

## EXPERIMENT A9: REDOX TITRATION

### Learning Outcomes

Upon completion of this lab, the student will be able to:

- 1) Apply the principles of titration that were previously discussed & performed to an oxidation-reduction reaction.
- 2) Evaluate the percentage of hypochlorite in bleach.

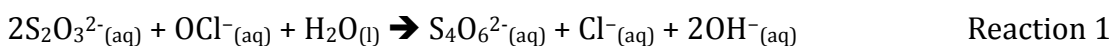
### Introduction

Oxidation-Reduction reactions, known in short as redox reactions, involve transfer of electrons. One reactant loses electrons, and is therefore oxidized. The electrons lost by this reagent are transferred to the second reagent, which accepts these electrons and is therefore reduced. The oxidation number of an element in the reagent getting oxidized increases and the oxidation number of an element in the reagent getting reduced decreases.

These types of reactions are common in electrochemistry, a topic that will be discussed in greater detail in a later section of General Chemistry.

In this experiment, the amount of hypochlorite ion-  $\text{OCl}^-$ , the active ingredient in bleach, will be measured by performing a redox titration. As in any titration, the stoichiometry of the chemical equation of the reaction will enable the determination of the amount of the unknown reagent.

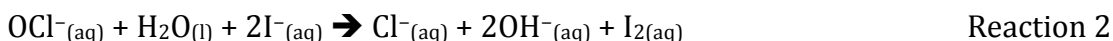
The hypochlorite ion will be titrated with thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ ) according to the following overall reaction written in its ionic form:



Reaction 1 shows that one mole of hypochlorite completely reacts with two moles of thiosulfate. This stoichiometric relationship becomes the basis for the required calculations.

However, Reaction 1 does not provide the complete picture of the chemistry of the reaction between hypochlorite and thiosulfate.

A third important reagent that is used for the electron transfer process (keep in mind that this is a redox reaction and must therefore involve electron transfer) is iodide ( $\text{I}^-$ ). When hypochlorite ions react with iodide ions, the following reaction first takes place:



The  $I_2$  formed in Reaction 2 reacts with the thiosulfate according to the following reaction:



When Reaction 2 and Reaction 3 are combined, the overall reaction obtained is Reaction 1. So, in reality it is the  $I_2$  that is titrated with thiosulfate. Since moles of  $I_2$  formed in Reaction 2 are the same as the moles of  $OCl^-$ , the stoichiometry between  $OCl^-$  and  $S_2O_3^{2-}$  is the same as that between  $I_2$  and  $S_2O_3^{2-}$ .

In this titration, the iodide and bleach (containing  $OCl^-$ ) will be in the Erlenmeyer flask and the burette will contain the thiosulfate.

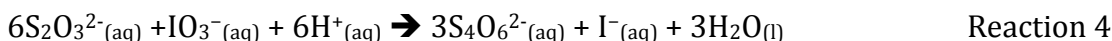
As is the case in any titration, the end point is determined visually by using indicators (see Experiment VII: Vinegar Titration). The redox titration discussed here uses starch as an indicator in an interesting manner.

When all the reagents are combined, the solution in the Erlenmeyer flask initially has a reddish-brown color, which is a result of the combination of  $I^-$  and  $I_2$  (from Reaction 2). Once the titration is begun, the addition of the thiosulfate decreases the amount of  $I_2$  as it is converted to  $I^-$  (according to Reaction 3) and the color of the solution becomes more yellow than brown. If starch (which is a colorless solution) is added at this point, it forms a complex with the remaining  $I_2$  and the solution takes on a deep blue to violet color. When the titration is completed, all the  $I_2$  will have been converted to  $I^-$ , releasing the starch in its free form and rendering the solution colorless.

Therefore the transformation of the deep blue colored solution to a colorless solution is used as a visual indication of the end point of this titration.

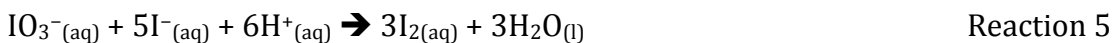
As discussed above, the moles of hypochlorite present in bleach is determined from the stoichiometric relationship between hypochlorite and thiosulfate (1 : 2 according to Reaction 1). The moles of the thiosulfate will be determined from its molarity and the volume used for the titration. Therefore it is important to know the exact molarity of the thiosulfate.

The molarity of the prepared thiosulfate solution must first be determined by titrating it against a primary standard (see Experiment VII). The primary standard used in the current experiment is iodate ( $IO_3^-$ ). The reaction between thiosulfate and iodate is as follows:



According to Reaction 4, six moles of thiosulfate are needed to completely react with one mole of iodate.

