Halogens and Their Compounds

Introduction

The chemistry of the halogens and their compounds is extraordinarily rich and complex. Although the free elements are far too reactive to be naturally occurring, all the halogens are manufactured industrially and have a wide variety of uses. Chlorine ($\text{Cl}_2$) ranks in the top ten of industrial chemicals with an annual production of about 20 billion pounds, most of which is generated by the electrolysis of brine (concentrated sodium chloride) by the chloralkali industry. More than 50% of this production of free chlorine is utilized in the manufacture of other chemicals — e.g., dry-cleaning fluids, pharmaceuticals, refrigerants, herbicides, pesticides, and plastics (primarily, polyvinylchloride, or PVC). Other major uses are as a bleach in the paper and textile industries and as a disinfectant in municipal water supplies and sewage treatment. The use of chlorine for disinfection of water is largely responsible for the almost complete eradication of water-borne diseases — e.g., cholera and hepatitis — that plagued societies for centuries. The active chemical that kills bacteria in disinfection is not chlorine, but hypochlorous acid ($\text{HClO}$), which is formed from the reaction of chlorine gas with water:

$$\text{Cl}_2(\text{g}) + \text{H}_2\text{O} \rightarrow \text{HCl} + \text{HClO}$$

Uncharged hypochlorous acid can then diffuse easily through bacterial cell walls and destroy the enzyme system of the pathogen.

Fluorine ($\text{F}_2$) is industrially produced by electrolysis in a molten salt reaction because the process must be carried out in the absence of water. Fluorine is extremely reactive and very dangerous; the technology to produce, store, transport, and use it originated primarily from the production of fissionable uranium for atomic bombs. Fluorine is used to produce many products that contain carbon-fluorine covalent bonds. The chlorofluorocarbons, known by the trade name Freons, are nontoxic, inert, and nonflammable and are extensively used as heat transfer fluids in refrigerators and air conditioners. Unfortunately, there is definite evidence that Freons are not inert in the stratosphere, and it has been shown that photochemical breakdown of these compounds produces chlorine radicals that catalytically destroy ozone. Recently, there has been unprecedented international agreement to phase out the production of chlorofluorocarbons and to carry out research to find substitutes for these fluids. The stability of carbon-fluorine bonds is also utilized in a variety of nonstick coatings, such as Silverstone®. These coatings...
are fluorocarbon polymers, such as Teflon (polytetrafluoroethylene), and are extremely inert and resistant to high temperatures.

The halides, such as sodium chloride, iodide, and calcium fluoride, are by far the most common halogen compounds found in nature. The oceans contain a remarkably constant concentration of common salt (sodium chloride), with very much smaller concentrations of various bromides and fluorides. It is interesting to note that the salt composition of the ocean is the result of a gigantic, global, acid-base titration between acids that have leaked out of the interior of the earth (e.g., HCl) and bases that have been set free by the weathering of primary rock. The production of common table salt for human consumption was undoubtedly one of the first chemical industries. It has been argued that the earliest roads were made for the transportation of salt and that the earliest cities were established as centers of the salt trade. Sources of salt have even been the object of military campaigns! Sodium chloride is certainly one of the most important electrolytes in body fluids, particularly in blood plasma and interstitial fluid. The addition of small amounts of other halides (e.g., iodide and fluoride) in the human diet is also now very common. Iodide ion is necessary for the production of thyroxine in the thyroid gland, and an insufficiency of iodide ion in the diet leads to a condition known as goiter. To assure the presence of enough iodide ion in the diet, sodium or potassium iodide is often added to table salt. The fluoridation of water is now a relatively common practice. At the very low concentration of one part per million, fluoride ion helps prevent tooth decay without causing discoloration.

One of the most controversial aspects of halogen chemistry is the toxicity problem associated with many of the organic compounds containing carbon-halogen bonds. Halogenated hydrocarbons, such as chloroform, the Freons mentioned earlier, ethylene dibromide in gasoline, DDT, PCB, and PBBs, have all been shown to be toxic in animal systems. Although the complete biochemistry is not yet clear, it seems that the damaging effects are caused as the carbon-halogen bond is broken down in the liver, forming toxic substances. The knowledge of the potential health problems of these halogenated products has led to limits and, in some instances, a complete ban in production of these substances.

