

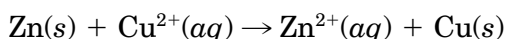
1. Determination of Iron by Redox Titration

Objective

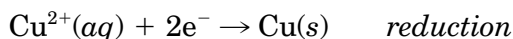
In this experiment, one of the main types of chemical reactions, oxidation/reduction (or redox) reactions, will be used in the titration analysis of an iron compound.

Introduction

Oxidation/reduction processes form one of the major classes of chemical reactions. In **redox reactions**, electrons are transferred from one species to another. For example, in the following simple reaction



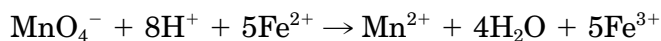
electrons are transferred from elemental metallic zinc to aqueous copper(II) ions. This is most easily seen if the overall reaction is written instead as two *half-reactions*, one for the oxidation and one for the reduction:



In this experiment you will use potassium permanganate, KMnO_4 , as the titrant in the analysis of an unknown sample containing **iron**. Although this method can easily be applied to the analysis of realistic iron *ores*—the native state in which an element is found in nature—for simplicity your unknown sample will contain only iron in the +2 oxidation state. In acidic solution, potassium permanganate rapidly and quantitatively *oxidizes* iron(II) to iron(III), while itself being *reduced* to manganese(II). The half reactions for the process are:



When these half-reactions are combined to give the overall balanced chemical reaction equation, a factor of *five* has to be used with the iron half-reaction so that the number of electrons lost in the overall oxidation will equal the number of electrons gained in the reduction:



Potassium permanganate has been one of the most commonly used oxidizing agents because it is extremely powerful, as well as inexpensive and readily available. It does have some drawbacks, however. Because KMnO_4 is such a strong oxidizing agent, it reacts with practically *anything* that can be oxidized: this tends to make solutions of KMnO_4 difficult to store without decomposition

or a change in concentration. Because of this limitation, it is common to prepare, standardize, and then use KMnO_4 solutions for an analysis all on the same day. It is *not* possible to prepare directly KMnO_4 standard solutions determinately by mass: solid potassium permanganate cannot be obtained in a completely pure state due to the high reactivity mentioned above. Rather, potassium permanganate solutions are prepared to be an approximate concentration, and are then standardized against a known primary standard sample of the same substance which is to be analyzed in the unknown sample.

Potassium permanganate is especially useful among titrants since it requires no indicator to signal the endpoint of a titration. Potassium permanganate solutions—even at fairly dilute concentrations—are intensely colored purple. The product of the permanganate reduction half-reaction, manganese(II), in dilute solution shows almost *no* color. Therefore, during a titration using KMnO_4 , when one drop *excess* of potassium permanganate has been added to the sample, the sample will take on a pale red/pink color (since there are no more sample molecules left to convert the purple MnO_4^- ions to the colorless Mn^{2+} ions).

SAFETY PRECAUTIONS

- **Wear safety glasses at all times while in the laboratory.**
- **Potassium permanganate is a strong oxidizing agent and can be damaging to skin, eyes, and clothing. Wash after handling.**
- **Potassium permanganate solutions will stain skin and clothing if spilled.**
- **Sulfuric acid solutions are damaging to the skin, eyes, and clothing—especially if allowed to concentrate through evaporation of water. If the sulfuric acid solution is spilled on the skin, wash immediately and inform the instructor.**
- **Iron salts may be irritating to the skin. Wash after handling.**

Apparatus/Reagents Required

Potassium permanganate, ferrous ammonium sulfate, 3 *M* sulfuric acid, buret and clamp, 250-mL Erlenmeyer flasks, 1-L glass bottle with cap, iron unknown sample

Procedure

A. Preparation of Potassium Permanganate Solution

Clean out a 1-L glass bottle and its cap. Wash first with soap solution, then rinse with tap water to remove all the soap. Finally rinse with several small portions of distilled water. Then place approximately 600 mL of distilled water in the bottle.

In a small beaker, weigh out 2.0 ± 0.1 g of potassium permanganate crystals (*Caution!*). Using a funnel, transfer the permanganate crystals to the 1-L bottle. Cap the bottle *securely* and shake the mixture to dissolve the permanganate. Potassium permanganate is often very *slow* in dissolving: continue shaking the solution until you are absolutely certain that all the permanganate crystals have dissolved completely.

B. Preparation of the Iron Standards

Clean out three 250-mL Erlenmeyer flasks with soap and water, giving a final rinse with several small portions of distilled water. Label the flasks as Samples 1, 2, and 3.

The primary standard iron(II) compound to be used for the standardization of the potassium permanganate solution is the salt ferrous ammonium sulfate hexahydrate (Mohr's salt), $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, which is almost universally abbreviated as FAS.

Place approximately 3 g of primary standard FAS into a small, clean dry beaker. Determine the mass of the beaker and FAS to at least the nearest milligram (0.001 g), or better, if an analytical balance is available, make the mass determination to the nearest 0.1 milligram (0.0001 g).

Using a funnel, carefully transfer approximately *one-third* of the FAS in the beaker (approximately 1 g) to the Erlenmeyer flask labeled Sample 1. Distilled water from a wash bottle can be used to rinse the salt into the flask if the funnel should clog.

Weigh the beaker containing the remainder of the FAS. The difference in mass from the previous weighing represents the mass of FAS transferred to the Sample 1 Erlenmeyer flask.

Using a funnel, carefully transfer approximately *half* the FAS remaining in the beaker (one-third of the original FAS sample) to the Erlenmeyer flask labeled Sample 2. Again, rinse the FAS from the funnel into the flask with distilled water from a wash bottle.

