This section describes the chemistry of halogens with the main group elements such as the alkali metals, alkaline earth metals, and Groups 13 and 14. The word halogen itself means "salt former" in Greek. Halogens such as chlorine, bromine and iodine have properties that enable them to react with other elements to form important salts such as sodium chloride, also known as table salt.

Properties of Halogens

Elements such as fluorine, chlorine, bromine, iodine, and astatine belong to Group 17, the halogen group. At room temperature fluorine is a yellow gas, chlorine is a pale green gas, bromine is a red liquid, and iodine is a purple solid. Astatine is a radioactive element, and exists in nature only in small amounts. All the halogens exist as diatomic molecules. They have high ionization energies and form the most electronegative group of elements. Their electron configuration, \( ns^2np^5 \), allows them to easily react with Group 1 and 2 metals; each halogen tends to pick up one electron, and the Group 1 and Group 2 elements each tend to lose one or two electrons, respectively. Halogens therefore react most vigorously with Group 1 and Group 2 metals of all main group elements.

Reaction with Water

From a standard reduction potential table, it is determined that iodine and bromine cannot oxidize water to oxygen because they have smaller reduction potentials than oxygen. Thus, iodine and bromine do not react with water. However, fluorine and chlorine have larger reduction potentials, and can oxidize water.

Fluorine reacts with water vapor to form oxygen and ozone:

\[
2F_2(g) + 2H_2O(g) \rightarrow 4HF(g) + O_2(g)
\]

\[
3F_2(g) + 2H_2O(g) \rightarrow 6HF(g) + O_3(g)
\]

The reaction of water with chlorine, shown below, proceeds very slowly.

\[
Cl_2 + H_2O \rightarrow H^+ + Cl^- + HClO
\]

Chlorine and bromine are moderately soluble in water. These solutions form solid hydrates within an ice lattice. These solutions are good oxidizing agents. Chlorine reacts reversibly with water to produce acids as in the following example, in which chloric acid and hydrochloric acid are formed:

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

Iodine is slightly soluble in water. It has the lowest standard reduction potential of the halogens, and is therefore the least powerful oxidizing agent. Air and other reagents can oxidize acidified solution of iodide ions.
Reaction with Hydrogen

All the halogens react directly with hydrogen, forming covalent bonds and—at sufficient levels of purity—colorless gases at room temperature. Hydrogen reacts with fluorine, chlorine, bromine, and iodine, forming HF, HCl, HBr, and HI, respectively. The bond strength of these molecules decreases down the group: \( \text{HF} > \text{HCl} > \text{HBr} > \text{HI} \).

Iodine and hydrogen react non-spontaneously to produce hydrogen iodide:

\[
\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}
\]

All the hydrogen halides are soluble in water, in which they form strong acids (with the exception of \( \text{HF} \)). The general equation of hydrogen halide for the acid reaction is given below:

\[
\text{HX} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{X}^-
\]

Group 1: The Alkali Metals

All the alkali metals react vigorously with halogens to produce salts, the most industrially important of which are NaCl and KCl.

\[
2\text{Na}(s) + \text{Cl}_2(g) \rightarrow 2\text{NaCl}(s)
\]

Sodium Chloride is used as a preservative for meat and to melt the ice on the roads (via freezing point depression). KCl is important for plant fertilizers because of the positive impact of potassium on plant growth. These metal halides form white ionic crystalline solids and are all soluble in water except LiF, because of its high lattice enthalpy attributed to strong electrostatic attraction between Li\(^+\) and F\(^-\) ions.

Group 2: The Alkaline Earth Metals

The alkaline earth metals react to form hydrated halides. These halides are ionic except for those involving beryllium (the least metallic of the group). Because alkaline earth metals tend to lose electrons and halogen atoms tend to gain electrons (Table P2), the chemical reaction between these groups is the following:

\[
\text{M} + \text{X}_2 \rightarrow \text{MX}_2
\]

where

- \( \text{M} \) represents any metal from Group 2
- \( \text{X} \) represents fluorine, chlorine, bromine or iodine.

Anhydrous calcium chloride has strong affinity for water, absorbing enough to dissolve its own crystal lattice. It can be produced directly from limestone, or as a by-product by Solvay Process.
Group 13: The Boron Family

All the Group 13 elements react with Halogens to form trihalides.

- All halides of boron are Lewis acids
- Aluminum halides adopt a dimeric structure

**Aluminum Halides**

Aluminum Fluoride, $\text{AlF}_3$, is an ionic compound with a high melting point. However, most of the other aluminum halides form molecules with the formula $\text{Al}_n\text{X}_m$ ($\text{X}$ represents chlorine, bromine, or iodine). When two $\text{AlX}_3$ units (or, more generally, any two identical units) join together, the resulting molecule is called a dimer. Aluminum halides are very reactive Lewis acids. They accept electrons and form acid-base compound called adducts, as in the following example:

$$\text{AlCl}_3 + (\text{C}_2\text{H}_5)_2\text{O} \rightarrow \text{Al}(\text{C}_2\text{H}_5)_2\text{OCl}_3$$

In this reaction, $\text{AlCl}_3$ is the Lewis acid and $(\text{C}_2\text{H}_5)_2\text{O}$ is the Lewis base.

Group 14: The Carbon Family

Group 14 elements form halides with general formula $\text{MX}_4$ ($\text{CCl}_4$, $\text{SiCl}_4$, $\text{GeCl}_4$, $\text{SnCl}_4$, $\text{PbCl}_4$), although some elements such as Ge, Sn, Pb can also form dihalides ($\text{MX}_2$). The tetrahalides of carbon, such as $\text{CCl}_4$, cannot be hydrolyzed due to non-availability of vacant valence d-orbitals, but other tetrahalides can be hydrolyzed.