It is hoped that you have gained a perspective on the incredible diversity and importance of the chemistry of the halogens and their compounds from this brief introduction. The experiments that follow can only touch the surface of this area of science, but they do represent some of the major principles of halogen chemistry.

---

**Background Chemistry**

- The elements in the halogen group are all nonmetals that exist at normal temperatures and pressures as diatomic molecules. The trends in properties expected for a family of elements in the periodic table are very evident in the halogens, as can be seen in Table 1.
- The outstanding characteristic of the halogens is the large number of compounds they form with other elements. In chemical reactions, the halogens readily accept one electron per halogen atom to form singly charged anions (e.g., F\(^-\) and Cl\(^-\)) or readily share their single,
Astatine, the other member of the halogen group, does not appear in Table 1 because it is extremely radioactive and has never been obtained in the pure form. An unpaired electron to form covalent bonds. As a result of this strong tendency to attract electrons, the halogens are all strong oxidizing agents. Fluorine (F₂), the first member of the family, is somewhat different from the other halogens primarily because of the small size and very high electronegativity of the fluorine atom. Fluorine is the most reactive of all the nonmetals and is one of the strongest oxidizing agents known. Fluorine cannot be prepared in aqueous solutions because it reacts rapidly with water:

\[ 2F_{2(g)} + 2H_2O \rightarrow 4HF + O_{2(g)} \]

Chlorine, bromine, and iodine all undergo redox reactions with water. For example, chlorine, with an oxidation number of 0, reacts as follows:

\[ Cl_2 + H_2O \rightarrow HCl + HClO \]

In this reaction, it can be seen that in one product, HCl, the oxidation number is -1, and in the other, HClO, the chlorine has an oxidation number of +1. As a result, a saturated solution of chlorine in water (chlorine water) is about 30% hypochlorous acid (HClO). The disinfectant properties of chlorine when used in water and sewage treatment are due to the presence of the hypochlorous acid, which is also a powerful oxidizing agent. Commercial liquid bleach is made by bubbling chlorine into sodium hydroxide solution:

\[ Cl_2 + 2NaOH \rightarrow NaCl + NaOCl + H_2O \]

In the resulting reactions, the active ingredient is sodium hypochlorite (NaOCl). Iodine has the unique property of reacting with excess iodide in aqueous solution to give the triiodide ion

\[ I_2 + I^- \rightarrow I_3^- \]

This ion has the very unusual property of reacting with soluble starch to give a blue-black-colored complex in which I₅⁻ and additional I₂ molecules form I₅⁻ chains:

\[ I_5^- + I_2 \rightarrow [I-I-I-I-I]^- \]
These I₅⁻ chains just happen to be the right size to fit down the middle of the amylose sugar helix (pictured in Figure 1).

Figure 1 The Starch-Iodine Complex

The pronounced color of this complex has led to its use as an excellent detection reaction for iodine and for oxidizing agents that can oxidize I⁻ to I₂.

One of the most common types of reactions of the halogens is the formation of halides in which each halogen atom gains one electron to become F⁻, Cl⁻, Br⁻, or I⁻. Almost all metals, metalloids, and nonmetals will react with halogens to produce halides. The properties of halides vary tremendously depending on which element enters into combination with the halogen. Alkaline metal halides (e.g., sodium chloride) are ionically bonded, white, crystalline solids that are very soluble in water and dissociate to give hydrated ions. Nonmetal halides (e.g., phosphorus trichloride) are generally covalent compounds with polar covalent bonds because of the high electronegativity of the halogen atom. The combination of halogens with carbon produces covalent organic compounds, many of them having properties that make them useful as solvents, refrigerants, anesthetics, pesticides, and plastics.

There are many compounds in which the halogen atoms have a positive oxidation number, the great majority of them in the form of oxyanions and oxyacids. Table 2 shows most of the known compounds of this type, together with the nomenclature and some examples of common stable salts.

