

EXPERIMENT 14
DETERMINATION OF IRON BY PERMANGANATE TITRATION

PURPOSE:

1. To illustrate an oxidation-reduction titration with potassium permanganate
2. To determine the percent mass of iron in an unknown.

PRINCIPLES:

Oxidation and reduction reactions, commonly called redox reactions, are processes that always occur together. A redox reaction is any reaction in which there is a change in the oxidation states of the atoms in going from reactants to products.

- Oxidation:
 - is recognized by an increase in the oxidation state of an element, and
 - results from a loss of electrons.
- Reduction
 - is recognized by a decrease in the oxidation state of an element, and
 - results from a gain of electrons.

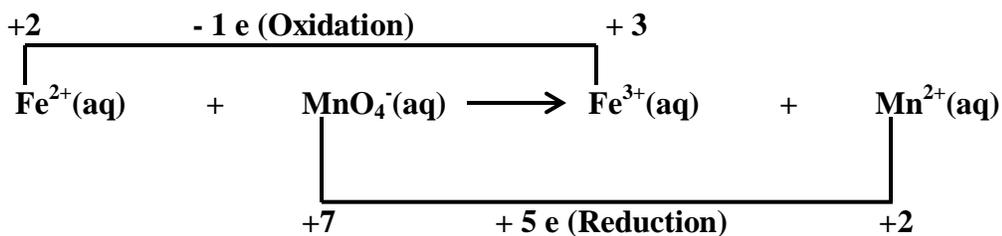
In a redox reaction:

- The element that is oxidized causes the reduction of another element and, as such, is referred to as a reducing agent.
- The element that is reduced causes the oxidation of another element and, as such, is referred to as an oxidizing agent.

When balancing redox reactions, we must balance both:

- The number of each type of atom, and
- The total charge on both the reactant(s) and the product(s) sides.

In this experiment the Fe^{2+} ion is oxidized to Fe^{3+} and Mn^{7+} is reduced to Mn^{2+} .



In order to use the stoichiometry involved in this reaction, the redox equation that represents this reaction must be balanced. Balancing redox reactions occurring in aqueous solutions is done by the half-reaction method. The half-reaction method for balancing redox reactions occurring in aqueous solutions (acidic or basic) involves several steps:

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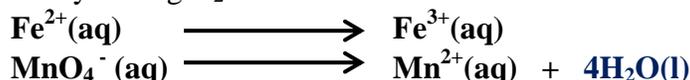
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1. Separate the overall equation into two half-reaction:

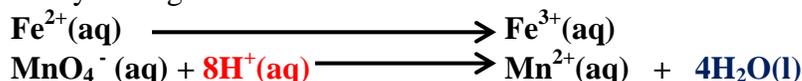
- Oxidation: $\text{Fe}^{2+}(\text{aq}) \longrightarrow \text{Fe}^{3+}(\text{aq})$
- Reduction: $\text{MnO}_4^- (\text{aq}) \longrightarrow \text{Mn}^{2+}(\text{aq})$

2. Balance the number of each type of atom in each half-reaction:

- Balance all elements other than H and O
(Note that all elements other than H and O are balanced)
- Balance O by adding H_2O

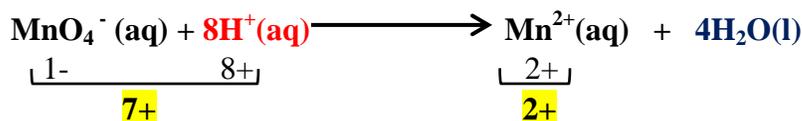


- Balance H by adding H^+ if the solution is acidic



3. Balance the total charge in each half-reaction:

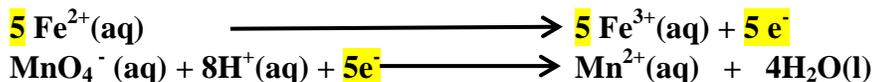
- Calculate the sum of the charges on both sides of the equation in each half-reaction.