As was the case with Reaction 1, Reaction 4 does not provide the complete picture of the chemistry of this reaction. In Reaction 4 as well, the iodate (like the hypochlorite in Reaction 1) is combined with iodide ( $I^-$ ) to facilitate the electron transfer process. The chemical reaction between iodate and iodide is as follows:



The  $I_2$  formed in Reaction 5 reacts with the thiosulfate according to the following reaction:



When Reaction 5 and Reaction 3 are combined, the overall reaction obtained is Reaction 4. So once again, in reality it is the  $I_2$  that is titrated with thiosulfate. Since three moles of  $I_2$  are formed in Reaction 5 and each mole of  $I_2$  is titrated with two moles of  $S_2O_3^{2-}$  according to Reaction 3, it then follows that six moles of  $S_2O_3^{2-}$  are needed to completely react with one mole of  $IO_3^-$ .

In this titration, the iodide and bleach (containing  $OCl^-$ ) will be in the Erlenmeyer flask and the burette will contain the thiosulfate.

The indicator used for the end point determination of Reaction 4 is also starch. The color of the mixture in the Erlenmeyer flask ( $IO_3^-$  and  $I^-$ ) will be reddish brown. Once the titration begins and as the  $I_2$  is converted to  $I^-$  (according to Reaction 3), the color will become more yellow. Starch added at this point will complex with the remaining  $I_2$  in the flask and give the solution a deep blue to violet color. Once all the  $I_2$  has been converted to  $I^-$  by the  $S_2O_3^{2-}$  the solution will become colorless, as the starch is not complexed with  $I_2$ .

## Experimental Design

A primary standard of iodate of concentration 0.0500 M must first be prepared. This solution will be used to titrate the provided thiosulfate solution of unknown molarity. The data from this titration will be used to determine the exact molarity of the thiosulfate solution. This thiosulfate solution will then be used to titrate the hypochlorite in the bleach. The mass percent of hypochlorite in the bleach solution will then be calculated.

## Reagents and Supplies

Starch solution, sodium thiosulfate solution ( $\sim$  molarity = 0.2 M), solid potassium iodate, 2 M sulfuric acid, 10% potassium iodide solution, 6 M acetic acid, bleach

(See posted Material Safety Data Sheets)

Volumetric flask

## Procedure

### PART 1: STANDARDIZATION OF AQUEOUS SODIUM THIOSULFATE SOLUTION

1. Calculate the mass of potassium iodate ( $\text{KIO}_3$ ) needed to make 25.00 mL of 0.0500 M solution.
2. Weigh an amount of potassium iodate as close to the number calculated in step 1 as possible. Record the exact mass.
3. Prepare the 0.0500 M  $\text{KIO}_3$  solution using a 25.00 mL volumetric flask.
4. Obtain about 10 mL of each of the following solutions: 1% starch, 2 M sulfuric acid, 10% aqueous potassium iodide, and sodium thiosulfate solution. Clearly label each container.
5. Set up two microburettes and label one as the thiosulfate burette and the other as iodate burette.
6. Rinse, condition, and fill each burette with the appropriate reagent.
7. Record the initial burette readings of both the burettes.
8. Add about 1 mL of iodate from the burette into a 25-mL Erlenmeyer flask. Record the final burette reading.
9. Add the following reagents into the above Erlenmeyer flask:
  - a. 5 mL of deionized water
  - b. Six drops of 2 M  $\text{H}_2\text{SO}_4$
  - c. 2 mL of 10% KI
10. The solution in the Erlenmeyer flask should be reddish brown in color. Begin titrating this solution with the thiosulfate.
11. If any reagent is stuck to the sides of the flask, rinse the flask with deionized water to ensure mixing of all the reagents.
12. When the solution in the Erlenmeyer flask is pale yellow, add 2 mL of deionized water and 15 drops of 1% starch solution. This solution should now be deep blue to violet in color.
13. Continue titrating with the thiosulfate until the solution turns colorless. Record the final burette reading of the thiosulfate burette.
14. Repeat steps 7 to 13 two to three more times.

