Experiments

EXPERIMENT 4
Graphical Investigation of Reaction Stoichiometry

4.1. Safety

Copper sulfate pentahydrate is harmful if swallowed and can cause irritation to skin, eyes and respiratory tract. At high concentrations, this compound can affect the liver and kidneys. Methanol is flammable and should be heated with care. Bunsen burners, hot glassware, and metal ring stands can cause painful and serious burns to skin.

Before Laboratory Questions

These questions should be used to help you write your notebook and should be answered in some form before you go to the laboratory.

(1) What is the purpose of this experiment?
(2) How do you plan to determine the stoichiometry of the reaction based on the metal assigned (i.e., iron, zinc, or aluminum)?
(3) What materials are required for this experiment? Are any chemicals needed? Which materials must be obtained from the stockroom, which must be obtained from the instructor, and which are in your laboratory drawer?
(4) What are the steps for this experiment?
(5) Create a table that will allow you to input the following information for the samples.
   - mass of the metal used
   - moles* of the metal used
   - volume of the copper solution added
   - concentration of the copper solution
   - mass of copper generated
   - moles* of copper generated
   - person performing experiment

   *These values must be calculated. The details of the calculations should be shown in your notebook for you to receive credit.

4.2. Introduction

In this experiment, we will investigate reaction stoichiometry graphically. The copper ion exists in a +1 or +2 oxidation state in aqueous solutions (i.e., the solvent is water). Similarly, in aqueous solution, the iron ion exists in a +2 or +3 oxidation state, while the zinc ion exists predominately in the +2 oxidation state and the aluminum ion exists in the +3 oxidation state. (The zinc(I) ion can exist in exotic solids, but is rarely observed in solution since it is readily oxidized to give zinc(II) ions.) Thus, the possible reactions that can occur between solid iron and aqueous copper(I) are

$$\mathrm{Fe}\,(s) \;+\; 2\,\mathrm{Cu}^{+}\,(aq) \;\rightarrow\; \mathrm{Fe}^{2+}\,(aq) \;+\; 2\,\mathrm{Cu}\,(s) \tag{4.1}$$

and

$$\mathrm{Fe}\,(s) \;+\; 3\,\mathrm{Cu}^{+}\,(aq) \;\rightarrow\; \mathrm{Fe}^{3+}\,(aq) \;+\; 3\,\mathrm{Cu}\,(s)\;, \tag{4.2}$$

while those between solid iron and aqueous copper(II) are

$$\mathrm{Fe}\,(s) \;+\; \mathrm{Cu}^{2+}\,(aq) \;\rightarrow\; \mathrm{Fe}^{2+}\,(aq) \;+\; \mathrm{Cu}\,(s) \tag{4.3}$$

and

$$2\,\mathrm{Fe}\,(s) \;+\; 3\,\mathrm{Cu}^{2+}\,(aq) \;\rightarrow\; 2\,\mathrm{Fe}^{3+}\,(aq) \;+\; 3\,\mathrm{Cu}\,(s)\;. \tag{4.4}$$

Similarly the reactions between solid zinc and aqueous copper ions are

$$\mathrm{Zn}\,(s) \;+\; 2\,\mathrm{Cu}^{+}\,(aq) \;\rightarrow\; \mathrm{Zn}^{2+}\,(aq) \;+\; 2\,\mathrm{Cu}\,(s) \tag{4.5}$$

and

$$\mathrm{Zn}\,(s) \;+\; \mathrm{Cu}^{2+}\,(aq) \;\rightarrow\; \mathrm{Zn}^{2+}\,(aq) \;+\; \mathrm{Cu}\,(s)\;; \tag{4.6}$$

while those between solid aluminum and aqueous copper ions are

$$\mathrm{Al}\,(s) \;+\; 3\,\mathrm{Cu}^{+}\,(aq) \;\rightarrow\; \mathrm{Al}^{3+}\,(aq) \;+\; 3\,\mathrm{Cu}\,(s) \tag{4.7}$$

and

$$2\,\mathrm{Al}\,(s) \;+\; 3\,\mathrm{Cu}^{2+}\,(aq) \;\rightarrow\; 2\,\mathrm{Al}^{3+}\,(aq) \;+\; 3\,\mathrm{Cu}\,(s)\;; \tag{4.8}$$

We will probe reaction stoichiometry by reacting various masses of a solid metal (either iron, zinc, or aluminum) with a solution of copper ions (assuming the the copper ions are in excess). We will then use a graphical analysis to determine which of the above equations is appropriate for the reactions being performed. Experiment 5 will study oxidation/reducation reactions in more detail.

