"All in the Family" Properties of Halogens

Periodic Trends and the Properties of the Elements

Introduction

In every family there are similarities and differences. The same is true in chemical families as well. Elements that share similar chemical properties are arranged in vertical columns, called groups or families, in the modern periodic table. For example, the Group 17 elements, consisting of fluorine, chlorine, bromine, iodine, and astatine, are called the halogens. What are the similarities and differences in the chemical properties of the halogens and their compounds?

Concepts

- Halogens
- Groups or families
- Periodic table
- Periodic trends

Activity Overview

The purpose of this demonstration is to explore the similarities and differences in the chemical properties of the halogens. The reactions of chlorine, bromine, and iodine with sodium chloride, sodium bromide, and sodium iodide will be investigated in order to determine the periodic trend for the reactivity of the halogens. Chlorine, bromine, and iodine will be identified by their unique colors in water and hexane.

Materials

Bromine water, Br_2 in H_2O, 10 mL†
Chlorine water, Cl_2 in H_2O, 10 mL†
Iodine solution, I_2, 0.04 M, 10 mL
Hexanes, C_6H_{14}, 60 mL
Sodium bromide solution, NaBr, 0.1 M, 10 mL
Sodium chloride solution, NaCl, 0.1 M, 10 mL
Sodium iodide solution, NaI, 0.1 M, 10 mL
Sodium thiosulfate solution, 4%, 500 mL§
Water, distilled or deionized
Bottles (with caps), square glass, 30-mL, 6
Graduated cylinders, 10- and 25-mL
Marking pencil or pen
Periodic table

†Prepare fresh within one day of use—see the *Preparation of Solutions* section. Do not store excess solution.
§Recommended for disposal of excess halogen solutions.

Safety Precautions

Conduct this activity in a hood or in a well-ventilated laboratory only. Bromine water and chlorine water are toxic by ingestion and inhalation. Do not breathe bromine and chlorine vapors. Bromine water and dilute iodine solution are also skin and eye irritants. Avoid contact of all chemicals with eyes and skin. Hexane is a flammable organic liquid. Do not allow any flames in the laboratory during this activity. Wear chemical splash goggles, chemical-resistant gloves, and chemical-resistant apron. Wash hands thoroughly with soap and water before leaving the lab. Please review current Material Safety and Data Sheets for additional safety, handling, and disposal information.

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Preparation of Solutions

For best results, prepare chlorine water and bromine water within one week of use. Avoid storing large quantities—prepare only as much as is needed. Carry out all reactions in the hood.

Chlorine Water: To prepare 100 mL of chlorine water, mix 13 mL of 5% sodium hypochlorite solution (bleach) with 30 mL of 1 *M* hydrochloric acid. Dilute to 100 mL with distilled water and stir to mix. Store in a labeled glass bottle or stoppered flask until needed. Work with chlorine water in the hood.

Bromine Water: To prepare 100 mL of bromine water, mix 30 mL of 1 *M* sodium bromide solution with 30 mL of 1 *M* hydrochloric acid. Add 15 mL of 5% sodium hypochlorite solution (bleach) followed by 25 mL of distilled water and stir well to mix. Store in a labeled glass bottle or stoppered flask until needed. Work with bromine water in the hood.

Procedure

1. Label six square glass bottles 1–6.
2. Using a graduated cylinder, measure and add 5 mL of chlorine water to each bottle 1 and 2. Cap the bottles.
3. Draw a line to mark the level of liquid in bottles 1 and 2, and mark off a line at the same height in each bottle 3–6.
4. Add bromine water to the 5-mL line in each bottle 3 and 4.
5. Add iodine solution to the 5-mL line in each bottle 5 and 6.
6. Record the color of each aqueous halogen solution in Data Table A.
7. Using a clean graduated cylinder, measure and add approximately 10 mL of hexane to each test tube 1–6.
8. Place a stopper in each test tube and carefully invert each tube several times to mix the liquids. There should be two layers—the top organic layer (hexane), and the bottom aqueous layer (water).
9. For each aqueous halogen/hexane mixture, record the colors of the upper and lower liquid layers in Data Table A.
10. Add 5 mL of sodium bromide solution to the chlorine mixture in bottle 1. Cap the bottle and carefully invert several times to mix the liquids. Observe any reaction that occurs—look for changes in color to either layer. Record all observations in Data Table B. If no change is apparent, write no reaction (*NR*) in the data table.
11. Using the information in the following chart, repeat step 10 for all of the possible halogen–sodium halide combinations in bottles 2–5. Record detailed observations as each solution is added. Complete Data Table B.