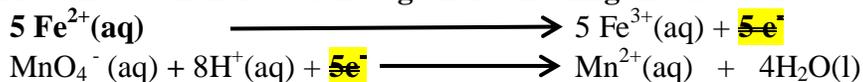
- Make the sum of the charges on both sides of the equation equal in each reaction, by adding as many electrons as necessary.



4. Make the number of electrons in both half-reactions equal by multiplying the first half-reaction by 5.



5. Add the two half-reactions together canceling the electrons.



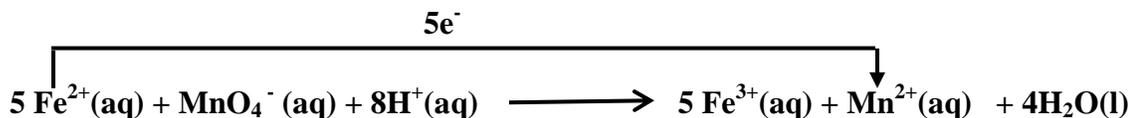
The resulting equation illustrates the balanced net ionic equation for this reaction.



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It follows that the permanganate ion (MnO_4^{2-}) is the oxidizing agent since it is the recipient of electrons taken from the Fe^{2+} ion.



Note that a source of H^+ ions is required for this redox reaction to occur. As such, this redox reaction will be carried out in an aqueous acidic solution.

You will be adding H_2SO_4 and H_3PO_4 , as sources of H^+ ions, to the solution containing the Fe^{2+} ions. The solution containing the Fe^{2+} ions will be titrated with a solution of standardized KMnO_4 solution, which contains the MnO_4^- ion.

As you recall from previous titrations, the **equivalence point** of a titration (sometimes referred to as the “**theoretical end point**”) is defined as the exact volume of one reactant (delivered from a buret) that reacts, according to the balanced equation, with an exact amount (volume or mass) of another reactant measured in a flask. When the equivalence point (“theoretical end point”) is reached, the reactants have reacted in a stoichiometric fashion and the solution will be colorless since both ions produced (Fe^{3+} and Mn^{2+}) are colorless.

For the redox titration using the permanganate ion as a titrant, the experimental end point of the titration is signaled without the use of an indicator. When the titration begins, the highly purple colored KMnO_4 solution (containing the MnO_4^- ion), that is added from a buret, reacts with the excess Fe^{+2} in the flask so quickly, that the purple/pink color of the added KMnO_4 solution disappears immediately. When the Fe^{+2} is nearly used up, the purple/pink color of the added KMnO_4 solution will not disappear so quickly. Once the Fe^{+2} is all used up, a slight excess of the MnO_4^- ion will turn the solution faint pink in color, signaling the “**experimental end point**”.

It follows that it is not possible to get the equivalence point exactly and that the **experimental end point** is determined by adding a **very small excess of the KMnO_4 solution** to the flask that is just sufficient to see the change in color of the solution from colorless to very faint pink. The purpose of adding H_3PO_4 to the reaction mixture is to provide a source of PO_4^{3-} ions which complexes with the Mn^{+2} product and sharpens the end point.

The unknowns in this experiment contain iron in the form of iron(II) ammonium sulfate, hexahydrate, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, mixed with another substance which is inert and does not participate in the redox reaction.

CAUTION:

DO NOT WASTE THE PERMANGANATE SOLUTION

ALL SOLUTIONS CONTAINING KMnO_4 (Potassium permanganate) SHOULD BE DISPOSED OF IN THE APPROPRIATE WASTE CONTAINER IN THE FUME HOOD.

DO NOT DISPOSE OF THE PERMANGANATE SOLUTION IN THE SINK

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PROCEDURE:

1. Obtain an unknown sample containing iron and record the unknown number in your Laboratory Notebook.

2. Set out three clean and dry 125 mL Erlenmeyer flasks.

If any of the flasks are dirty, clean them, rinse them with deionized water and dry them **thoroughly**. Your instructor will instruct you in the proper procedure for drying the flasks, **if necessary**.