4.3. Chemical equations

Eqs. (4.1) − (4.6) represent chemical equations which use chemical formulas to describe a chemical reaction. For example, eq. (4.1) states that 1 mole of solid iron will react with 2 moles of aqueous copper(I) ions to yield 2 moles of solid copper and 1 mole of ferrous ion. The right arrow is the symbol defined to mean *reacts to yield*. Any chemical formula written to the left of the right arrow is called a *reactant*. Any chemical formula written to the right of the right arrow is called a *product*. The physical state of each species should be given in any complete chemical equation, since the physical state can change the thermodynamics of the reaction. Mass and charge conservation are achieved by placing numbers in front of the chemical formulas. The chemical equation is said to be *balanced* when both the mass and the charge are conserved (i.e., the mass and charge of the reactants equals the mass and charge of the products). **A chemical equation must be balanced to be used for stoichiometric calculations.**

4.3.1. Using chemical equations

Chemical equations are important, since these equations give the mole ratios necessary to perform stoichiometric calculations. For example, with a balanced chemical equation, we can predict the amount of product we should obtain from a given chemical reactant. This amount is known as the *theoretical yield* of a product. The first step in calculating the theoretical yield is to determine which of the reactants is the *limiting reactant*, or the reactant that will be consumed completely during the reaction. The limiting reactant is found by

(1) Determining the molar ratio of one reactant to another reactant using the balanced chemical equation.
(2) Determining the number of moles of each reactant experimentally available using molar masses.
(3) Determine the same molar ratio in (1) using the experimental moles in (2).
(4) If the value in (3) is greater than the value in (1), then the denominator is limiting. If the value in (3) is equal to the value in (1), then neither reactant is limiting. If the value in (3) is less than the value in (1), then the numerator is limiting.

Once the limiting reactant is known, then this reactant is used to calculate all stoichiometric quantities.

For example, if we wanted to determine the theoretical yield of solid copper obtained from the reaction of 0.855 g of Zn (s) with 1.352 g of $CuSO_4$ (aq) (which acts as the source of cuprous ions), we first use eq. (4.6) to determine the molar ratio of Zn (s) to $CuSO_4$ (aq). From eq. (4.6), we have

$$\frac{n(\mathrm{Zn}, s)}{n(\mathrm{CuSO_4}, aq)} = \frac{1 \text{ mol Zn}}{1 \text{ mol CuSO}_4} = 1 \text{ mol Zn (mol}^{-1} \text{ CuSO}_4) \tag{4.9}$$

Now, we convert both masses to moles using the molar mass of the chemicals (i.e., Step 2). Since the molar mass of Zn is 65.384 g/mol, we obtain a starting molar amount n_{Zn} of

$$n_{\mathrm{Zn}} \;=\; 0.855 \text{ g Zn} \left(\frac{1 \text{ mol Zn}}{65.384 \text{ g Zn}}\right) \;=\; 0.0130\overline{8} \text{ mol Zn} .$$

Similarly, the molar mass of $CuSO_4$ is 159.607 g/mol. Thus, the molar amount n_{CS} of the $CuSO_4$ reactant is

$$n_{\mathrm{CS}} \;=\; 1.352 \text{ g CuSO}_4 \left(\frac{1 \text{ mol CuSO}_4}{159.607 \text{ g CuSO}_4}\right) \;=\; 8.471 \times 10^{-3} \text{ mol CuSO}_4 .$$