Test Tube	**1**	**2**	**3**	**4**	**5**	**6**
Halogen	Cl_2	Cl_2	Br_2	Br_2	I_2	I_2
Sodium Halide Solution	NaBr	NaI	NaCl	NaI	NaCl	NaBr

Disposal

Please consult your current *Flinn Scientific Catalog/Reference Manual* for general guidelines and specific procedures governing the disposal of laboratory waste. At the end of the demonstration, bottles 1 and 3 contain bromine and bottles 2, 4, 5, 6 contain iodine. The contents of the test tubes may be rinsed into a large waste beaker for reduction using 4% sodium thiosulfate, according to Flinn Suggested Disposal Method #12a.

Tips

- Review the recommended safety precautions for working with dilute solutions of the halogens. Never, ever "sniff" halogen solutions. Chlorine water, in particular, is dangerous because it is colorless and the presence of chlorine may not be obvious.
- The small amounts of chlorine and bromine water used in this demonstration may be safely worked with in capped bot

tles at a laboratory bench in a *well-ventilated* lab. Prepare and dispense the halogen solutions in an operating fume hood. Cap the bottles before carefully transferring them to a demonstration table or lab bench.

- Set up a large 1-L waste beaker containing 500 mL of 4% sodium thiosulfate solution in the hood for reduction of the residual halogen waste solutions.
- Teachers who have covered the basics of oxidation and reduction may want to incorporate these concepts in their discussion of the chemical properties of the halogens. Fluorine is the strongest oxidizing agent, while iodide ion is the strongest reducing agent among the halide anions.
- For best results, dilute the commercially available 0.05 *M* iodine solution to a 0.04 *M* solution. The 0.04 *M* solution provides for a lighter color that is easier to see.
- Fluorine is the most reactive halogen. In fact, it is the most reactive of all nonmetals—the strongest oxidizing agent known—and extremely poisonous. For these reasons, fluorine was the last of the halogens to be discovered in its free element form. Chlorine, bromine, and iodine had all been isolated as their free elements by 1830. The element fluorine, however, was not successfully prepared until 1886 by the French chemist Henri Moissan. In the period between 1830 and 1886, several scientists died during unsuccessful attempts to prepare elemental fluorine. Many more scientists, including Moissan, suffered serious health effects due to fluorine poisoning. Henri Moissan was awarded the Nobel Prize for Chemistry in 1906 for the discovery of fluorine.

Discussion

The *halogens* are a reactive group of nonmetals. The first two members of the group, fluorine and chlorine, are gases at room temperature. As the atomic mass of the halogens increases, the physical state of the elements also changes—bromine is a liquid at room temperature, while iodine and astatine are solids. This change from gas to liquid to solid as the atomic mass of the halogens increases is easily observed. There are other "periodic" trends in the properties of the halogens that are not as easily observed or measured. Thus, it is known that the atomic size (radius) of the halogens increases going down the column of elements, but that the ionization energy decreases in the same direction. *Periodic trends* in the physical properties of the halogens are mirrored by trends in their chemical properties as well.

The halogens exist in nature mainly in the form of salts of their anions. Calcium fluoride, for example, occurs in mineral deposits, while sodium chloride, sodium bromide, and sodium iodide occur naturally in seawater. (Astatine is a radioactive, unstable, and very rare element.) In the form of their free elements, the halogens readily combine with many other elements, including metals, hydrogen, and oxygen. Indeed, the halogens do not exist in nature in their uncombined form. The halogens are prepared for industrial use by passing an electric current through solutions of their salts. In the laboratory they can be made by treating halide salts with strong oxidizing agents. When the halogens are prepared in this way, they are found to exist as diatomic molecules—F_2, Cl_2, Br_2, and I_2. The free halogens are generally quite toxic and must be handled with caution.

One of the many types of reactions that the halogens (X_2) undergo are single replacement reactions with sodium halides (NaY), as shown in Equation 1.

$$2NaY + X_2 \rightarrow Y_2 + 2NaX \qquad \textit{Equation 1}$$

These reactions will take place in one direction only. The reaction of a halogen X_2 with a different sodium halide (NaY) will occur only if X_2 is more reactive than Y_2. If X_2 is less reactive than Y_2, the reaction shown in Equation 1 will not take place. The *activity series* of the halogens lists the halogens in order from the most reactive to the least reactive. By comparing the pairwise reactions of chlorine, bromine, and iodine with the salts sodium chloride, sodium bromide, and sodium iodide, it is possible to determine the periodic trend in the chemical reactivity of the halogens.