<table>
<thead>
<tr>
<th>Oxyacid</th>
<th>Name</th>
<th>Can it Be Isolated?</th>
<th>Oxidation No. of Halogen</th>
<th>Example of Salts</th>
</tr>
</thead>
<tbody>
<tr>
<td>HClO</td>
<td>hypochlorous acid</td>
<td>no</td>
<td>+1</td>
<td>hypochlorites, (NaClO)</td>
</tr>
<tr>
<td>HBrO</td>
<td>hypobromous acid</td>
<td>no</td>
<td>+1</td>
<td>hypobromites (not stable)</td>
</tr>
<tr>
<td>HIO</td>
<td>hypoiodous acid</td>
<td>no</td>
<td>+1</td>
<td>hypoiodites (not stable)</td>
</tr>
<tr>
<td>HClO₂</td>
<td>chlorous acid</td>
<td>no</td>
<td>+3</td>
<td>chlorites (not stable)</td>
</tr>
<tr>
<td>HClO₃</td>
<td>chloric acid</td>
<td>no</td>
<td>+5</td>
<td>chlorates (KClO₃)</td>
</tr>
<tr>
<td>HBrO₃</td>
<td>bromic acid</td>
<td>no</td>
<td>+5</td>
<td>bromates (NaBrO₃)</td>
</tr>
<tr>
<td>HIO₃</td>
<td>iodic Acid</td>
<td>yes</td>
<td>+5</td>
<td>iodates (KIO₃)</td>
</tr>
<tr>
<td>HClO₄</td>
<td>perchloric acid</td>
<td>yes</td>
<td>+7</td>
<td>perchlorates (LiClO₄)</td>
</tr>
<tr>
<td>HBrO₄</td>
<td>perbromic Acid</td>
<td>no</td>
<td>+7</td>
<td>perbromates (KBrO₄)</td>
</tr>
<tr>
<td>HIO₄</td>
<td>periodic acid</td>
<td>yes</td>
<td>+7</td>
<td>periodates (KIO₄)</td>
</tr>
</tbody>
</table>

From CHEM/100K: Small Scale Experiments for General Chemistry, Stephen Thompson. Copyright © 1990 by Stephen Thompson. Published by Prentice-Hall, Inc. All rights reserved.
Section A  From Fluorine to Astatine: A Basic Introduction to the Halogens

Objectives

To become familiar with some of the structures, properties, and reactions of the halogens (listed in the table below).

Caution: All of the halogens are very toxic and should be handled with great care — even iodine!

Even though you will be working with extraordinarily small amounts of all the materials in this series of experiments, please be careful. Sulfuric acid is corrosive, and silver compounds will turn the skin black. If you get any of these chemicals on your skin, wash well with cold water and check with your instructor.

Group VIIA

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
<th>Atomic No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>fluorine</td>
<td>9</td>
</tr>
<tr>
<td>Cl</td>
<td>chlorine</td>
<td>17</td>
</tr>
<tr>
<td>Br</td>
<td>bromine</td>
<td>35</td>
</tr>
<tr>
<td>I</td>
<td>iodine</td>
<td>53</td>
</tr>
<tr>
<td>At</td>
<td>astatine</td>
<td>85</td>
</tr>
</tbody>
</table>

Discussion

This family of elements, collectively called the halogens, represents one of the most typical group of nonmetallic elements in the periodic chart. The electron configurations of the halogens reveal that each element in this group has 7 valence electrons, one short of an octet.

- Write the electron configuration for an atom of chlorine.
- Which are the valence electrons?

At normal temperatures and pressures, all the halogens form diatomic molecules in which they complete their octet by sharing electrons.

- Write the chemical formula for a molecule of iodine and draw its Lewis structure.

At room temperature and pressure, fluorine and chlorine are gases, bromine is a red-brown liquid, and iodine is a shiny black solid that sublimes readily to give a violet vapor. Astatine is so radioactive that it has never been isolated in the pure form. The longest-lived isotope (\(^{210}\)At), has a half-life of 8.3 hours.

- Why should a group of elements exhibit a progression from the gaseous to the solid state?
- Explain why the halogens are so reactive.

