Chlorine is a halogen in group 17 and period 3. It is very reactive and is widely used for many purposes, such as as a disinfectant. Due to its high reactivity, it is commonly found in nature bonded to many different elements.

Chlorine, which is similar to fluorine but not as reactive, was prepared by Sheele in the late 1700's and shown to be an element by Davy in 1810. It is a greenish-yellow gas with a disagreeable odor (you can detect it near poorly balanced swimming pools). Its name comes from the Greek word chloros, meaning greenish-yellow. In high concentration it is quite toxic and was used in World War I as a poison gas.

### Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic Number</td>
<td>17</td>
</tr>
<tr>
<td>Atomic Weight</td>
<td>35.457</td>
</tr>
<tr>
<td>Electron Configuration</td>
<td>[Na]3s^23p^5</td>
</tr>
<tr>
<td>1st Ionization Energy</td>
<td>1251 kJ/mol</td>
</tr>
<tr>
<td>Ionic Radius</td>
<td>181 pm</td>
</tr>
<tr>
<td>Density (Dry Gas)</td>
<td>3.2 g/L</td>
</tr>
<tr>
<td>Melting Point</td>
<td>-101°C</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>-34.05°C</td>
</tr>
<tr>
<td>Specific Heat</td>
<td>0.23 g cal/g°C</td>
</tr>
<tr>
<td>Heat of Vaporization</td>
<td>68 g cal/g</td>
</tr>
<tr>
<td>Heat of Fusion</td>
<td>22 g cal/g</td>
</tr>
<tr>
<td>Critical Temperature</td>
<td>114°C</td>
</tr>
<tr>
<td>Standard Electron Potential</td>
<td>1.358V</td>
</tr>
</tbody>
</table>

At room temperature, pure chlorine is a yellow-green gas. Chlorine is easily reduced, making it a good oxidation agent. By itself, it is not combustible, but many of its reactions with different compounds are exothermic and produce heat. Because chlorine is so highly reactive, it is found in nature in a combined state with other elements, such as NaCl (common salt) or KCl (sylvite). It forms strong ionic bonds with metal ions.
Like fluorine and the other members of the halogen family, chlorine is diatomic in nature, occurring as $\text{Cl}_2$ rather than Cl. It forms -1 ions in ionic compounds with most metals. Perhaps the best known compound of that type is sodium chloride, common table salt (NaCl).

Small amounts of chlorine can be produced in the lab by oxidizing $\text{HCl}$ with $\text{MnO}_2$. On an industrial scale, chlorine is produced by electrolysis of brines or even sea water. Sodium hydroxide (also in high demand) is a by-product of the process.

In addition to the ionic compounds that chlorine forms with metals, it also forms molecular compounds with non-metals such as sulfur and oxygen. There are four different oxides of the element. Hydrogen chloride gas (from which we get hydrochloric acid) is an important industrial product.

### Reactions with Water

Usually, reactions of chlorine with water are for disinfection purposes. Chlorine is only slightly soluble in water, with its maximum solubility occurring at 49° F. After that, its solubility decreases until 212° F. At temperatures below that range, it forms crystalline hydrates (usually $\text{Cl}_2\text{I}$) and becomes insoluble. Between that range, it usually forms hypochlorous acid ($\text{HOCl}$). This is the primary reaction used for water/wastewater disinfection and bleaching.

$$\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HCl}$$

At the boiling temperature of water, chlorine decomposes water

$$2\text{Cl}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{HCl} + \text{O}_2$$

### Reactions with Oxygen

Although chlorine usually has -1 oxidation state, it can have oxidation states of +1, +3, +4, or +7 in certain compounds, such as when it forms oxoacids with the alkali metals.

<table>
<thead>
<tr>
<th>Oxidation State</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1</td>
<td>$\text{NaClO}$</td>
</tr>
<tr>
<td>+3</td>
<td>$\text{NaClO}_2$</td>
</tr>
<tr>
<td>+5</td>
<td>$\text{NaClO}_3$</td>
</tr>
<tr>
<td>+7</td>
<td>$\text{NaClO}_4$</td>
</tr>
</tbody>
</table>

### Reactions with Hydrogen

When $\text{H}_2$ and $\text{Cl}_2$ are exposed to sunlight or high temperatures, they react quickly and violently in a spontaneous reaction. Otherwise, the reaction proceeds slowly.
\[H_2+Cl_2 \rightarrow 2HCl\]

HCl can also be produced by reacting Chlorine with compounds containing Hydrogen, such as Hydrogen sulfide

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### Reactions with Halogens

Chlorine, like many of the other halogens, can form interhalogen compounds (examples include BrCl, ICl, ICl₂). The heavier elements in one of these compounds acts as the central atom. For Chlorine, this occurs when it is bounded to fluorine in CIF, CIF₃, and CIF₅.

