Reading assignment: Burdge, Chemistry 4th edition, section 4.6.

Goals

We will study an example of a redox titration in order to determine the concentration of sodium hypochlorite, the active ingredient in commercial bleach.

Safety Note: Safety glasses and laboratory coats are required when performing this experiment

Equipment and Materials

50.00-mL buret, 250-mL volumetric flask, 25.00-mL volumetric pipette, pipette pump, 200-mL or 300-mL Erlenmeyer flask, 10-mL graduated cylinder, 100-mL graduated cylinder, 100-mL beaker, commercial bleach solution (4-6% hypochlorite), 10% potassium iodide solution (KI), 2.0-M hydrochloric acid solution (HCl), ~0.26 M sodium thiosulfate solution ($Na_2S_2O_3$), starch solution.

Discussion

An aqueous solution of sodium hypochlorite (NaOCl) is a slightly yellow liquid, and is commonly known as bleach. Aside from its uses as a bleaching agent, sodium hypochlorite solutions are also used as sterilizing agents and in water treatment. Industrial uses include agriculture, food, paper production, and textiles. Sodium hypochlorite is also added to waste water to reduce odors.

The concentration of sodium hypochlorite in bleach solutions can be determined by titration. A desirable method would be to find a titrant that reacts with NaOCl to form a colored product. But there are no simple colorimetric titrant-indicator systems that work well. Therefore, we must use a multi-step method to titrate sodium hypochlorite.

In the first step sodium hypochlorite, hydrochloric acid, iodide ion, and starch are combined to form a starch–triiodide complex. In this step there are three reactions that take place:

(1) Hydrochloric acid reacts with sodium hypochlorite to form hypochlorous acid:

$$\mathrm{NaOCl(aq) + HCl(aq) \longrightarrow \underset{\text{hypochlorous acid}}{HOCl(aq)} + NaCl(aq)}$$

(2) Hypochlorous acid reacts with iodide when the solution is acidic:

$$\mathrm{HOCl\ (aq) + HCl\ \ (aq) + 3I^{-}\ (aq) \longrightarrow \underset{\text{triiodide}}{I_3^{-}}\ (aq) + 2Cl^{-}\ (aq) + H_2O\,(l)}$$

Tridiodide, I_3^-, is a dark red complex. A dark blue complex is formed when triiodide is combined with starch.

(3) $$\underset{\text{triiodide ion}}{I_3^{-}} + \text{starch} \rightarrow \underset{\text{triiodide starch complex (dark blue)}}{[I_3^{-}][\text{starch}]}$$

The result of these three reactions is that when sodium hypochlorite is present the starch-triiodide complex is produced. This is useful because the result of these three reactions is the formation of a dark blue complex that has a concentration that is proportional to the amount of sodium hypochlorite in the solution.

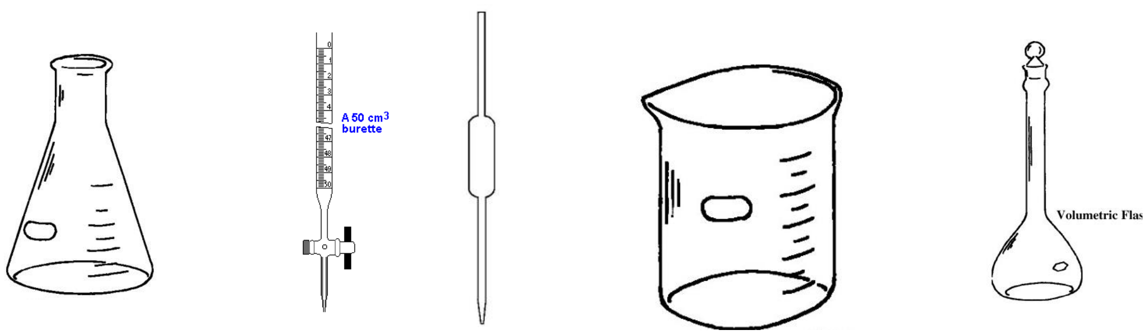
In the next step, the starch-triiodide product is titrated by sodium thiosulfate to form a colorless solution of iodide, dithionate, and uncomplexed starch:

(4) $$\underset{\text{triiodide starch complex (dark blue)}}{[I_3^{-}][\text{starch}]} + \underset{\text{thiosulfate}}{2S_2O_3^{2-}} \longrightarrow \underset{\text{iodide ion colorless}}{3I^{-}} + \underset{\text{dithionate}}{S_4O_6^{2-}} + \text{starch}$$

If iodide is added in excess to the hypochlorous acid then all of the hypochlorous acid will be reacted, forming the dark blue starch-triiodide complex. The hypochlorite acts as a limiting reagent, determining how much triiodide is produced. We can then titrate the triiodide-starch complex with the thiosulfate to determine the concentration of the complex formed. This can then be used to calculate the initial concentration of hypochlorite.

Procedure

SAFETY PRECAUTIONS
Safety glasses or goggles must be worn throughout this experiment. Bleach is a strong oxidizing agent and should be washed from skin. Bleach can also damage clothing. For that reason, take care not to splash any of the bleach solution on clothing.



300 mL Erlenmeyer Flask	50 mL buret	25 mL volumetric pipet	beaker	250 mL volumetric flask

1. Students perform titrations individually. Dilution of the bleach (Step 3 below) can be performed in pairs.

2. Obtain about 60 mL of sodium thiosulfate solution using a clean and dry 100-mL beaker. Record the concentration of this solution on the Data Sheet. Rinse a 50-mL buret with tap water and then distilled or deionized water. Rinse the buret with a few milliliters of the sodium thiosulfate solution. Fill the buret to just above the 0 mL mark with sodium thiosulfate solution. Allow a few milliliters to pour through the buret tip so that any trapped air can be flushed through. Read and record the initial buret level to the nearest 0.05 mL.

3. Perform a 10-fold quantitative dilution of bleach. This step can be performed with a partner and the diluted bleach shared. Use a clean 25-mL volumetric pipet to deliver 25.00 mL of bleach solution into a clean 250-mL volumetric flask. Add distilled or deionized water to the mark of the volumetric flask. Be sure to mix the solution well to ensure that it is homogeneous. The bleach should now be one-tenth its original concentration and can be used in your titrations. Rinse the pipet with distilled or deionized water to remove the bleach solution.

4. The titration takes place in a large Erlenmeyer flask. Using the 25-mL volumetric pipet, carefully add 25.00 mL of diluted bleach (from Step 3) to the Erlenmeyer flask.

5. Using a 100-mL graduated cylinder, add about 15 mL of distilled or deionized water to the reaction flask.

6. Using a 100-mL graduated cylinder, add about 20 mL of 10% potassium iodide solution to the reaction flask.

7. Pour about 2 mL of starch solution in a 10-mL graduated cylinder. This starch solution will be added to the Erlenmeyer flask later.

8. Using a 100-mL graduated cylinder, add about 20 mL of hydrochloric acid solution to the reaction flask. Begin the titration promptly after adding this solution to the mixture.

9. Begin titrating the bleach solution with sodium thiosulfate solution. Add the thiosulfate solution to the Erlenmeyer flask while swirling until the solution in the flask becomes a pale yellow color. Be sure not to add so much that the solution becomes clear. You are looking for a pale yellow color. Once the solution turns pale yellow get the starch solution ready. Don't write down the volume on the burette at this point; you'll be adding more thiosulfate solution in a few moments. There may be a dark precipitate of crystals of solid iodine if you are slow in getting to this stage.

10. Add the 2 mL of starch solution from the graduated cylinder to the Erlenmeyer flask. The color of the solution should now be dark blue.

11. Continue the titration dropwise (this means one drop at a time, slowly) with constant swirling until the solution becomes clear. This clear solution signals the endpoint of the titration. Record the buret volume level in the data sheet to the nearest 0.05 mL. The contents of the Erlenmeyer flask should be poured into the proper waste container.