Connecting to the National Standards

This laboratory activity relates to the following National Science Education Standards (1996):

Unifying Concepts and Processes: Grades K–12
Evidence, models, and explanation
Constancy, change, and measurement
Content Standards: Grades 9–12
Content Standard A: Science as Inquiry
Content Standard B: Physical Science, structure and properties of matter, chemical reactions
Content Standard F: Science in Personal and Social Perspectives; natural and human-induced hazards

Sample Data
Data Table A. Color and Appearance of the Halogens

Bottles	Halogen	Color of Aqueous Solution	Appearance of Hexane/Water Mixture
1, 2	Cl_2	*Colorless*	*Two liquid layers. Both layers are clear and colorless.*
3, 4	Br_2	*Light orange-yellow*	*Two liquid layers. Top layer is orange; bottom layer is yellow.*
5, 6	I_2	*Dark orange*	*Two liquid layers. Top layer is purple; bottom layer is orange.*

Data Table B. Reactions of Halogens and Sodium Halides

Bottle	Halogen	Sodium Halide	Observations
1	Cl_2	**NaBr**	*Top layer is orange; bottom layer is yellow.*
2	Cl_2	**NaI**	*Top layer is purple; bottom layer is orange.*
3	Br_2	**NaCl**	*NR* *(No change in colors of top and bottom layers.)*
4	Br_2	**NaI**	*Top layer is purple; bottom layer is light orange.*
5	I_2	**NaCl**	*NR* *(No change in colors of top and bottom layers.)*
6	I_2	**NaBr**	*NR* *(No change in colors of top and bottom layers.)*

Answers to Discussion Questions

1. Describe the hazards and safety precautions for working with halogens in the lab.

Chlorine and bromine water are toxic by inhalation and ingestion. Work with these solutions in a well-ventilated lab only. Never breathe chlorine and bromine vapors. Bromine and iodine water are eye and skin irritants. Avoid contact of all chemicals with eyes and skin. Wear chemical splash goggles and chemical-resistant gloves and apron.

2. How can each halogen—Cl_2, Br_2, and I_2—be detected in the aqueous layer and in the organic (hexane) layer?

Chlorine is colorless in both water and in hexane. Bromine is yellow in water, darker orange in hexane. Iodine is dark orange/brown in water, purple in hexane.

3. Did chlorine react with sodium bromide? With sodium iodide? Describe the evidence for any chemical reaction that occurred and the possible identity of the product(s).

Chlorine reacted with both sodium bromide and sodium iodide. Evidence for reaction was the appearance of an orange color (elemental bromine) in the top organic layer when chlorine was mixed with sodium bromide, and appearance of a purple color (elemental iodine) in the top organic layer when chlorine was mixed with sodium iodide.

4. Did bromine react with sodium chloride? With sodium iodide? Describe the evidence for any chemical reaction that occurred and the possible identity of the product(s).

Bromine reacted with sodium iodide but not with sodium chloride. Evidence for reaction with iodide ion was the appearance of a purple color (elemental iodine) in the top organic layer when bromine was mixed with sodium iodide. No change was observed in the colors of the top and bottom layers when bromine was mixed with sodium chloride.

5. Did iodine react with sodium chloride? With sodium bromide? Describe the evidence for any chemical reaction that occurred and the possible identity of the product(s).

Iodine did not react with either sodium chloride or sodium bromide. No changes were observed in the original colors of the top and bottom layers when the sodium halide salts were added.

6. Write a balanced chemical equation for each chemical reaction that occurred in bottles 1–6.

$2NaBr + Cl_2 \rightarrow Br_2 + 2NaCl$ *Bottle # 1*

$2NaI + Cl_2 \rightarrow I_2 + 2NaCl$ *Bottle # 2*

$2NaI + Br_2 \rightarrow I_2 + 2NaBr$ *Bottle # 4*

7. Explain, based on the results of this demonstration, which halogen was most reactive and least reactive, respectively. Write the activity series for the halogens, including fluorine, from highest to lowest.

Chlorine is the most reactive of the halogens, because it reacted with both sodium bromide and sodium iodide. Iodine is the least reactive of the halogens, because it did not react with either sodium chloride or sodium bromide. The activity series of the halogens is fluorine > chlorine > bromine > iodine.

8. (*a*) Write a general statement that describes the periodic trend in the reactivity of nonmetals within a group or family in the Periodic Table. (*b*) Predict which Group 16 element, oxygen or sulfur, should be more reactive.