NOTE:

The reason for the Erlenmeyer flasks to be dry is that the iron unknown will be weighed out in these flasks. If the flasks contain moisture, some of the Fe^{+2} in the unknown will be oxidized to Fe^{+3} and reduce the amount of Fe^{+2} that reacts with the permanganate solution.

3. Obtain a 50.0 mL buret and clean it thoroughly with deionized water.

4. Obtain about 100 mL of the standardized permanganate solution in a clean, dry 250 mL beaker. Record the molarity of the permanganate solution.

5. Prepare your buret for the titration as follows:

a. Rinse the buret twice with about 5 mL of the permanganate solution, draining it into a beaker at your bench.

DO NOT DISPOSE OF THE PERMANGANATE SOLUTION IN THE SINKS!

b. Fill the buret a little above the "0" line.

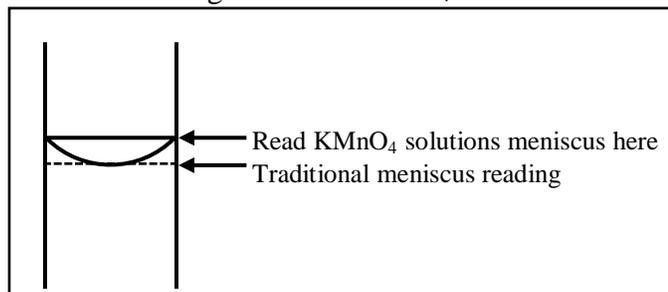
c. Open the stopcock and drain the permanganate solution in order to completely fill the tip of the buret and flush out any air bubbles.

- The liquid level will drop below the "0" line.
- It is not necessary to refill it to exactly 0.00 mL; however it is necessary to record exactly the starting volume to the nearest ± 0.01 mL.

d. Since the KMnO_4 solution is a deeply colored purple solution, it is difficult to read the level of the titrant in the buret in the traditional manner (bottom of meniscus)

In any titration in which KMnO_4 solution is used as a titrant, it is common practice to read the level of the KMnO_4 solution in the buret consistently at the top of the meniscus (see below).

Reading buret for KMnO_4 solutions



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6. Weigh out the unknown as follows:

- Using the weighing bottle technique and the analytical balance, accurately weigh for the first run (trial run) **no more than 0.5 g** of the unknown into a dry Erlenmeyer flask.
- Record the mass to the nearest ± 0.0001 g.

7. Titrate your first sample (trial run)

- Add approximately 50 mL of 1 M H_2SO_4 and swirl gently to dissolve the solid unknown completely
- Add about 4 mL to 5 mL of 85% H_3PO_4 . The addition of H_3PO_4 sharpens the end point and it makes it easier to detect the faint pink end point.
- Record the initial starting volume in the buret.
- Begin the addition of the permanganate solution from the buret, swirling the flask during the addition.
- Stop the addition of the permanganate solution when the pink color persists.
- Record the final volume in the buret.

8. Titrate the additional samples accurately.

- If you added under 10 mL of permanganate to titrate the trial sample, weigh out proportionally more of the solid unknown for all additional titrations to ensure that your volumes of permanganate required to reach the end point are more than 10 mL.. Ideally, this volume of the titrant used should be around 20 mL
- You will weigh out two or three additional samples into dry Erlenmeyer flasks, **one at a time**.

DO NOT WEIGH OUT MORE THAN ONE SAMPLE AT A TIME TO AVOID ANY OXIDATION OF THE Fe^{2+} to Fe^{3+} . (See Step 2).

