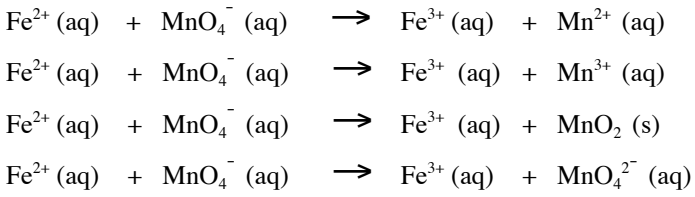
# Determination of the Stoichiometry of a Redox Reaction

## PRE-LAB ASSIGNMENT:

**Reading:** Section 4.4 – 4.6 and 20.1-20.2 in Brown, LeMay, Bursten, and Murphy.

1. Balance the following reactions: (getting these right will save you a lot of time later!)



$Fe^{2+}(aq) + MnO_4^-(aq) \rightarrow Fe^{3+}(aq) + Mn^{2+}(aq)$

$Fe^{2+}(aq) + MnO_4^-(aq) \rightarrow Fe^{3+}(aq) + Mn^{3+}(aq)$

$Fe^{2+}(aq) + MnO_4^-(aq) \rightarrow Fe^{3+}(aq) + MnO_2(s)$

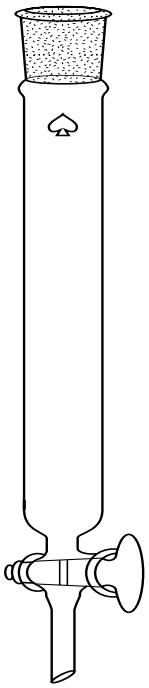
$Fe^{2+}(aq) + MnO_4^-(aq) \rightarrow Fe^{3+}(aq) + MnO_4^{2-}(aq)$

2. For lab this week you will need to prepare your own potassium permanganate solution (see Procedure, part A). How much $KMnO_4$ salt will you need to weigh in order to make a 0.01M $KMnO_4$ solution in a 250.0 mL volumetric flask? Show your work.

## INTRODUCTION

While expanding your experience with **titrations** and **redox reactions**, this experiment will allow you to use a titration to determine the stoichiometry of $Fe^{2+}$ reacting with potassium permanganate, $KMnO_4$. From the stoichiometry you will be able to determine the identities of the reaction products.

**Titration:** A titration is a process in which a solution of known concentration is mixed with a solution of unknown concentration and a specific chemical reaction between the two reactants is carried just to completion. If the balanced equation for the reaction is known, the concentration of the unknown reagent can be determined with excellent accuracy. The point at which the titration reaction is complete, with no excess of either reactant, is called the equivalence point. Effective titrations require accurate methods for measuring solution volumes, usually with a buret, and the "end point" of the reaction. The "end point" of the reaction is an observable change in a measurable quantity of the reaction solution, often a color change. The "end point" (observable change) should be very close to the equivalence point at which an exactly stoichiometric amount of the known reactant has been added.



In the following procedure we will use the deep purple color of the $KMnO_4$ to follow the progress of the reaction. When the permanganate ion reacts with $Fe^{2+}$ the products are colorless. Thus, as the $KMnO_4$ solution is added to carry out the reaction, the deep purple color is dissipated. However, as soon as the equivalence point is reached, excess purple $MnO_4^-$ ion accumulates in the reaction solution and can be visually detected. The color of $MnO_4^-$ ion is so intense that it can be seen at very low ($\sim 2 \times 10^{-6}$ M) concentration and our "end point" (appearance of purple color) is very close to the true equivalence point of the reaction.

**Redox Reactions:** Potassium permanganate, $KMnO_4$, is commonly used as an oxidizing agent for oxidation-reduction titrations. Its oxidizing properties also make $KMnO_4$ useful in medicine, for instance, as an antiseptic and an antidote for many poisons. In redox titrations, the very strong oxidation potential of $KMnO_4$ makes it useful for the determination of a wide variety of inorganic and organic species including Sn, Fe, V, Mo, W, U, Ti, $HNO_2$, and oxalic acid. The product of the reduction of $KMnO_4$ depends on the reaction conditions. In our reaction, the product formed from $Fe^{2+}(aq)$ is $Fe^{3+}(aq)$ and possible products from the $MnO_4^-$ ion are $Mn^{2+}(aq)$, $Mn^{3+}(aq)$, $MnO_2(s)$, or $MnO_4^{2-}$. The reaction product and the number of electrons gained by $KMnO_4$ must be known before using the reagent in analytical determinations. Thus, you will use your titration in a slightly different manner than that described above. You will have two solutions of known concentration and will start with an unknown reaction equation. As part of the pre-lab assignment, you will write balanced equations for all of the likely reactions. Then hopefully you will be able to fit your results to only one of the equations.