Although the halogens form a family (Group VIIA in the Periodic Chart) with periodic properties, fluorine (F\(_2\)) the first member, exhibits some differences from the other elements. These differences are largely due to the small size and high electronegativity of the fluorine atom. F\(_2\) is extraordinarily reactive because of the very strong tendency to grab electrons and become fluoride ion F\(^-\).
If a metal such as sodium is exposed to gaseous fluorine, there is an instantaneous violent reaction that produces a white saltlike product. The reaction is

\[ 2\text{Na}_6 + \text{F}_2 \rightarrow 2\text{Na}^+ + 2\text{F}^- \]

This is an example of a redox reaction in which the Na atom has lost an electron in becoming a Na\(^+\) ion:

\[ 2\text{Na} \rightarrow 2\text{Na}^+ + 2e^- \]

This part of the reaction is a loss of electrons (by Na) and is called oxidation. The fluorine atoms in F\(_2\) each gained an electron to become fluoride ions F\(^-\):

\[ \text{F}_2 + 2e^- \rightarrow 2\text{F}^- \]

This gain of electrons by F\(_2\) is called reduction. If the two parts, reduction and oxidation, are added up, we obtain the redox reaction table:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Oxidation</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>2Na \rightarrow 2Na(^+) + 2e(^-)</td>
<td>oxidation</td>
<td>2Na \rightarrow 2Na(^+) + 2F(^-)</td>
</tr>
</tbody>
</table>

Note: The product is the ionically bonded salt sodium fluoride (NaF).

One more piece of jargon — but a useful one. In the above redox reaction, the chemical species that grabs the electrons (F\(_2\)) is called the oxidizing agent, and the species that gives the electrons (Na) is called the reducing agent. F\(_2\) is one of the most powerful oxidizing agents known.

Fluorine is far too nasty to make in this laboratory, but you can at least write some of its reactions.

- Write a balanced net ionic equation for the reaction between F\(_2\) and Cl\(^-\). Divide the reaction into 2 parts and decide which is reduction and which is oxidation.
- What species is the reducing agent in this reaction?

When aluminum metal is heated and dropped into fluorine gas, there is an explosion.

- Write the equation for this reaction.
- What color do you think the product is?

## Section B  The Synthesis and Reactions of Chlorine

**Objectives**  
(1) To carry out a microscale preparation of chlorine gas (Cl\(_2\))  
(2) To investigate some of its redox reactions.
Discussion  

The solutions you will need for this experiment and the following experiments can be found in the 24-well tray or at Reagent Central. At your place is a plastic reaction surface that provides a white and a black background for viewing the chemistry. The synthesis of gases will be done in a plastic petri dish, which acts as a miniature environmental chamber.

The chemical reaction for the synthesis of chlorine is the action of dilute acid (hydrochloric acid) on commercial bleach solution (e.g., regular Clorox®). Bleach (according to the label) is 5.25% active ingredient, which is sodium hypochlorite (NaOCl), and 94.75% inactive ingredient, which is presumably water. The reaction equation is

\[ \text{NaOCl} + 2\text{HCl} \rightarrow \text{Cl}_2(g) + \text{NaCl} + \text{H}_2\text{O} \]

It is worth noting that the misuse of bleach solutions in household situations is common enough to warrant a hazardous chemical warning on the label. The label reads: “Strong oxidizer. Flush drains before and after use. Do not use or mix with other chemicals, such as toilet bowl cleaners, rust removers, acid- or ammonia-containing products. To do so will release hazardous gases.”

Procedure

1. Place the petri dish onto the plastic surface against a white background.
2. Drop 1 drop of diluted bleach solution (already diluted to 50%) into the center of the dish.
3. In a circle around the drop of bleach, drop separately 1 drop of 0.1M KI (potassium iodide), 1 drop of dye (bromocresol green), and 1 drop of starch/0.1M KI solution.
4. Also place in the dish, close to the center, a small circle of filter paper that has been wet with 1 drop of 0.1M KI and that has had the excess liquid removed by dabbing it with a piece of folded microtowel.