12. Perform two more titrations by repeating steps 3-11. You may need to use the same Erlenmeyer flask.

13. The density of the bleach solution should be measured or given to you by the instructor.

14. After completing your final titration pour any unused reagents into the appropriate waste container. The buret should be rinsed with distilled or deionized water. All glassware should be returned to the appropriate location.

Calculations

To calculate the molarity of the sodium hypochlorite solution we use the titration volume, molarity of the thiosulfate titrant, stoichiometry of the reactions, and volume of the sample of diluted bleach solution.

1. Calculate the number of moles of titrant (sodium thiosulfate) for each titration:

$$\text{moles} \quad Na_2S_2O_3 = \left(\text{molarity of } Na_2S_2O_3 \text{ solution}\right) \ \text{x} \ \left(\text{volume of } Na_2S_2O_3 \text{ solution}\right)$$

2. The moles of hypochlorite are found from the stoichiometry of the reaction with thiosulfate. The stoichiometry of the equation shows that there are two moles of thiosulfate ion per mole of hypochlorous acid. Note that the moles of HOCl are equal to the moles of NaOCl and OCl^-.

$$H^+(aq) + HOCl(aq) + 2S_2O_3^{2-}(aq) \longrightarrow S_4O_6^{2-}(aq) + Cl^-(aq) + H_2O(aq)$$

$$\text{moles HOCl} = \text{moles } S_2O_3^{2-} \ \text{x} \left(\frac{1 \text{ mol HOCl}}{2 \text{ mol } S_2O_3^{2-}}\right)$$

3. The bleach solution that we titrated was diluted by a factor of 10. Multiply the moles of the hypochlorous acid by 10 to take this factor into account. This will give the number of moles of HOCl in 25.00 mL of undiluted bleach.

4. Sodium hypochlorite (NaOCl) is the form of the hypochlorite that is reported on bleach bottles, not hypochlorous acid. The sodium hypochlorite mass percent is found from the mass of sodium hypochlorite in 25.00 mL and the mass of the 25.00 bleach solution:

$$\text{mass } \% = \left(\frac{\text{mass of NaOCl}}{\text{mass of bleach solution}} \right) \text{ x } 100$$

5. The mass of the NaOCl is found from the moles of NaOCl and the molar mass of NaOCl:

$$\text{mass of NaOCl} = (\text{moles of NaOCl}) \text{ x } (\text{molar mass of NaOCl})$$

6. The mass of 25.00 mL of bleach solution is found from its density and the volume (25.00 mL):

$$\text{mass of bleach solution} = (\text{density of bleach}) \text{ x } (\text{volume of solution})$$

7. Perform a Q test on your mass percent values and calculate an average mass percent concentration. How close is your result to the value listed on the bottle?

N	3	4	5
Q*	0.970	0.829	0.710

*95% confidence

$$Q_{calc} = \left| \frac{gap}{range} \right|$$

Observations and Notes

The Determination of Hypochlorite in Bleach

Date ______________

Name_______________________________

Table 1: Reagent Data

Brand name of bleach	____________________
Density of bleach	____________________ $g \cdot mL^{-1}$
Volume of diluted bleach used in each titration	____________________ mL
Concentration of sodium thiosulfate	____________________ $mol \cdot L^{-1}$

Titration Data

	Trial 1	Trial 2	Trial 3
Final buret volume	____________ mL	____________ mL	____________ mL
Initial buret volume	____________ mL	____________ mL	____________ mL
Volume delivered	____________ mL	____________ mL	____________ mL
Volume delivered (L)	____________ L	____________ L	____________ L

Calculations

Moles of $Na_2S_2O_3$ in titration	____________	____________	____________
Moles of NaOCl in titration	____________	____________	____________
Moles of undiluted NaOCl	____________	____________	____________
Mass of 25.00 mL of NaOCl	____________ g	____________ g	____________ g
Mass of 25.00 mL bleach solution	____________ g	____________ g	____________ g
Mass % of NaOCl from experiment	____________	____________	____________
Average mass % of NaOCl from experiment (Q test)	____________		

Mass % of NaOCl from label ______________