Thus, from the experimental masses we obtain a zinc to copper sulfate molar ratio of

$$\frac{n_{Zn}}{n_{CS}} = \frac{1.30\overline{8} \times 10^{-2} \text{ mol Zn}}{8.471 \times 10^{-4} \text{ mol CuSO}_4} = 1.54 \text{ mol Zn(mol}^{-1} \text{ CuSO}_4) . \tag{4.10}$$

Since the molar ratio in eq. (4.10) is greater than that in eq. (4.9), $CuSO_4$ is the limiting reactant. Finally, the mass m_{Cu} of solid copper expected from this reaction can now be calculated by converting the moles of copper sulfate (the limiting reactant) to moles of copper and then using the molar mass of copper to proceed from the moles of copper to the mass of copper.. Thus,

$$m_{\mathrm{Cu}} \;=\; 8.471 \times 10^{-3} \text{ mol CuSO}_4 \left(\frac{1 \text{ mol Cu}}{1 \text{ mol CuSO}_4}\right)\left(\frac{63.546 \text{ g Cu}}{1 \text{ mol Cu}}\right) \;=\; 0.5382 \text{ g Cu} .$$

Since $CuSO_4$ is limiting in this instance, no copper sulfate remains after the reaction. However, Zn (s) is in excess and, therefore, will still be present after the reaction is complete. The mass of Zn (s) remaining can also be determined by determining the mass of Zn (s) used during the reaction. This mass is determined by starting with the moles of the limiting reagent $CuSO_4$, using the reaction equation [i.e., eq. (4.6)] to go from moles of $CuSO_4$ to moles of Zn, and then using the molar mass of Zn (s) to obtain the mass of Zn reacted. Subtracting this mass from the initial mass of Zn yields the amount of unreacted Zn. We will leave this calculation for you to perform. (The answer is 0.554 g of Zn (s) reacted and, therefore, 0.301 g of Zn (s) remaining.)

4.4. Calculations Involving Concentration

Most chemical reactions do not occur between chemicals in the solid phase. Mobility is required, so reactions are often performed with one or both chemicals dissolved in a solvent. A solution is a homogeneous mixture of two or more molecules or ions with one of the molecules (or ions) being the solvent and all others being the solutes. Solutes are dissolved into the solvent. However, before we can begin to study solution chemistry, an understanding of concentration must first be developed. Concentration is the ratio of amount of *solute* to the amount of *solvent* or *solution*. In Experiment 2, you measured the density of alcohol/water solutions and plotted these data as a function of *percent concentration* by volume of alcohol. However, percent concentration is not the most useful measure of concentration when working with chemical reactions. *Molar concentration*, or ***molarity*** M, of a solution is defined as the number of moles of the solute per liter of solution, and is the most widely used measure of concentration. Below, we have shown two examples that illustrate how molarity is calculated and how molarity is used in solution chemistry.

4.4.1. Calculation of molarity

If 8.5 grams of ammonia (having a molar mass of 17.031 g/mole) is dissolved in water to a final volume of 500 mL (3 significant figures), the molarity would be determined by first calculating the number of moles of NH_3 in solution and by then dividing the number of moles by the total volume of the solution. In other words,

$$\text{moles NH}_3 \;=\; 8.5 \text{ g NH}_3 \left(\frac{1 \text{ mol NH}_3}{17.031 \text{ g NH}_3}\right) \;=\; 0.49\overline{9} \text{ mol NH}_3$$

$$\text{molarity NH}_3 \;=\; \frac{0.49\overline{9} \text{ mol NH}_3}{500 \text{ mL}} \left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) \;=\; 1.0 \text{ mol NH}_3/\text{L} = 1.0 \text{ M}$$

Note that the answer is written (correctly) to indicate 2 significant figures.

4.4.2. Molarity in solution chemistry

If you wanted to make 750 mL (3 significant figures) of a 0.200 M aqueous solution of sodium chloride, one would calculate the number of grams of solid sodium chloride by the following steps:

(1) Determine the number of moles of NaCl needed to prepare the solution.
(2) Determine the molar mass of NaCl.
(3) Multiply the number of moles of NaCl needed by the molar mass of NaCl to obtain the grams of NaCl required.