Note: The paper circles are in a box at Reagent Central.
5. Get ready to put the top on. Drop 1 drop of HCl onto the bleach solution. Quickly put the top on.

- Watch and record what happens.
- Make a picture of which solution is where — it’s easy to get them mixed up.
- From your observations, what can you deduce about the gases?
Caution: Do not add the NH₃ to any of the other drops.

- Describe carefully the appearance of the filter paper circle.
  What must be happening here?
  Chlorine gas is still present in excess in the dish!
- Describe the color change of the dye.

Note: This reaction is typical of the oxidizing power of chlorine towards organic dyes in general.

6. Terminate the reaction by adding 1 drop of 2M NH₃ to the dish.
7. Place the petri dish onto a black background.
- Describe what happens.

Note: You have formed an aerosol of ammonium chloride (NH₄Cl) that consists of tiny white particles of the salt settling on the plastic surface.

8. Flood the dish by adding distilled water from your wash bottle.
  Swirl to dilute the remaining drops.
9. Pour the liquid into the waste cup.
10. Wash thoroughly with tap water at the sink.
11. Rinse once with distilled water, and dab dry with a microtowel.

Section C  A Small-Scale Pilot Plant for the Manufacture of Chlorine by the Industrial Process

Objectives  ▶ To construct a small-scale pilot plant for the manufacture of chlorine.

Discussion  ▶ Chlorine is manufactured on a very large scale by the electrolysis of sodium chloride solution (brine). 
  Electrolysis is a process in which a redox reaction is made to occur by means of an outside source of electrical energy in the form of direct current. 
  The design of the pilot plant is critical because it is necessary to separate the two products of the electrolysis — chlorine gas and sodium hydroxide — before they can react and disappear.

Procedure

The pilot plant is pictured in the following diagram. Refer to the diagram as you complete each step to ensure that your pilot plant is built properly.

Note: The design features of the pilot plant have been carefully chosen to duplicate those in the industrial process.
1. Obtain pins and pencil lead from Reagent Central.
2. To construct the plant, cut 3 straw pieces, 1 piece about 8 cm long, and 2 pieces about 6 cm long.
3. Use your 1/4" punch to make 2 holes about 0.5-0.7 cm apart in the 8 cm straw.
4. Push the short straws through the holes in the long straw.
5. Make a hole in one of the 6 cm straws with the pin so that you can insert the pencil lead without breaking it.
6. Now push the pin into first the 8 cm straw and on through the other 6 cm straw.

**Note:** The pencil lead and pin in the straws is the electrode system. The pin is the cathode, defined as the place where reduction occurs. The pencil lead is the anode, defined as the place where oxidation occurs.

7. Fill a clean well of a 24-well tray about 3/4 full with brine. Add 3 drops of dye (bromocresol green) to the brine and stir.
8. Dip the electrode system into the brine.
9. Clip the alligator clips to the electrodes but do not attach the clips to the battery yet.
10. Place a small drop of starch/KI solution on the wall inside each straw (about 1 cm down).
11. Place a cap on the anode straw.
12. Now attach the clips to the battery.
   - Report your observations.

13. Remove one clip from the battery terminal after 3 or 4 seconds (or you will generate too much chlorine gas).
   - Now write the part of the redox reaction that is occurring at the **anode**.
   - What evidence do you have for the reaction?

The part of the redox reaction at the **cathode** is the reduction of water:
\[2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-\]

- Explain why the indicator dye in the brine changed color.
- Explain carefully how the products of the electrolysis reaction were kept from reacting with each other.
- Write the equation for the redox reaction accomplished during this electrolysis.

14. Terminate by unclipping all clips.
15. Lay the wires to one side.

*Note:* Try not to get brine on the clips or they will corrode!

16. Carefully lift off the cap, add 1 drop of \(\text{NH}_3\) to it, and put it back on the same straw.

- What will be formed in the straw?

17. Leave the straw for a few minutes and then clean up. Remove the pencil lead, wash it, wipe it with a towel, and retain for the next experiment. Put the straw pieces into the waste straw box.

