

# All in the Family

## The Halogens and Their Compounds

### Introduction

In every family there are both 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. The Group VIIA elements, for example, 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

- Periodic table
- Halogens
- Activity series
- Groups or families
- Periodic trends
- Single replacement reactions

### Background

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 is a solid. 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 ionic compounds containing halide 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.) The halogens readily combine with many other elements, including metals, hydrogen, and oxygen. Indeed, the halogens do not exist in nature as free elements. The halogens are prepared for industrial use by passing an electric current through sodium halide solutions. 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 so-called single replacement reactions with metal halides (MY), as shown in *Equation 1*.



These reactions will take place in one direction only. The reaction of one halogen ( $X_2$ ) with a different metal halide (MY) 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 pair-wise reactions of chlorine, bromine, and iodine with sodium chloride, sodium bromide, and sodium iodide, it should be possible to determine the periodic trend in the chemical reactivity of the halogens.

### Experiment Overview

The purpose of this experiment is to explore the similarities and differences in the chemical properties of the halogens. In Parts A and B, the reactions of chlorine, bromine, and iodine with sodium chloride, sodium bromide, and sodium iodide will be studied in order to determine the activity series of the halogens. In Part C, the solubility of metal chlorides, bromides, and iodides will be examined.

### Pre-Lab Questions

1. Read the entire procedure and the recommended safety precautions. What hazards are associated with the use of halogens in the lab? How can these hazards be avoided?
2. Chlorine is used in water treatment plants and in swimming pools. Why is chlorine added to drinking water and to swimming pool water? Based on your answer to Question #1, suggest a possible disadvantage to the use of chlorine in water treatment.
3. The following table shows the boiling points of the halogens. Describe in words the periodic trend that is observed.

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

### Materials

Ammonia water, $NH_3$ , 1.0 M, 6 mL	Sodium iodide solution, NaI, 0.1 M, 2 mL
Bromine water, $Br_2$ in $H_2O$ , 1 mL	Marking pencil or pen
Chlorine water, $Cl_2$ in $H_2O$ , 1 mL	Pipets, Beral-type (or eyedroppers), 9
Iodine solution, $I_2$ , 0.05 M, 1 mL	Test tubes, 12 × 75 mm, 6
Hexane, $C_6H_{14}$ , 6 mL	Test tube rack
Silver nitrate solution, $AgNO_3$ , 0.1 M, 3 mL	Stirring rod (optional)
Sodium bromide solution, NaBr, 0.1 M, 2 mL	Stoppers for test tubes, 6
Sodium chloride solution, NaCl, 0.1 M, 2 mL	Water, distilled or deionized

### Safety Precautions

*Bromine water and chlorine water are toxic by ingestion and inhalation. Do not breathe bromine and chlorine vapors. Bromine and iodine water are skin and eye irritants. Avoid contact of all chemicals with eyes and skin. Hexane is a flammable organic liquid. Do not allow hexane to come in contact with heat, flames or other sources of ignition. Wear chemical splash goggles and chemical-resistant gloves and apron.*

## Procedure

### Part A. Color and Appearance of the Halogens

Hexane is an organic solvent that does not dissolve in water. Chlorine, bromine, and iodine will be identified by their color and appearance in both water and hexane.

1. Place six clean test tubes in a test tube rack. Label the tubes 1–6.
2. Use a pipet to add 10 drops of chlorine water ( $\text{Cl}_2$ ) to tubes 1 and 2.
3. Use a different pipet to add 10 drops of bromine water ( $\text{Br}_2$ ) to tubes 3 and 4.
4. Use a third pipet to add 10 drops of iodine solution ( $\text{I}_2$ ) to tubes 5 and 6.
5. Record the color of each aqueous halogen solution in Data Table A.
6. Add approximately 20 drops of hexane to each tube 1–6.
7. Place a stopper on each tube. Hold the stopper in place with a finger and carefully invert each tube several times to mix the liquids.
8. Use Data Table A to record your observations of each halogen mixture after hexane has been added. (How many layers are present? Which layer is which? What color(s) are they?)

