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- 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 ($S_2O_3^{2-}$) according to the following overall reaction written in its ionic form:

$$2S_2O_3^{2-}{}_{(aq)} + OCl^-{}_{(aq)} + H_2O_{(l)} \rightarrow S_4O_6^{2-}{}_{(aq)} + Cl^-{}_{(aq)} + 2OH^-{}_{(aq)} \qquad \text{Reaction 1}$$

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 (I^-). When hypochlorite ions react with iodide ions, the following reaction first takes place:

$$OCl^-{}_{(aq)} + H_2O_{(l)} + 2I^-{}_{(aq)} \rightarrow Cl^-{}_{(aq)} + 2OH^-{}_{(aq)} + I_{2(aq)} \qquad \text{Reaction 2}$$

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

$I_{2(aq)} + 2S_2O_3^{2-}{}_{(aq)} \rightarrow 2I^-{}_{(aq)} + S_4O_6^{2-}{}_{(aq)}$ Reaction 3

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:

$6S_2O_3^{2-}{}_{(aq)} + IO_3^-{}_{(aq)} + 6H^+{}_{(aq)} \rightarrow 3S_4O_6^{2-}{}_{(aq)} + I^-{}_{(aq)} + 3H_2O_{(l)}$ Reaction 4

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:

$IO_3^-{}_{(aq)} + 5I^-{}_{(aq)} + 6H^+{}_{(aq)} \rightarrow 3I_{2(aq)} + 3H_2O_{(l)}$ Reaction 5

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

$I_{2(aq)} + 2S_2O_3^{2-}{}_{(aq)} \rightarrow 2I^-{}_{(aq)} + S_4O_6^{2-}{}_{(aq)}$ Reaction 3

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 (~ 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 (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 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 H_2SO_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 H_2SO_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 KIO_3 (grams)	
Volume of KIO_3 solution (mL)	25.00

Iodate solution

	Trial 1	**Trial 2**	**Trial 3**	**Trial 4**
Initial burette reading (mL)				
Final burette reading (mL)				

Thiosulfate solution

	Trial 1	**Trial 2**	**Trial 3**	**Trial 4**
Initial burette reading (mL)				
Final burette reading (mL)				

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

Bleach

	Trial 1	**Trial 2**	**Trial 3**	**Trial 4**
Mass of empty Erlenmeyer flask (grams)				
Mass of Erlenmeyer flask + bleach (grams)				

Thiosulfate solution

	Trial 1	**Trial 2**	**Trial 3**	**Trial 4**
Initial burette reading (mL)				
Final burette reading (mL)				

Calculations

PART 1: STANDARDIZATION OF AQUEOUS SODIUM THIOSULFATE SOLUTION

Molar mass of KIO_3 =

Mass of KIO_3 =

Moles of KIO_3 =

Volume of KIO_3 solution prepared = 25.00 mL = 0.02500 L

Molarity of KIO_3 = $\frac{moles}{Volume}$ =

	Trial 1	**Trial 2**	**Trial 3**	**Trial 4**
Volume of IO_3^- (liters)				
Volume of $S_2O_3^{2-}$ (liters)				

Molarity of thiosulfate (show calculation for each trial):

$6S_2O_3^{2-}{}_{(aq)} + IO_3^-{}_{(aq)} + 6H^+{}_{(aq)} \rightarrow 3S_4O_6^{2-}{}_{(aq)} + I^-{}_{(aq)} + 3H_2O_{(l)}$

Trial 1

Trial 2

Trial 3

Trial 4

	Molarity of $S_2O_3^{2-}$
Trial 1	
Trial 2	
Trial 3	
Trial 4	
Average	

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

$2S_2O_3^{2-}{}_{(aq)} + OCl^-{}_{(aq)} + H_2O_{(l)} \rightarrow S_4O_6^{2-}{}_{(aq)} + Cl^-{}_{(aq)} + 2OH^-{}_{(aq)}$

At equivalence point: 1 mole of OCl^- = 2 moles of $S_2O_3^{2-}$

Average molarity of $S_2O_3^{2-}$ (from part 1) =

	Trial 1	**Trial 2**	**Trial 3**	**Trial 4**
Volume of $S_2O_3^{2-}$ (liters)				
Moles of $S_2O_3^{2-}$ (M × V)				
Moles of OCl^-				
Molar Mass of OCl^- (g/mol)				
Mass of OCl^- (grams)				
Mass of bleach (grams)				
Mass percent of OCl^- in bleach (%)				

Average mass percent of hypochlorite in bleach = ____________________