**An Example Analysis**: The approach used in this experiment can be illustrated with a parallel example using perchlorate ion, $ClO_4^-$, as the oxidizing agent. In the titration of $Fe^{2+}$ with $ClO_4^-$, the two possible chlorine-containing products are $Cl_2$ and $Cl^-$. The possible half reactions are shown as equations 1 to 3 and the balanced equations for the two possible reactions are equations 4 and 5 (verify the balancing of these reactions as practice). From these balanced reactions, we can see that the stoichiometry of the reaction in terms of moles $Fe^{2+}$ to moles $ClO_4^-$ can be used to determine the products of the reaction: 7:1 for $Cl_2$ as the product or 8:1 for $Cl^-$ as the product.

**Oxidation** is the loss of electrons

**Reduction** is the gain of electrons

$$Fe^{2+} \rightarrow Fe^{3+} + 1e^- \quad \text{oxidation half-reaction} \quad (1)$$

and

$$ClO_4^- \rightarrow 1/2\ Cl_{2\,(g)} \quad \text{reduction half-reaction} \quad (2)$$

or

$$ClO_4^- \rightarrow Cl^- \quad \text{reduction half-reaction} \quad (3)$$

$$7\ Fe^{2+} + ClO_4^- + 8\ H^+ \rightarrow 7\ Fe^{3+} + 1/2\ Cl_{2\,(g)} + 4\ H_2O \quad (4)$$

or

$$8\ Fe^{2+} + ClO_4^- + 8\ H^+ \rightarrow 8\ Fe^{3+} + Cl^- + 4\ H_2O \quad (5)$$

To determine the actual stoichiometry, the titration experiment was carried out. A carefully weighed sample of 0.3532 g of ferrous sulfate $FeSO_4 \cdot 7H_2O$ (F.W. 278.03 g $mol^{-1}$) was titrated with a 0.01062 M solution of $KClO_4$. The endpoint was reached when 14.99 mL of $KClO_4$ was added . This result was used to determine the stoichiometry of the reaction as shown below. The resulting stoichiometry of 8:1 indicates that the product of the reaction was $Cl^-$ and for every mole of $ClO_4^-$, 8 electrons were transferred.

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**Problem Solving:** (keeping at least one extra significant figure and rounding at the end)

The number of moles of $Fe^{2+}$ is

$$0.3532 \text{ g of } FeSO_4 \cdot 7H_2O \left(\frac{1 mole}{278.03 g}\right) = 1.2704 \times 10^{-3} \text{ mol } Fe^{2+}$$

The number of moles of $ClO_4^-$ added is

$$14.99 \text{ mL of } KClO_4 \left(\frac{1L}{1000mL}\right) \left(\frac{0.01062 mol}{L}\right) = 1.5919 \times 10^{-4} \text{ mol } ClO_4^-$$

The ratio of $Fe^{2+}$ to $ClO_4^-$ is

$$\frac{\text{moles } Fe^{2+}}{\text{moles } ClO_4^-} = \frac{1.2704 \times 10^{-3} \text{ mol}}{1.5919 \times 10^{-4} \text{ mol}} = 7.980$$

The stoichiometry is, therefore, 8:1, so reaction (5) is the proper reaction.

**Precision** How well your data relate to one another.
**Accuracy** How well your data relate to the right answer.

**Quantitative Laboratory Work**: Now that you have some experience in the chemistry lab, you are ready to try quantitative determinations. The procedure is designed to approximate "real world" analytical work. You will prepare all of your own reagent solutions, carry out the analysis as many times as you feel is necessary and report your best estimate of the "correct" result.

**PROCEDURE:**[1] Ferrous ammonium sulfate hexahydate, $Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$ will be used as the source of the iron(II) ion, and potassium permanganate, $KMnO_4$, will be the source of the permanganate ion.

A. **Preparation of the standard 0.01 M $KMnO_4$ solution**: Prepare an *approximately* 0.01 M $KMnO_4$ solution by weighing, to four significant figures, enough solid $KMnO_4$ salt to prepare 250 mL of solution. Weigh the $KMnO_4$ into a clean, dry weighing bottle. Quantitatively transfer the $KMnO_4$ into a 250-mL volumetric flask using a long stemmed funnel, washing the weighing bottle several times with deionized water from a wash bottle. Add approximately 100 mL of water to the flask and swirl the mixture to dissolve the solid. Dilute to the mark, adding the last few mL with a Pasteur pipet to avoid going over the mark. With the stopper firmly in place, mix well by inverting the volumetric flask at least a dozen times.