These steps are illustrated below.

$$\begin{aligned}
\text{moles NaCl} &= 750 \text{ mL solution} \left(\frac{0.200\text{moles NaCl}}{1 \text{ L solution}}\right) \left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) \\
&= 0.150\overline{0} \text{ moles NaCl}
\end{aligned}$$

$$\begin{aligned}
\text{molar mass NaCl} &= 23.00 \text{ g/mol of Na} \left(\frac{1\text{mole Na}}{1\text{mole NaCl}}\right) \\
&\quad + 35.45 \text{ g/mol of Cl} \left(\frac{1\text{mole Cl}}{1\text{mole NaCl}}\right) \\
&= 58.45 \text{ g/mol NaCl}
\end{aligned}$$

$$\begin{aligned}
\text{grams NaCl} &= 0.150\overline{0} \text{ moles NaCl} \times 58.45 \text{ g/mol of NaCl} = 8.76\overline{7} \text{ g NaCl} \\
&= 8.77 \text{ g NaCl}
\end{aligned}$$

4.5. Experiment 4. Reaction of aqueous copper ions with elemental iron or zinc

Note that in this experiment your calculations will be based on both your data and the data of your assigned laboratory partners. The procedure for this study is as follows:

(1) During the pre-laboratory meeting, your laboratory instructor will assign laboratory partners and a set of masses for your group. You will also be assigned a metal (either iron, zinc, or aluminum) and a copper solution (E04A or EO4B). Place the correct amount of metal sample into a clean, dry 150 mL beaker.
(2) Add 30.0 mL of the aqueous copper solution (assume that the solution is 1.0 M in copper ions) to a clean, dry Erlenmeyer flask.
(3) Heat the copper solution to **almost** boiling and then slowly add this solution to the beaker containing the metal sample. (If the addition is performed too quickly, the solution will froth and material will be lost during the reaction.)
(4) When the reaction has ceased, allow the copper product to settle. Then carefully decant the liquid from above the product.
(5) Add approximately 10 mL of distilled water to the product and swirl the beaker to mix. Again, allow the product to settle and decant. This washes the product to remove trace amounts of aqueous metal cation. Repeat with a second 10 mL portion of distilled water.
(6) Add 5 mL of methanol and swirl. Allow the product to settle and decant. Repeat with a second 5 mL portion of methanol. Methanol is used here to remove any excess water because the vapor pressure of methanol is higher than that for water.
(7) Heat the beaker in a hot water bath (or on a hot plate) to remove any remaining methanol. If necessary, carefully break up any clumps of copper with the spatula tip. (Check the spatula to ensure that you are not removing any copper from the beaker.)
(8) When the product is thoroughly dry, weigh the product. Tell your laboratory partners the mass of the product generated.
(9) Transfer the product to the container provided by your laboratory instructor for use in Experiment 6.
(10) Repeat the experiment for the second mass.
(11) Before you leave the laboratory, be sure to copy all of the data from your laboratory partners. Do not forget to note which data comes from which partner.

Table 4.1: Table of critical values $Q_{90\%}$, $Q_{95\%}$, and $Q_{99\%}$ for Dixon's Q-test at 90%, 95% and 99% confidence levels, respectively, for a set of n quantities. Adapted from [2].

n	3	5	7	8	9	10	15	20
$Q_{90\%}$	0.941	0.642	0.507	0.468	0.437	0.412		
$Q_{95\%}$	0.970	0.710	0.568	0.526	0.493	0.466	0.384	0.342
$Q_{99\%}$	0.994	0.821	0.680	0.634	0.598	0.568		

4.6. Statistical analysis

Sometimes in a set of experimental data, measured quantities will be obtained that are numerically distant from the other data. Such a measured quantity is called an outlier and can sometimes be removed from the data set. The most common test to determine if a data point can be removed from the data set is the *Q-test*. (We should note that for a small data set ($\leq$ 10 points), the Q-test should only be used to test a single data point.) To apply a Q-test to a set of data [2]