## Section D  
Electrochemical Writing with a Halogen

**Objectives**  
To carry out an electrolysis to generate iodine by using a pencil lead as a stylus.

**Discussion**  
This experiment is an interesting variation on the electrolytic production of a halogen that you just completed.

**Procedure**

1. Obtain a piece of aluminum foil and a piece of filter paper from Reagent Central.
2. Lay the foil down on the plastic surface and place the paper on top of it.
3. Drop 2 or 3 drops of starch/KI solution onto the paper. Let it spread out into the pores of the paper.
4. Clip one electrical wire to the edge of the foil. Clip the pencil lead to the other wire.
5. Decide how you are going to clip the wires to the battery and which electrode will be the stylus, then do so.
6. Make contact between the stylus and the paper and write your name.
7. Unclip the battery.
8. With your tweezers, turn the paper over and add 1 drop of dye solution (bromocresol green) to the paper.

- Write the redox equation and the two parts that are the reduction and the oxidation.
- Is the aluminum foil the cathode or the anode in this experiment?

Section E  Precipitation Reactions and Titration of a Halide

Objectives  ► To investigate, both qualitatively and quantitatively, the reaction of halides with silver nitrate (AgNO₃) to produce sparingly soluble silver halides as precipitates.

Discussion  ► The precipitation reactions are the basis for a simple quantitative analysis of halides by means of volumetric titrations.

Procedure

1. Use the plastic surface with a black background to carry out a dropwise study of the reaction of silver nitrate solution with HCl, NaCl, KBr, and KI solutions.

- Describe colors and textures and write the net ionic equations wherever you see a chemical reaction.

In this next experiment, you are going to be doing a quantitative volumetric experiment as accurately as possible. This means that all the drops used in the reaction have to be exactly the same volume.

Note:  The only way to insure this is to use the same microburet for all solutions. Good wash and transfer technique is critical to obtaining accurate results.

2. Clean and dry a well in the 24-well tray.
3. Transfer about 1 mL of 0.1M NaCl solution to the well.
4. Wash a microburet several times with distilled water and expel all water. Suck up a little NaCl solution, roll it around the bulb to wash the bulb completely, then expel it. Now suck up the rest of the NaCl solution.
5. Carefully clean a 1 × 12 well strip.
6. Now drop 1 drop of the 0.1M NaCl solution from the microburet into each of the 12 wells, making sure that the drop actually drops into the well.
7. Add 1 drop of 1% potassium chromate indicator solution to each well.

*Note:* The volume of this solution is not critical, so just go ahead and use the dropper that the solution is in.

8. Expel the NaCl solution from the microburet, wash it several times with distilled water, and then use good transfer technique to rinse and fill it with some 0.02M AgNO₃ solution.

9. Now you're ready to carry out a serial titration. This involves adding 1 drop of AgNO₃ to the first well, 2 drops to the second, and so on. Stir the solution in each well with a microstirrer.

- Describe what you see and report the number of drops of 0.02M AgNO₃ required to make the indicator change color.

The overall chemical reaction for this titration is

\[
\text{NaCl} + \text{AgNO}_3 \rightarrow \text{AgCl}_{(s)} + \text{NaNO}_3
\]

with a simple 1:1:1 stoichiometry.

10. The reddish-brown color that occurs at the *endpoint* is due to the precipitation of silver chromate,

\[
\text{K}_2\text{CrO}_4 + 2\text{AgNO}_3 \rightarrow \text{Ag}_2\text{CrO}_4_{(s)} + 2\text{KNO}_3
\]

which will only occur when all the chloride ion has reacted with silver ion, and there is an excess of AgNO₃ in the solution.

- What is the limiting reagent in the titration before the endpoint?

This precipitation titration (sometimes called a Mohr titration) is a quantitative analysis for the halide (NaCl), provided the exact concentration of the titrant (AgNO₃) is known.

- Calculate the molarity of the NaCl solution.

11. 1 × 12 well strip thoroughly with water. If any solid remains, add 1 drop of NH₃ and remove with a cotton swab. Place swab in waste solution to dilute the ammonia, then wash again with cold water.

Section F  Redox Analysis of Commercial Bleach

**Objectives**

- To carry out an analysis of a commercial chlorine bleach.

