A Volumetric Analysis (Redox Titration) of Hypochlorite in Bleach

In this laboratory exercise, we will determine the concentration of the active ingredient in Household Bleach; Hypochlorite Ion (ClO\(^-\)). We will do this using a titrimetric analysis in which the hypochlorite is treated with Iodide (I\(^-\)), resulting in the production of elemental Iodine (I\(_2\)). This is then titrated with Thiosulfate (S\(_2\)O\(_3^{2-}\)) to a Starch Indicator Endpoint; a blue to colorless color change. The Thiosulfate itself is standardized against primary grade Iodate (IO\(_3^-\)). All of these chemical processes are redox reactions and so this analysis is call a Redox Titration.

Generally, Redox Titrations involve Standard Solutions of Oxidants or Reductants; the titrant. The analyte, prepared to be in a single oxidation state, is treated with the Standard Solution such that a change in oxidation state is effected by the Oxidant or Reductant. This change of oxidation state accompanies a change in the Indicator, signaling the endpoint of the titration has been reached.

As an example, aqueous Iron can be analyzed using a redox titration. The Iron can exist in two oxidation states in Water; Fe\(^{2+}\) and Fe\(^{3+}\). An Analysis for aqueous Iron (Fe) might involve pre-treatment of the sample with a pre-reductant to ensure all the Iron is in the Fe\(^{2+}\) oxidation state.

\[
\text{Fe}^{2+}(\text{aq}) \quad \text{&} \quad \text{Fe}^{3+}(\text{aq}) \quad \overset{\text{Pre-Reductant}}{\rightarrow} \quad \text{Fe}^{2+}(\text{aq})
\]

The resulting solution of Ferrous Ions (Fe\(^{2+}\)) can then be titrated with a Standard Permanganate (MnO\(_4^-\)) solution (oxidant) causing the Ferrous Ions to be Oxidized to Ferric Ions (Fe\(^{3+}\)):

\[
5 \text{Fe}^{2+} + \text{MnO}_4^- + 8 \text{H}^+ \rightarrow 5 \text{Fe}^{3+} + \text{Mn}^{2+} + 4 \text{H}_2\text{O}
\]

The endpoint of this redox titration is indicated by a color change from clear to pink; due to the slight excess of purple Permanganate that exists when you add one additional drop of titrant beyond the equivalence point. And, at the equivalence point:

\[
\# \text{ mole Fe} = \frac{5 \text{ mole Fe}}{1 \text{ mole MnO}_4^-} \times V_{\text{std}} \times M_{\text{std}}
\]
In an Iodometric Redox Titration, the analyte is first treated with the Iodide Ion (I$^-$), a weak reducing agent, to produce Elemental Iodine, I$_2$.

\[
\text{Analyte (aq)} + 2 \text{I}^- \rightarrow \text{Reduced Analyte (aq)} + \text{I}_2(\text{aq}) \quad \text{(Eq. 1)}
\]

Note the Iodide is oxidized from an Oxidation State of -1 to an Oxidation State of 0.

The elemental Iodine then combines with any excess Iodide present to produce I$_3^-$, a species that forms a Blue colored complex with Starch:

\[
\text{I}_2(\text{aq}) + \text{I}^- (\text{aq}) \rightarrow \text{I}_3^- (\text{aq}) \quad \text{(Eq. 2)}
\]

This is then titrated with Standardized Thiosulfate (S$_2$O$_3^{2-}$) to reduce the Iodine back to an Oxidation State of -1:

\[
\text{I}_3^- (\text{aq}) + 2 \text{S}_2\text{O}_3^{2-} (\text{aq}) \rightarrow 3 \text{I}^- (\text{aq}) + \text{S}_4\text{O}_6^{2-} (\text{aq}) \quad \text{(Eq. 3)}
\]

What change in Oxidation State does the Sulfur undergo when Thiosulfate is oxidized to Tetrathionate (S$_4$O$_6^{2-}$)?

The endpoint of the titration is detected by using a Starch indicator. Starch, a complex carbohydrate, forms a blue-colored complex with I$_3^-$ ion. So, at the point where the I$_3^-$ is consumed by the titration, the titration solution turns from blue to colorless. The starch indicator is added to the solution near the end of the titration, at the point where dilute iodine imparts a pale yellow color to the solution. There are two reasons why the indicator is not added at the beginning of the titration when the iodine concentration is high. First, a diffuse endpoint would result from the slow dissociation of the starch-iodine complex if a large amount of iodine were absorbed in the starch. Second, iodometric titrations are carried out in strongly acid media, a situation that promotes the reaction between oxidizing agents and iodide. Unfortunately starch has a tendency to hydrolyze (decompose) in acidic media, destroying its indicator qualities.

Other sources of error in iodometric titrations include the decomposition of Thiosulfate and the air-oxidation of excess Iodide by the Oxygen in the Air. Cloudiness, a result of the formation of colloidal Sulfur will indicate the decomposition of Thiosulfate has occurred. In acidic solutions, the decomposition of Thiosulfate is aided by bacterial attack. Therefore, all water and glassware used in the preparation of Thiosulfate solutions should be sterilized to reduce the likelihood of bacterial attack, and the Thiosulfate solution should be stored in a refrigerator to slow microbial growth. The Thiosulfate solution should be discarded if any bacteria or mold growth is observed. However, if the Thiosulfate solution is prepared on the day it is used, these precautions can be neglected. During the titration, the analyte solution should be continuously stirred in order to prevent a local excess of Thiosulfate from building-up. Finally, a large excess of Iodide is added to the analyte solution to encourage the titration reaction to go to completion. Unreacted Iodide does not interfere with the reaction, however Iodide can be air-oxidized if the titration is not performed immediately. Consequently, one should prepare only one analyte sample at a time, and the titration should be completed rapidly to minimize air-oxidation.
In this experiment, the level of Sodium Hypochlorite (NaClO), the active ingredient in Household Bleach, is determined iodometrically by reacting it with an excess of Iodide and then titrating the Iodine produced with Standard Sodium Thiosulfate.