PART 2: TITRATION OF THE HYPOCHLORITE IN BLEACH WITH THE STANDARDIZED SODIUM THIOSULFATE SOLUTION

1. Obtain about 10 mL of the following solutions: 1% starch, 6 M acetic acid, 10% aqueous potassium iodide, standardized sodium thiosulfate solution from part 1, and bleach. Clearly label each container.
2. Set up two microburettes and label one as the thiosulfate burette and the other as bleach.
3. Rinse, condition, and fill each burette with the appropriate reagent.
4. Record the initial burette readings of both the burettes.
5. Record the mass of a clean, empty, and dry 25-mL Erlenmeyer flask.
6. Add about 0.1 mL of bleach (about two to four drops) from the burette into the above Erlenmeyer flask. Record the final burette reading.
7. Measure the mass of the Erlenmeyer flask containing the bleach and record this value.
8. Add the following reagents into the above Erlenmeyer flask:
  - a. 2 mL of deionized water
  - b. 1 mL of 2 M  $\text{H}_2\text{SO}_4$
  - c. 2 mL of 10% KI
9. The solution in the Erlenmeyer flask should be reddish brown in color. Begin titrating this solution with the thiosulfate.
10. If any reagent is stuck to the sides of the flask, rinse the flask with deionized water to ensure mixing of all the reagents.
11. When the solution in the Erlenmeyer flask is pale yellow, add 10 drops of 1% starch solution. This solution should now be deep blue to violet in color.
12. Continue titrating with the thiosulfate until the solution turns colorless. Record the final burette reading of the thiosulfate burette.
13. Repeat steps 4 to 12 two to three more times.

**Data Table****PART 1: STANDARDIZATION OF AQUEOUS SODIUM THIOSULFATE SOLUTION**

Mass of $\text{KIO}_3$ (grams)	
Volume of $\text{KIO}_3$ solution (mL)	25.00

**Iodate solution**

	<b>Trial 1</b>	<b>Trial 2</b>	<b>Trial 3</b>	<b>Trial 4</b>
Initial burette reading (mL)				
Final burette reading (mL)				

**Thiosulfate solution**

	<b>Trial 1</b>	<b>Trial 2</b>	<b>Trial 3</b>	<b>Trial 4</b>
Initial burette reading (mL)				
Final burette reading (mL)				

PART 2: TITRATION OF THE HYPOCHLORITE IN BLEACH WITH THE STANDARDIZED SODIUM THIOSULFATE SOLUTION

**Bleach**

	<b>Trial 1</b>	<b>Trial 2</b>	<b>Trial 3</b>	<b>Trial 4</b>
Mass of empty Erlenmeyer flask (grams)				
Mass of Erlenmeyer flask + bleach (grams)				

**Thiosulfate solution**

	<b>Trial 1</b>	<b>Trial 2</b>	<b>Trial 3</b>	<b>Trial 4</b>
Initial burette reading (mL)				
Final burette reading (mL)				



## Calculations

### PART 1: STANDARDIZATION OF AQUEOUS SODIUM THIOSULFATE SOLUTION

Molar mass of  $\text{KIO}_3 =$

Mass of  $\text{KIO}_3 =$

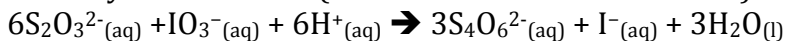
Moles of  $\text{KIO}_3 =$

Volume of  $\text{KIO}_3$  solution prepared = 25.00 mL = 0.02500 L

Molarity of  $\text{KIO}_3 = \frac{\text{moles}}{\text{Volume}} =$

	<b>Trial 1</b>	<b>Trial 2</b>	<b>Trial 3</b>	<b>Trial 4</b>
Volume of $\text{IO}_3^-$ (liters)				
Volume of $\text{S}_2\text{O}_3^{2-}$ (liters)				

Molarity of thiosulfate (show calculation for each trial):



Trial 1

Trial 2

Trial 3

Trial 4

	<b>Molarity of <math>\text{S}_2\text{O}_3^{2-}</math></b>
Trial 1	
Trial 2	
Trial 3	
Trial 4	
<b>Average</b>	

PART 2: TITRATION OF THE HYPOCHLORITE IN BLEACH WITH THE STANDARDIZED SODIUM THIOSULFATE SOLUTION



At equivalence point: 1 mole of  $\text{OCl}^-$  = 2 moles of  $\text{S}_2\text{O}_3^{2-}$

Average molarity of  $\text{S}_2\text{O}_3^{2-}$  (from part 1) =

	<b>Trial 1</b>	<b>Trial 2</b>	<b>Trial 3</b>	<b>Trial 4</b>
Volume of $\text{S}_2\text{O}_3^{2-}$ (liters)				
Moles of $\text{S}_2\text{O}_3^{2-}$ ( $M \times V$ )				
Moles of $\text{OCl}^-$				
Molar Mass of $\text{OCl}^-$ (g/mol)				
Mass of $\text{OCl}^-$ (grams)				
Mass of bleach (grams)				
Mass percent of $\text{OCl}^-$ in bleach (%)				

**Average mass percent of hypochlorite in bleach = \_\_\_\_\_**