(1) Arrange the data set in increasing order.
(2) Compute Q_{gap} by taking the absolute difference between the outlier in question and the closest data point.
(3) Compute Q_{range} by taking the difference between the largest measured quantity and the smallest measured quantity.
(4) Determine Q for the outlier using

$$Q = \frac{Q_{gap}}{Q_{range}} \ . \tag{4.11}$$

(5) For this experiment, you must be able to reject a data point with 95% confidence. Thus, you will be comparing to $Q_{95\%}$ for your tests.
(6) If $Q > Q_{95\%}$, then you can reject the data point and not include this point in the least squares analysis of the data.

4.7. References

1. J. E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 5th ed. (Wiley, New York, 2007).
2. G. D. Christian, *Analytical Chemistry*, 6th ed. (Wiley, New York, 2003).

After Laboratory Questions
These questions should be used to help you write your notebook and should be answered after the experiment is complete.

(1) Graph the mass of solid metal used as a function of the mass of copper generated. Tape a copy of this graph on both pages (original and duplicate) in your notebook. Perform a linear least square analysis on the data and record the regression equation using the correct units on all parameters (i.e., slope and intercept). Be sure to include the uncertainty in each parameter. If you have to throw out any data points, show how you verified that the point could be removed.
(2) Graph the moles of solid metal used as a function of the moles of copper generated. Tape a copy of this graph on both pages (original and duplicate) in your notebook. Perform a linear least square analysis on the data and record the regression equation using the correct units on all parameters (i.e., slope and intercept). Be sure to include the uncertainty in each parameter. If you have to throw out any data points, show how you verified that the point could be removed.
(3) For both graphs, explain what the slope indicates.
(4) Is the intercept zero (or close to zero) for each of the regression equations? Explain why or why not?
(5) Why is the slope different for the regression equation involving moles and that involving mass?
(6) From these results, which equation [i.e., eqs. (4.1) − (4.8)] represents the reaction that your group performed?

4.8. Reminders

Remember to get your results signed before leaving the laboratory and to submit your laboratory notebook pages. Remember to submit your remaining notebook pages for Experiment 3.

4.9. Project 4 Laboratory Report suggestions

Below are some suggestions for what should be included in each section of the laboratory report. Remember that a written document should flow. Therefore, do not write a sentence on each suggestion, since this will be penalized.

- Abstract
  - Describe the experiment.
  - Give the final results in words.
- Introduction
  - Explain the reactions using chemical equations in **proper format**.
  - Discuss the advantages and disadvantages of graphical analysis.
  - Discuss anything else that might be necessary to introduce the results that you observed.
- Experiment
  - Explain the experimental technique without copying from the manual.
- Results and discussion
  - Graphically present the data. (If you include the data in tabular format, points will be deducted from your laboratory report, as there is too much data to present in a table.)

- Explain each graph and discuss what the linear least squares analysis lets you conclude from each graph.
- Discuss the sources of uncertainty in each of the linear least squares analyses. If you removed a point from the data set, explain why and what could have led to the outlier point.

4.10. Practice problems

The problems below are excellent practice problems for the laboratory quiz and the laboratory practical. Since these problems will not be graded, the answers are given in Appendix I. With these as example problems, you can make-up additional problems by changing the volume and molarity of the copper solution, by changing from copper(II) to copper(I), by changing the mass of the metal, or by changing the metal (i.e., iron, aluminum, or zinc).

(1) If 1.321 grams of solid iron is reacted with 32.4 mL of 1.0 M aqueous copper(II) to generate iron(III) and solid copper, what is the limiting reactant?

(2) If 0.432 grams of solid aluminum is reacted with 35.3 mL of 1.50 M aqueous copper(I) to generate aluminum(III) and solid copper, how much copper was generate?

(3) If 1.85 grams of solid zinc is reacted with 36.3 mL of 0.550 M aqueous copper(II) to generate solid zinc, what is the total mass of the filtered and dried solid?