\[
\text{ClO}^-(aq) + 3 \text{I}^-(aq) + 2 \text{H}^+(aq) \rightarrow \text{Cl}^- + \text{I}_3^- + \text{H}_2\text{O} \quad \text{(Eq. 4)}
\]

\[
\text{I}_3^-(aq) + 2 \text{S}_2\text{O}_3^{2-}(aq) \rightarrow 3 \text{I}^- + \text{S}_4\text{O}_6^{2-} \quad \text{(Eq. 5)}
\]

Note the Hypochlorite is reduced to Chloride, Cl\(^+1\) to Cl\(^-1\), in this process.

Bleach, as the name implies, is a substance that will whiten. “Chlorine” bleaches contain Sodium Hypochlorite as the oxidizing agent that causes whitening. Commercial chlorine bleach will be at least 5.25% Sodium Hypochlorite. Other bleaches contain Calcium Hypochlorite (Bleaching Powder) or Peroxides.

In chlorine bleaches, the hypochlorite is in equilibrium with Chlorine:

\[
\text{HClO} + \text{Cl}^- + \text{H}^+ \rightleftharpoons \text{Cl}_2 + \text{H}_2\text{O}
\]

An acidic environment favors the production of Chlorine.

The Thiosulfate titrant solution itself must be Standardized against primary Potassium Iodate (KIO\(_3\)):

\[
\text{IO}_3^-(aq) + 8 \text{I}^- + 6 \text{H}^+(aq) \rightarrow 3 \text{I}_3^- + 3 \text{H}_2\text{O} \quad \text{(Eq. 6)}
\]

\[
\text{I}_3^- + 2 \text{S}_2\text{O}_3^{2-}(aq) \rightarrow 3 \text{I}^- + \text{S}_4\text{O}_6^{2-} \quad \text{(Eq. 7)}
\]

This titration reaction has a (6 mole S\(_2\)O\(_3^{2-}\) / 1 mole IO\(_3^-\)) stoichiometry for the standardization process.
Pre-Lab Calculation

1. Suppose thiosulfate titrant is made as described below and standardized against a 0.0500 M solution of potassium iodate, also as described below. If the initial burette reading is 0.15 mL and the final reading is 29.52 mL, what is the molarity of the sodium thiosulfate titrant? Show all work.

2. Suppose a bleach sample (10.2564 g) is titrated with the standardized titrant from question 2, as described in the procedure below. The initial burette volume is 0.05 mL and the final volume is 30.50 mL. What is the % sodium hypochlorite (NaClO, F.W. 74.4422 g/mol) in the bleach? Show all work.
Procedure

Preparation of Sodium Thiosulfate Titrant

Clean a 1-L bottle with soap, rinse several times with tap water, and then distilled water. Weigh approximately 6.25g sodium thiosulfate pentahydrate crystals, Na$_2$S$_2$O$_3$$\cdot$5H$_2$O. Transfer to the clean 1-L bottle, add about 250 mL distilled water, add 0.025 g sodium carbonate, shake thoroughly until the solution is homogeneous. (A small amount of sodium carbonate is added to keep the solution neutral or slightly alkaline and thereby stabilize it against decomposition to elemental sulfur.)

Standardization of Sodium Thiosulfate Titrant

The thiosulfate solution should be standardized and used on the day it is prepared. Rinse a 50-mL buret several times with small portions of solution and then fill. Adjust the volume to near the zero mark, record the initial volume to the nearest 0.01 mL. Using a volumetric pipet, add a 10-mL aliquot of the 0.0500M Potassium Iodate solution provided for you to a clean 250-mL Erlenmeyer flask. Add about 2 g solid potassium iodide, swirl to dissolve. Add, with rapid mixing, 5 mL of 6M H$_2$SO$_4$. Mix thoroughly. Prepare only one sample at a time.

Titrate immediately with the thiosulfate solution, being sure to continuously swirl the solution. Titrate until the solution becomes a pale yellow color. Add 2 – 3 mL starch solution, titrate until the blue color just disappears (this should occur about 0.5 mL after adding the starch solution). The starch is not added until just before the endpoint is expected, because otherwise the high concentration of Iodine produces a reddish color that does not disperse at the endpoint.

Repeat the standardization with two more samples. Calculate the average molarity and standard deviation of your Na$_2$S$_2$O$_3$ solution.

Determination of Hypochlorite in Bleach

Choose one brand of commercial bleach and record its name and reported percentage active ingredient on the label.

Prepare each sample one at a time. Weigh approximately 10 g bleach unknown and transfer to a clean 250-mL volumetric flask. Dilute to the mark with distilled water and mix thoroughly. Using a volumetric pipet, transfer 3 50-mL aliquots of the bleach solution to individual Erlenmeyer flasks containing 50 mL distilled water.

Prepare each of the three samples immediately before titration. Add ~10 mL glacial acetic acid and ~2 g KI to the sample and mix thoroughly. Titrate immediately with the standardized Na$_2$S$_2$O$_3$ solution, swirling the flask constantly. When the color has faded to a pale yellow, add about 2 mL starch solution and continue the titration drop-by-drop until the solution just becomes colorless. Repeat with the two additional unknown samples.

Calculate the w/w% Sodium Hypochlorite present in your unknown bleach sample.