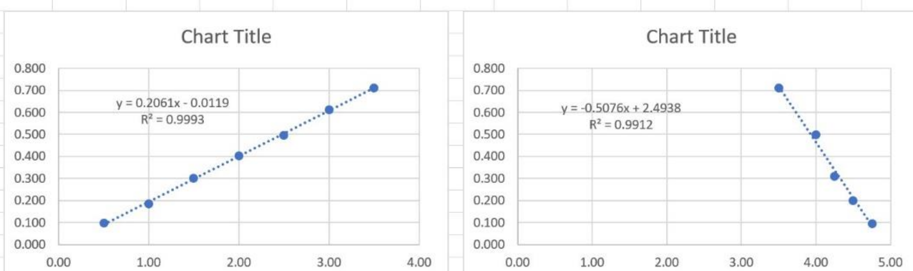
4. Set the wavelength of the spectrophotometer to λ_{max} and again recalibrate it to zero using the blank. Since all remaining measurements will be taken at this wavelength, no further recalibration is required.
5. Measure the absorbance of each of the eleven prepared mixtures. Record this data in your notebook.
6. When completely finished, dispose of your waste in the designated waste bottle.

Part C: Data Analysis

1. Using Microsoft Excel or Google Sheets, graph your absorbance vs. volume of phenanthroline used. Treat ascending and descending values as two separate data sets, which will give you two separate graphs in the same file.
2. Add a best-fit trendline to each graph, and obtain the equations of these lines.
3. Solve for the optimum volumes, (the point of intersection of these lines) using your two equations, with the method of simultaneous equations.
4. From the point of intersection, you can determine the volume of reactants that yields the maximum absorbance (hence the maximum amount of complex formed). Remember, since the concentrations of the reactant solutions are equal, the volume ratio is equal to the mole ratio.
5. Use this volume ratio to determine the simplest whole number ratio of Fe^{+2}:Phen , which is the stoichiometric ratio for this reaction.

Example Calculation:

Vol Phen	Absorbance
0.50	0.097
1.00	0.185
1.50	0.301
2.00	0.403
2.50	0.496
3.00	0.611
3.50	0.710
4.00	0.497
4.25	0.310
4.50	0.199
4.75	0.094



Use the method of simultaneous equations to solve for x. That will give the volume of phenanthroline that will produce the maximum amount of product.

Example Calculation
The total volume in each test tube was 5 mL.

Y = 0.2061 x – 0.0119 Y = -0.5076 x + 2.4938

0.2061 x – 0.0119 = -0.5076 x + 2.4938

Now solve for x:

0.2061 x – 0.0119 = -0.5076 x + 2.4938

0.7137 x = 2.5057 x = (2.5057 / 0.7137) = 3.511

x = 3.511 mL optimum volume of phen = 3.511 mL

optimum volume of Fe^{2+} = 5.00 mL – 3.51 mL = 1.49 mL

The mole ratio (same as volume ratio) determined by this calculation is:

$Fe^{2+}_{1.49}$: $Phen_{3.51}$ now get whole-number subscripts $Fe^{2+}_{\frac{1.49}{1.49}}$: $Phen_{\frac{3.51}{1.49}}$

Round off to whole numbers (3.51 / 1.49 = 2.36, round to 2)

Fe^{2+}_{1} : $Phen_{2}$