The reactivity of nonmetals within a family decreases as you go down a column in the periodic table. Based on this trend, oxygen should be more reactive than sulfur.

9. The following table shows the boiling points of the halogens. Describe in words and give a possible explanation for the trend that is observed.

Halogen	F_2	Cl_2	Br_2	I_2
Boiling point	–188 °C	–34 °C	58 °C	184 °C

The boiling points of the halogens increase in a regular manner as the molar mass increases. As the size of the molecules increases, there are more electrons and a greater surface area for attraction of the molecules by dispersion forces. The greater the attractive forces between molecules, the more energy is required to convert the molecules from the liquid phase to the gas phase, and the higher the boiling point of the liquid.

10. Chlorine is used in water treatment plants and in swimming pools. Why is chlorine added to drinking water and to swimming pool water? What is the chief disadvantage of using chlorine?

Chlorine is added as a disinfectant to water. Because of its high chemical reactivity, chlorine oxidizes and kills bacteria and other microbes. The chief disadvantage to the use of chlorine in water treatment is that chlorine is toxic—exposure to large concentrations of chlorine vapor is potentially lethal. There is also growing awareness of the environmental hazard of chlorine. Chlorine reacts with many organic compounds, including those in our bodies, to form chlorinated organic compounds, many of which are also toxic and bioaccumulate in fish and wildlife.

Reference

This activity was adapted from an experiment in *The Periodic Table*, Volume 4 in the *Flinn ChemTopic™ Labs* series; Cesa, I., Editor; Flinn Scientific: Batavia, IL (2002).

Flinn Scientific—Teaching Chemistry™ eLearning Video Series

A video of the *“All in the Family” Properties of Halogens* activity, presented by Irene Cesa, is available in *Periodic Trends and the Properties of the Elements*, part of the Flinn Scientific—Teaching Chemistry eLearning Video Series.

Materials for *“All in the Family” Properties of Halogens* are available from Flinn Scientific, Inc.

Materials required to perform this activity are available in the *All in the Family—Periodic Trend Demonstration Kit* available from Flinn Scientific. Materials may also be purchased separately.

Catalog No.	Description
AP7281	All in the Family—Periodic Trend Demonstration Kit
S0368	Sodium Bromide Solution, 1 M, 500 mL
S0079	Sodium Hypochlorite Solution, 5%, 500 mL
H0013	Hydrochloric Acid, 1 M, 500 mL
H0002	Hexanes, 500 mL
S0237	Sodium Chloride Solution, 0.1 M, 500 mL
S0245	Sodium Iodide Solution, 0.1 M, 500 mL
I0048	Iodine Solution, 0.05 M, 100 mL
AP8449	Bottles, French Square-Style, 30-mL
GP2005	Graduated Cylinder, 10-mL
GP2010	Graduated Cylinder, 25-mL

Consult your *Flinn Scientific Catalog/Reference Manual* for current prices.

"All In the Family" Worksheet

Data Table A. Color and Appearance of the Halogens

Bottles	Halogen	Color of Aqueous Solution	Appearance of Hexane/Water Mixture
1, 2	Cl_2		
3, 4	Br_2		
5, 6	I_2		

Data Table B. Reactions of Halogens and Sodium Halides

Bottle	Halogen	Sodium Halide	Observations
1	Cl_2	NaBr	
2	Cl_2	NaI	
3	Br_2	NaCl	
4	Br_2	NaI	
5	I_2	NaCl	
6	I_2	NaBr	

Discussion Questions

1. Describe the hazards and safety precautions for working with halogens in the lab.

2. How can each halogen—Cl_2, Br_2, and I_2—be detected in the aqueous layer and in the organic (hexane) layer?

3. Did chlorine react with sodium bromide? With sodium iodide? Describe the evidence for any chemical reaction that occurred and the possible identity of the product(s).

4. Did bromine react with sodium chloride? With sodium iodide? Describe the evidence for any chemical reaction that occurred and the possible identity of the product(s).

5. Did iodine react with sodium chloride? With sodium bromide? Describe the evidence for any chemical reaction that occurred and the possible identity of the product(s).

6. Write a balanced chemical equation for each chemical reaction that occurred in bottles 1–6.

7. Explain, based on the results of this demonstration, which halogen was most reactive and least reactive, respectively. Write the activity series for the halogens, including fluorine, from highest to lowest.

8. (*a*) Write a general statement that describes the periodic trend in the reactivity of nonmetals within a group or family in the Periodic Table. (*b*) Predict which Group 16 element, oxygen or sulfur, should be more reactive.

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