Weigh the beaker containing the remaining FAS. The difference in mass from the previous weighing represents the mass of Sample 2 that was transferred to the Erlenmeyer flask.

Using a funnel as above, transfer as much as possible of the FAS remaining in the beaker to the Sample 3 Erlenmeyer flask. Finally weigh the empty beaker and any residual FAS that may not have been transferred completely. The difference in mass from the previous weighing represents the mass of Sample 3.

Add 25 mL of distilled water to each sample and swirl the flasks to dissolve the FAS.

Add 15 mL of 3 M sulfuric acid, H_2SO_4 , to each sample (*Caution!*). Sulfuric acid is added to the samples to provide the hydrogen ions, H^+ , required for the reduction of the permanganate ion.

C. Standardization of the Potassium Permanganate Solution

Clean out a buret with soap and water, and rinse with several portions of tap water, followed by several small rinsings with distilled water.

Rinse the buret with several 4–6-mL portions of the potassium permanganate solution. Tilt and rotate the buret so that the inside walls are completely rinsed with the permanganate, and allow the solution to run out of the tip of the buret to rinse the tip also. Discard the rinsings.

Finally, using a funnel *and with the buret below eye-level*, fill the buret to slightly *above* the zero mark with the permanganate solution. Allow a few mL of permanganate to run out of the tip of the buret to remove any air bubbles from the tip.

Since potassium permanganate solutions are so intensely colored, it is generally impossible to see the curved meniscus that the solution surface forms in the buret. In this case, it is acceptable to make your liquid level readings at the point where the *top* surface of the permanganate solution comes in contact with the wall of the buret. Remove the funnel from the buret and take the initial volume reading, to the nearest 0.02 mL. Record.

Place the Erlenmeyer flask containing Sample 1 under the tip of the buret, and begin adding potassium permanganate to the sample a few mL at a time, swirling the flask after each addition of permanganate. As the permanganate solution is added to the sample, red streaks may be visible in the sample until the permanganate has a chance to mix with and react with the iron(II) present.

Continue adding permanganate a few mL at a time, with swirling, until the red streaks begin to become more persistent. At this point, begin adding the permanganate *one drop* at a time, swirling the flask constantly to mix. The endpoint is the first appearance of a *permanent*, pale pink color.

After the endpoint has been reached, record the final buret reading (to the nearest 0.02 mL). Calculate the volume of potassium permanganate solution used to titrate FAS Sample 1.

Titrate FAS Samples 2 and 3 in a similar manner, recording initial and final volumes of potassium permanganate solution used to the nearest 0.02 mL.

From the mass of each FAS sample, and from the volume of KMnO_4 used to titrate the respective samples, calculate three values for the molarity of your potassium permanganate solution, as well as the average molarity. If any one of your individual molarities seems out-of-line from the other two, you should consult with the instructor about performing a fourth standardization titration (using an additional 1-g sample of FAS).

D. Analysis of the Iron Unknown

Your instructor will provide you with an iron unknown, and will inform you of the approximate sample size to weigh out. Prepare three samples of the iron unknown as you performed in Part B for the primary standard FAS, being sure to add the sulfuric acid required for the reaction, and being sure to keep the masses of the samples to the amount indicated by the instructor.

Titrate the iron unknown samples as described in Part C above, recording initial and final volumes to the nearest 0.02 mL. Calculate the volume of permanganate solution required to reach the pale pink endpoint for each sample.

From the volume required to titrate each unknown sample, and the average molarity of the KMnO_4 solution, calculate the number of moles of potassium permanganate required for each iron sample.

From the number of moles of potassium permanganate required for titration of each iron sample, calculate the number of moles of iron present in each unknown sample.

From the number of moles of iron present in each sample, and the molar mass of iron, calculate the mass of iron present in each unknown sample.

From the mass of iron present in each sample, and from each sample's mass, calculate the percent iron in each sample.

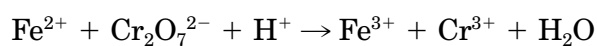
Calculate the average percent iron by mass present in your unknown sample.

Determination of Iron by Redox Titration

Date: Student name:
Course: Team members:
Section:
Instructor:

Prelaboratory Questions

1. Another common analysis for iron is titration of iron(II) with potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$. Divide the following reaction into half-reactions, balance the half-reactions, and combine the balanced half-reactions into the balanced overall equation for the reaction.



2. Use a chemical dictionary, handbook, or encyclopedia to write several *other* uses of potassium permanganate (other than in the analysis of iron samples as in this experiment).

3. If 26.23 mL of potassium permanganate solution is required to titrate 1.041 g of ferrous ammonium sulfate hexahydrate, $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, calculate the molarity of the KMnO_4 solution.
4. If a 2.893 g sample of an unknown containing iron requires 28.45 mL of the permanganate solution described in Prelaboratory Question 3 to reach the endpoint, calculate the % Fe in the unknown.

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Results/Observations

Standardization of KMnO_4 Solution

	Sample 1	Sample 2	Sample 3
Mass of FAS taken
Initial KMnO_4 volume
Final KMnO_4 volume
Volume KMnO_4 used
Moles iron present
Moles KMnO_4 present
Molarity of KMnO_4 solution
Mean molarity and average deviation		

Analysis of Unknown

	Sample 1	Sample 2	Sample 3
Mass of unknown taken
Initial KMnO_4 volume
Final KMnO_4 volume
Volume KMnO_4 used
Moles KMnO_4 present
Moles iron present
Mass of iron present
% of iron present
Mean % iron present and average deviation		