**Silicon Halides**

Silicon reacts with halogens to form compounds of the form $\text{SiX}_4$, where $\text{X}$ represents any common halogen. At room temperature, $\text{SiF}_4$ is a colorless gas, $\text{SiCl}_4$ is a colorless liquid, $\text{SiBr}_4$ is a colorless liquid, and $\text{SiI}_4$ forms colorless crystals. $\text{SiF}_4$ and $\text{SiCl}_4$ can be completely hydrolyzed, but $\text{SiBr}_4$ can be only partially hydrolyzed.

**Metal Halides**

Lead and tin are metals in Group 14. Tin occurs as both $\text{SnO}_2$ and $\text{SnO}_4$. $\text{SnCl}_2$ is a good reducing agent and is found in tinstone. $\text{SnF}_2$ was once used as additive to toothpaste but now is replaced by $\text{NaF}$.

Group 16: The Oxygen Family

**Oxygen and Sulfur Halides**

Sulfur reacts directly with all the halogens except iodine. It spontaneously combines with fluorine to form sulfur hexafluoride, $\text{SF}_6$, a colorless and inert gas. It can also form $\text{SF}_4$ which is a powerful fluorinating agent. Sulfur and chlorine form $\text{SCl}_2$, a red liquid, which is used in the production of the poisonous mustard gas. This reaction is
shown below:

\[3SF_4 + 4BCl_3 \rightarrow 4BF_3 + 3SCl_2 + 3Cl_2\]

Oxygen combines with fluoride to form the compounds OF\(_2\) and O\(_2\)F\(_2\). The structures of these molecules resemble that of hydrogen peroxide, although they are much more reactive.

**Halogen Oxides**

Common halogen oxides include \(\text{Cl}_2\text{O}\), \(\text{ClO}_2\), \(\text{Cl}_2\text{O}_4\), and \(\text{I}_2\text{O}_5\). Chlorine monoxide, the anhydride of hypochlorous acid, reacts vigorously with water as shown below, giving off chlorine and oxygen as products.

\[\text{Cl}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons 2\text{HOCl}\]

Chlorine dioxide and chlorine perchlorate form when sulfuric acid reacts with potassium chlorate. These compounds are similar to the nitrogen compounds \(\text{NO}_2\) and \(\text{N}_2\text{O}_4\). Iodine pentoxide forms iodic anhydride when reacted with water, as shown:

\[\text{I}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HIO}_3\]

**Halogen Oxoacids**

Compounds that are made up of both oxygen and hydrogen are considered to be oxygen acids, or oxoacids. Common oxoacids are shown in the table below.

<table>
<thead>
<tr>
<th>HClO</th>
<th>HBrO</th>
<th>HIIO</th>
</tr>
</thead>
<tbody>
<tr>
<td>HClO(_2)</td>
<td>HBrO(_3)</td>
<td>HIIO(_3)</td>
</tr>
<tr>
<td>HClO(_3)</td>
<td>HBrO(_4)</td>
<td>HIIO(_4)</td>
</tr>
<tr>
<td>HClO(_4)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Halogen Oxoanions**

The oxoanions of chlorine are following:

- Hypochlorite, OCl\(^-\)
- Chlorite, ClO\(_2\)^-\)
- Chlorate, ClO\(_3\)\(^-\)
- Perchlorate, ClO\(_4\)\(^-\)
All these compounds have common uses. For example, sodium chlorite is used as bleaching agent for textiles. Chlorate is a very good oxidizing agent and is very important in matches and fireworks.

Group 17: Other Halogens (Interhalogens)

Halogens have the ability to form compounds with other halogens (interhalogens). They are represented with the notation XY, in which the X and Y refer to two different halogens. Examples of this type of molecule include IBr and BrCl. They can also form polyatomic molecules such as XY$_3$, XY$_5$, XY$_7$, corresponding to molecules such as IF$_3$, BrF$_5$, and IF$_7$. Most interhalogen compounds such as ClF$_3$ and BrF$_3$ are very reactive.

References


Questions

1. Complete the following chemical reaction: \[Mg + Br_2 \rightarrow\]
2. Which halogens cannot oxidize water to oxygen, and why?
3. Name four chlorine oxoanions.
4. Which metal forms a dimer when reacted with halogen?
5. Complete the following acid reaction: \[HF + H_2O \rightarrow\]
6. Why is Aluminium Chloride a covalent compound, while Aluminium Chloride is ionic?

Answers

1. \[Mg + Br_2 \rightarrow MgBr_2\]
2. Iodine and bromine cannot oxidize water to oxygen because they have low electrode potential.
3. Hypochlorite, chlorite, chlorate, perchlorate
4. Aluminum
5. \[HF + H_2O \rightarrow H_3O^+ + F^-\]
6. \[(AlCl_3)\] is a molecular compound (molecular formula)

- Apparent charges Al (+3) and Cl (-1)
- Electronegativity of Al is 1.61
- Electronegativity of Cl is 3.16
The difference in electronegativities is 1.55
Therefore bonds are covalent

\((\text{AlF}_3)\) is an ionic compound (formula compound)

- Ionic charges Al (+3) and F (-1)
- Electronegativity of Al is 1.61
- Electronegativity of F is 3.98 (The fluorine atom is the most electronegative of all the elements)
- The difference in electronegativities is 2.37
- Therefore bonds are ionic