B. **Weigh a sample of ferrous ammonium sulfate hexahydrate**: Weigh approximately 0.5 g, to four significant figures, of $Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$ into a weigh boat. Transfer this sample into a 200 or 250 mL Erlenmeyer flask. Remember to keep track of the weight in each flask, since they will all be different. Add approximately 25 mL of 0.5 *M* sulfuric acid, $H_2SO_4$, and 25 mL of 2.0 *M* phosphoric acid, $H_3PO_4$, to the sample just before titrating. Place the flask on top of a stir plate, and let a stir bar assist you in keeping the solution well mixed.

C. **Titrate sample to a faint pink endpoint**: Be certain that your buret is clean (no droplets adhering to the inside upon draining) and the stopcock is tightened. Rinse the buret with about 3 mL of your standard $KMnO_4$ solution. Fill the buret using a plastic funnel. Clear all bubbles from the tip. Remove any drops from the tip. Record the initial volume, before starting each titration. The top of the meniscus will be read at the beginning and end of the titration. Read the volume to **two significant figures** past the decimal point (for example, 1.26 mL). Insert the tip of the buret well inside the neck of the Erlenmeyer flask. Titrate with $KMnO_4$ until the appearance of a very faint pink color that persists for 30 seconds. Note that as you approach this endpoint, the pink color will begin to persist for longer periods of time, before disappearing. At this point, it is advisable to add titrant **slowly.** You can even add partial drops from the buret tip - simply touch the flask to the droplet on the tip of the buret and then rinse the wall of the flask with a squirt of water from your wash bottle.

D. Repeat the titration two more times with fresh samples of $Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$.

E. Calculate the molar ratio for each of your three trials. Calculate the precision. If you have 98% precision or higher, then you are done titrating. If you have less than 98% precision, do a fourth trial and recalculate your precision based on all four titrations. If your precision is 98% or higher, you are finished. If your precision is below %98, titrate a fifth trial. Once this trial is complete calculate your precision for all 5 trials. If you have titrated more than three trials it is possible to use a statistical test to reject a questionable data point. The Q-Test is posted in lab and you can ask your instructor for help with your data to decide if a trial can be statistically rejected.

[1] Developed by T.W. Shattuck, Chemistry Department, Colby College, 1989.

## What should be in your notebook?

1. Calculated concentration of your $KMnO_4$ solution from the exact mass of $KMnO_4$ you weighed out.
2. All masses and volumes (initial, final, and difference) for each titration.
3. The average ratio for the moles of $Fe^{+2}$ to the moles of $MnO_4^-$.
4. For the molar ratio of all your trials: the Excel standard deviation, the percent relative standard deviation, and percent precision.
5. Calculated the percent relative experimental error and percent accuracy of your experimental work. What will you use for the "actual" value? That depends on which balanced redox reaction you've identified based on your experimental molar ratio.

## What should be attached to your discussion now but put into your lab notebook later?

1. The Report Table
2. The identified balanced redox reaction with all the work shown.

## What should be in your discussion?

Address <u>your</u> objective, report your results (including accuracy and precision) and the significance of each. Be sure to use proper significant figures in your discussion. Present the redox reaction most likely to represent the chemistry you observed and explain why.

The error discussion will naturally lead into why your calculated stoichiometry is not 100% precise or accurate. Be clear about whether you are talking about precision results or accuracy results throughout your discussion. <u>Specifically</u> how did random experimental error lead to the error in your results. You want to discuss two different sources of error. No more, no less.

Keep in mind that attachments to a discussion are supportive materials, that document your results. No reader should be sent to look at attachments to figure out what the results are and what they mean. If your results are important you need to present the values/findings and the significance of each within the discussion. This will be true for CH141 and CH142.

**Report Table:**

**Mass $KMnO_4$ , g _____ Molarity $KMnO_4$, M _____**

| Trial | $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ mass, g | Moles $Fe^{+2}$ | volume $KMnO_4$,mL | Moles $MnO_4^-$ | Molar Ratio: $Fe^{2+}/MnO_4^-$ |
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Average molar ratio: _____:1_____

Standard deviation of molar ratio: _____

% Relative standard deviation: _____

% Precision: _____

% Relative experimental error: _____

% Accuracy: _____