**Discussion**

- The sodium hypochlorite (NaOCl) in bleach is allowed to oxidize I⁻ to I₂. The I₂ concentration formed in this reaction can be determined
by titration with sodium thiosulfate (Na$_2$S$_2$O$_3$) solution using starch as an indicator.

**Procedure**

*Note:* Again, this experiment is a quantitative volumetric analysis and you must be careful to use good wash, rinse and transfer techniques and the same microburet for the dilutions and titration. Commercial bleach (e.g., Clorox$^\text{®}$) is available in a plastic bottle at Reagent Central.

1. Fill a clean, dry well in a 1 × 12 well strip with bleach.
2. Clean a microburet and suck some of the bleach up into the microburet.
3. Carry out a 10-fold dilution of the bleach by dropping 2 drops onto the plastic surface.
4. Wash the microburet several times with water and fill it 1/2 full with distilled water.
5. Add 18 drops of water to the 2 drops of bleach.
6. Expel the water from the microburet and suck up the diluted bleach solution from the surface. If you like, you can easily assure that it is mixed by expelling and sucking up again.
7. Drop 1 drop of the diluted bleach solution in 2 places on the plastic.

*Note:* You can do duplicate titrations very easily by this method!

8. Expel the diluted bleach solution from the microburet into a waste cup.
9. Wash the microburet thoroughly with water and use good wash and rinse technique to fill it 1/2 full with 0.01M Na$_2$S$_2$O$_3$ solution.
10. Now carry out a "pool" titration on the plastic by adding 1 drop of acetic acid and 2 drops of starch/KI solution to one of the drops of diluted bleach solution on the plastic. Stir and leave the stirrer lying in the pool.
11. Titrate the blue-black pool with the 0.01M Na$_2$S$_2$O$_3$ with constant stirring.

*Note:* Don’t forget to count drops of titrant as you go!

12. Do the same titration on the duplicate sample.

The chemistry is a little complicated, but its not too bad. Here are the reactions that occur. First, the bleach oxidizes the I$^-\text{ to I}_2$:

$$\text{ClO}^- + 2\text{I}^- + 2\text{H}^+ \rightarrow \text{Cl}^- + \text{I}_2 + \text{H}_2\text{O}$$

In the presence of I$^-$ (which was deliberately added in excess), triiodide ion I$_3^-$ is formed:
\[ I_2 + I^- = I_3^- \]

The \( I_3^- \) then reacts with the starch to form the blue-black complex. The \( I_3^- \) blue-black complex is then titrated with sodium thiosulfate, which reduces the \( I_3^- \) back to colorless \( I^- \), forming the tetrathionate ion \( S_4O_6^{2-} \) as a product:

\[ I_3^- + 2S_2O_3^{2-} = S_4O_6^{2-} + 3I^- \]

**Calculation of Sodium Hypochlorite Concentration in Bleach Sample**

- First, calculate the molarity of the \( I_3^- \) solution.

Let’s say that it took 12 drops of 0.01 M \( Na_2S_2O_3 \) to titrate the blue-black \( I_3^- \) to a colorless end point. Then the \( I_3^- \) molarity is

\[
0.01 \text{ M } Na_2S_2O_3 \times \frac{12 \text{ drops}}{1 \text{ drop}} \times \frac{1 \text{ mol } I_3^-}{2 \text{ mol } Na_2S_2O_3} = 0.06 \text{ M}
\]

The reason for the last factor is that each \( I_3^- \) reacts with two \( S_2O_3^{2-} \) ions in the titration reaction.

The calculated molarity is the molarity of the diluted bleach solution. You diluted the original bleach by 10 times. The molarity of the original commercial bleach is \( 10 \times 0.06 \text{ M} = 0.6 \text{ M} \). The original bleach contains NaClO, which has a formula weight of 74.5 g mol\(^{-1}\). Now all you have to do is calculate the number of grams of NaClO per liter, divide by 10, and obtain the number of grams per 100 mL of bleach. Phew! Check your bleach sample container to see if you can find the percentage of sodium hypochlorite in the commercial sample.