### Part B. Reactions of Halogens with Sodium Halides

9. Add 10 drops of sodium bromide ( $\text{NaBr}$ ) solution to the chlorine solution in tube 1. Replace the stopper on the tube and carefully invert the tube 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 NR (no reaction) in the data table.
10. Continue to add 10 drops of the appropriate sodium halide solution to each test tube, as shown in the following chart. Make and record detailed observations as you add each solution and mix the contents of each tube. Complete Data Table B.

Test Tube	1	2	3	4	5	6
Halogen	$\text{Cl}_2$	$\text{Cl}_2$	$\text{Br}_2$	$\text{Br}_2$	$\text{I}_2$	$\text{I}_2$
Sodium Halide	$\text{NaBr}$	$\text{NaI}$	$\text{NaCl}$	$\text{NaI}$	$\text{NaCl}$	$\text{NaBr}$

11. Dispose of the solutions as instructed by your teacher. Rinse the tubes with water before using them again in Part C.

**Part C. Solubility of Metal Halides**

12. Label three small test tubes 1–3.
13. Using a separate pipet for each solution, add 20 drops of 0.1 M sodium halide solution to the appropriate test tube, as shown below.

Test Tube	1	2	3
Sodium Halide	NaCl	NaBr	NaI

14. Use a labeled pipet to add 20 drops of 0.1 M silver nitrate solution ( $\text{AgNO}_3$ ) to each test tube, observing carefully as each drop is added. Record observations in Data Table C.
15. Use a labeled pipet to add 30 drops of ammonia water into each test tube, observing carefully as each drop is added. Gently swirl or stir the test tubes to mix the contents. Record observations in Data Table C. Allow any precipitate to settle for 1–2 minutes and record any additional observations.
16. Dispose of the solutions as instructed by your teacher.

Name: \_\_\_\_\_

Class/Lab Period: \_\_\_\_\_

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

Tubes	Halogen	Initial observations	Observations with hexane
1, 2	Cl <sub>2</sub>		
3, 4	Br <sub>2</sub>		
5, 6	I <sub>2</sub>		

**Data Table B. Reactions of Halogens with Sodium Halides**

Tube	Halogen	Sodium Halide	Observations
1	Cl <sub>2</sub>	NaBr	
2	Cl <sub>2</sub>	NaI	
3	Br <sub>2</sub>	NaCl	
4	Br <sub>2</sub>	NaI	
5	I <sub>2</sub>	NaCl	
6	I <sub>2</sub>	NaBr	

**Data Table C. Solubility of Metal Halides**

Tube	Sodium Halide	Observations with AgNO <sub>3</sub>	Observations with aqueous ammonia
1	NaCl		
2	NaBr		
3	NaI		

**Post-Lab Questions** (Use a separate sheet of paper to answer the following questions.)

1. How can each of the halogens— $\text{Cl}_2$ ,  $\text{Br}_2$ , and  $\text{I}_2$ —be detected in the aqueous layer and in the organic (hexane) layer? Based on your observations, are the halogens more soluble in water or in hexane?
2. Look at the results of the reactions of chlorine water in test tubes 1 and 2. Did chlorine react with sodium bromide? With sodium iodide? What evidence do you have for any reaction that occurred?
3. Look at the results of the reactions of bromine water in test tubes 3 and 4. Did bromine react with sodium chloride? With sodium iodide? What evidence do you have for any reaction that occurred?
4. Look at the results of the reactions of iodine water in test tubes 5 and 6. Did iodine react with sodium chloride? With sodium bromide? What evidence do you have for any reaction that occurred?
5. Using Equation 1 in the *Background* section as a guide, write a balanced chemical equation for each reaction that occurred in test tubes 1–6.
6. Based on laboratory results, which halogen is most reactive? Least reactive? Explain.
7. Using lab data, write the activity series for the halogens, from most active to least active.
8. Assuming other nonmetals behave the same as the halogens, write a general statement that describes the periodic trend in the reactivity of nonmetals as you go down a column in the Periodic Table.
9. Use your answer to Question #8 to predict which Group VIA element, oxygen or sulfur, should be more reactive.
10. What effect in general did silver nitrate have on each of the sodium halide solutions?
11. What effect did ammonia have on each precipitate?
12. Write a general statement that describes the similarities and differences in the solubility behavior of silver halides.
13. (Optional) Write the chemical equation for the double replacement reaction of silver nitrate with each of the three sodium halide solutions. Label the solid product with (s) and write the name and color of each precipitate.