- To each sample, add the acids as before:
 - Add 50 mL of 1 M H_2SO_4 and swirl gently to dissolve the unknown completely
 - Add 4 mL to 5 mL of 85% H_3PO_4
- Titrate the sample carefully by following the guidelines given below:
 - Add the permanganate solution slowly in order to mix it in thoroughly during the addition.
 - Do not let the permanganate color accumulate in the solution to any significant degree during the early stages of titration.
 - If any permanganate solution splatters on the walls of the flask, rinse it into the solution using a wash bottle. Avoid accidentally rinsing the end of the buret tip.
 - As you near the expected end point volume, add the permanganate solution drop wise.
 - To get the most accurate results, split drops. This is done in the following manner:
 - Allow a partial drop to form at the bottom of the buret tip,
 - touch the drop to the inner sides of the flask, and
 - rinse the drop into the solution.

DO NOT RINSE OFF THE BOTTOM OF THE BURET!

- Add the permanganate solution until a **faint pink color persists for 30 seconds or more**.
- Record the final volume of the permanganate solution in the buret.

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9. Repeat the titration for a total of two or three more samples.

10. Review the precision of your experimental data in the following manner:

- Divide the mL of the permanganate solution delivered from the buret, by the mass of the respective unknown used for the titration.
- This ratio should be the same (or reasonably close) for all your titrations.
- If you do not have at least two titrations with the same ratio ($< \pm 8\%$), reweigh another sample of unknown and titrate it.

Example:

Trial 1	Trial 2	Trial 3
$\frac{9.55 \text{ mL}}{0.3405 \text{ g}}$	$\frac{26.72 \text{ mL}}{0.8488 \text{ g}}$	$\frac{24.30 \text{ mL}}{0.7198 \text{ g}}$
28.05 mL/g	31.48 mL/g	33.76 mL/g
	6.75 % apart	
	$\frac{31.48 - 33.76}{33.76} \times 100 = 6.75 \%$	

Based on this example, we can conclude that:

- Trial 2 and Trial 3 are precise enough to provide the experimental data for calculations.
- No additional titration is required.
- Trial 1 needs to be discarded since it is 10.9 % apart from Trial 2 and 16.9 % apart from Trial 3
- The final answer (% Fe in the sample) will be calculated as the average of the % Fe obtained from Trial 2 and Trial 3

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CALCULATIONS:1. **Sample Calculation**

If 26.72 mL of 0.01934 M KMnO_4 are required to titrate the iron in a 0.8488 g sample of unknown, what is the mass percent iron in that unknown?

$$? \text{ moles MnO}_4^- = 26.72 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.01934 \text{ mol MnO}_4^-}{1 \text{ L}} = 5.168 \times 10^{-4} \text{ mol MnO}_4^-$$

$$? \text{ moles Fe}^{+2} = 5.168 \times 10^{-4} \text{ mol MnO}_4^- \times \frac{5 \text{ mol Fe}^{+2}}{1 \text{ mol MnO}_4^-} = 2.584 \times 10^{-3} \text{ mol Fe}^{+2}$$

$$? \text{ grams of Fe}^{+2} = 2.584 \times 10^{-3} \text{ mol Fe}^{+2} \times \frac{55.86 \text{ g}}{1 \text{ mol Fe}^{+2}} = 0.1436 \text{ g Fe}^{+2}$$

$$\% \text{ Fe}^{+2} = \frac{0.1436 \text{ g Fe}^{+2}}{0.8488 \text{ g sample}} \times 100 = \mathbf{16.92 \% Fe}^{+2}$$

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REPORT FORM

NAME: _____ UNKNOWN # _____ DATE: _____

Molarity of standardized KMnO_4 : _____ M

	Sample # 1	Sample # 2	Sample # 3	Sample # 4
Mass of Sample (g)				
Initial Buret Reading (mL)				
Final Buret Reading (mL)				
Volume of MnO_4^- used (mL)				
Moles of MnO_4^- used				
Moles of Fe^{+2} present				
Mass of Fe^{+2} present (g)				
% of Fe^{+2} in sample				
Average % of Fe^{+2} in sample				

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