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### Reactions with Metals

Chlorine reacts with most metals and forms metal chlorides, with most of these compounds being soluble in water. Examples of insoluble compounds include \(\text{AgCl}\) and \(\text{PbCl}_2\). Gaseous or liquid chlorine usually does not have an effect on metals such as iron, copper, platinum, silver, and steel at temperatures below 230°F. At high temperatures, however, it reacts rapidly with many of the metals, especially if the metal is in a form that has a high surface area (such as when powdered or made into wires).

**Example: Oxidizing Iron**

Chlorine can oxidizing iron

\[\text{Cl}_2 + \text{Fe} \rightarrow \text{FeCl}_2\]

Half Reactions:

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

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### Isotopes

\(\text{^35}Cl\) and \(\text{^37}Cl\) are the two natural, stable isotopes of Chlorine. \(\text{^36}Cl\), a radioactive isotope, occurs only in trace amounts as a result of cosmic rays in the atmosphere. Chlorine is usually a mixture of 75% \(\text{^35}Cl\) and 25% \(\text{^37}Cl\). Besides these isotopes, the other isotopes must be artificially produced. A table containing some common isotopes is found below:

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Atomic Mass</th>
<th>Half-Life</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{^35}Cl)</td>
<td>32.986</td>
<td>2.8 seconds</td>
</tr>
<tr>
<td>(\text{^34}Cl)</td>
<td>33.983</td>
<td>33 minutes</td>
</tr>
<tr>
<td>(\text{^35}Cl)</td>
<td>34.979</td>
<td>Stable ((\infty))</td>
</tr>
</tbody>
</table>
Production and Uses

Chlorine is a widely used chemical with many applications.

Water Treatment

Chlorine is used in the disinfection (removal of harmful microorganisms) of water and wastewater. In the United States, it is almost exclusively used. Chlorine was first used to disinfect drinking water in 1908, using sodium hypochlorite (NaOCl):

\[ \text{NaOCl} + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{NaOH} \]

Following widespread use of sodium hypochlorite to disinfect water, diseases caused by unclean water decreased greatly. Compared to other methods, it is effective at lower concentrations and is inexpensive.

Polyvinyl Chloride (PVC)

Polyvinyl Chloride is a plastic which is widely manufactured throughout the globe, and is responsible for nearly a third of the world’s use of chlorine. It is usually manufactured by first taking EDC (ethylene dichloride) and then making it into a vinyl chloride, the basic unit for PVC. From then on, vinyl chloride monomers are linked together to form a polymer. PVC becomes malleable at high temperatures, making it flexible and ideal for many purposes from pipes to clothing. However, PVC is toxic. When in gaseous form and inhaled, it can cause damage to the lungs, the body’s blood circulation, and nervous system. The production of PVC has many regulations surrounding it due to the many harmful effects that the plastic itself and the intermediates involved have on the environment and on human health.

Paper Bleaching

Paper is one of the most widely consumed products in the world. Before wood is made into a paper product, however, it must be turned into pulp (separated fibrous material). This pulp has a color that ranges from light to dark brown. Chlorine is used to bleach the pulp to turn it into a bright, white color, which makes it desirable for consumers. The process usually involves a number of steps, depending on the nature of the pulp.

Problems

1) Solve and balance the following equations

   a. \( \text{(H}_2\text{S} + \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \)
b. \( \text{Sb + Cl}_2 + \text{H}_2\text{O} \rightarrow \text{X} \)

2) Write the electron configuration for Chlorine.

3) What is the molecular geometry of the following? (See Valence Bond Theory)
   a. \( \text{ClO}_2 \)
   b. \( \text{ClF}_5 \)

4) What are the naturally occurring Chlorine isotopes?

5) When does Chlorine have an oxidation state of +5?

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**Answers**

1) Solve and balance the following equations:
   a. \( \text{H}_2\text{S} + 4\text{Cl}_2 + 4\text{H}_2\text{O} \rightarrow \text{H}_2\text{S}_4 + \text{HCl} \)
   b. \( 2\text{Sb} + 3\text{Cl}_2 + \text{H}_2\text{O} > 2\text{SbCl}_3 \)

2) The electron configuration of Chlorine is: \( 1s^22s^22p^63s^23p^5 \)

3) What is the molecular geometry of the following?
   a. \( \text{ClO}_2 \) -Bent or angular; \( \text{ClO}_2 \) is bonded to two ligands, has one lone pair and one unpaired electron.
   b. \( \text{ClF}_5 \) -Square pyramid; \( \text{ClO}_2 \) is bonded to five ligands and has one lone pair

4) The naturally occurring Chlorine isotopes are Chlorine-35 and Chlorine-36. While Chlorine-37 does occur naturally, it is radioactive and unstable.

5) Chlorine has an oxidation state of +5 when it reacts with oxoacids with the Alkali Metals.

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**References**

Contributors

- Judy Hsia (University of California, Davis)