

Chapter 10

Group 17: The Halogens

10.1 The Group 17 Elements: The Halogens¹

10.1.1 The elements

The Group 17 elements have a particular name: the *halogens* meaning *born of salt*. This is due to the formation of salts when they form compounds with a metal. Table 10.1 lists the derivation of the names of the halogens.

Element	Symbol	Name
Fluorine	F	Latin <i>fluere</i> meaning <i>to flow</i>
Chlorine	Cl	Greek <i>chlôros</i> meaning <i>pale green</i>
Bromine	Br	Greek <i>brômos</i> meaning <i>stench</i>
Iodine	I	Greek <i>odes</i> meaning <i>violet</i> or <i>purple</i>
Astatine	At	Greek <i>astatos</i> , meaning <i>unstable</i>

Table 10.1: Derivation of the names of each of the halogens.

10.1.1.1 Discovery

10.1.1.1.1 Fluorine

The mineral *fluorspar* (also known as *fluorite*) consists mainly of calcium fluoride and was described in 1530 by Agricola (Figure 10.1) for its use as a flux. Fluxes are used to promote the fusion of metals or minerals, and it was from this use that fluorine derived its name. In 1670 Heinrich Schwanhard found that when he mixed fluorspar with an acid the fumes produced (hydrogen fluoride) etched the glasses he was wearing. Despite many researchers investigating the chemistry of hydrogen fluoride (HF) the elemental form of fluorine was not isolated until 1886 when Henri Moissan (Figure 10.2) studied the electrolysis of a solution of potassium hydrogen difluoride (KHF₂) in liquid hydrogen fluoride (HF). The mixture was needed because hydrogen fluoride is a non-conductor. The device was built with platinum/iridium electrodes in a platinum holder and the apparatus was cooled to $-50\text{ }^{\circ}\text{C}$.

¹This content is available online at <<http://cnx.org/content/m34994/1.1/>>.



Figure 10.1: German author Georg Bauer (1494 - 1555), whose pen-name was the Latinized Georgius Agricola, was most probably the first person to be environmental conscious.



Figure 10.2: French chemist Ferdinand Frederick Henri Moissan (1852 - 1907) was awarded the Nobel Prize for his work with fluorine.

The generation of elemental fluorine from hydrofluoric acid proved to be exceptionally dangerous, killing or blinding several scientists who attempted early experiments on this halogen. The victims became known as *fluorine martyrs*.

10.1.1.1.2 Chlorine

Archaeological evidence has shown that sodium chloride (known as *table salt*) has been used as early as 3000 BC and brine (the saturated water solution) as early as 6000 BC. It is thought that hydrochloric acid was probably known to alchemist Jābir ibn Hayyān (Figure 10.3) around 800 AD, while aqua regia (a mixture of nitric acid and hydrochloric acid) began to be used to dissolve gold sometime before 1400 AD. Upon dissolving gold in aqua regia, chlorine gas is released along with other nauseating and irritating gases.



Figure 10.3: 15th century portrait of Abu Musa Jābir ibn Hayyān (721 - 815), also known by his Latinized name “Gerber”. He was a chemist, alchemist, astronomer and astrologer, engineer, geologist, philosopher, physicist, and pharmacist and physician.

Chlorine was first prepared and studied in 1774 by Carl Wilhelm Scheele (Figure 10.4), and therefore he is credited for its discovery despite his failing to establish chlorine as an element, mistakenly thinking that it was the oxide obtained from the hydrochloric acid. Regardless of what he believed, Scheele did isolate chlorine by reacting MnO_2 (as the mineral pyrolusite) with HCl , (10.1).

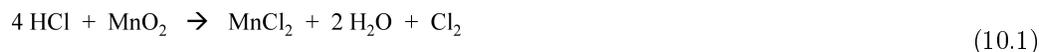




Figure 10.4: Swedish chemist Carl Wilhelm Scheele (1742 – 1786). Isaac Asimov called him "hard-luck Scheele" because he made a number of chemical discoveries before others who are generally given the credit.

10.1.1.1.3 Bromine

Bromine was discovered independently by two chemists Antoine Balard (Figure 10.5) in 1825 and Carl Jacob Löwig (Figure 10.6) in 1826.



Figure 10.5: French chemist Antoine Jérôme Balard (1802 - 1876).



Figure 10.6: German chemist Carl Jacob Löwig (1803 - 1890).

Balard found bromide salts in the ash of sea weed from the salt marshes of Montpellier. The sea weed was used to produce iodine, but also contained bromine. Balard distilled the bromine from a solution of seaweed ash saturated with chlorine. The properties of the resulting substance resembled that of an intermediate of chlorine and iodine; with those results he tried to prove that the substance was iodine monochloride (ICl), but after failing to do so he was sure that he had found a new element and named it *muride*, derived from the Latin word *muria* for brine.

In contrast, Löwig isolated bromine from a mineral water spring in Bad Kreuznach. Löwig used a solution of the mineral salt saturated with chlorine and extracted the bromine with Et_2O . After evaporation a brown liquid remained. Unfortunately, the publication of his results were delayed and Balard published first.

10.1.1.1.4 Iodine

Iodine was discovered by Bernard Courtois (Figure 10.7) in 1811 when he was destroying the waste material from the production of saltpeter (KNO_3) during gunpowder production. Saltpeter produced from French niter beds required sodium carbonate (Na_2CO_3), which could be isolated from seaweed washed up on the coasts of Normandy and Brittany. To isolate the sodium carbonate, seaweed was burned and the ash then washed with water; the remaining waste was destroyed by the addition of sulfuric acid (H_2SO_4). After adding too much acid, Courtois observed a cloud of purple vapor that crystallized on cold surfaces making dark crystals. Courtois suspected that this was a new element but lacked the money to pursue his observations. In supplying samples to his friends, Charles Desormes and Nicolas Clément, he hoped his research was to continue. On 29 November 1813, Desormes and Clément made public Courtois's discovery, describing the substance to a meeting of the Imperial Institute of France.



Figure 10.7: French chemist Bernard Courtois (1777 - 1838).

10.1.1.1.5 Astatine

The existence of *eka-iodine* had been predicted by Mendeleev (Figure 10.8), but astatine was first synthesized in 1940 by Corson (Figure 10.9), MacKenzie (Figure 10.10), and Segrè (Figure 10.11) at the University of California, Berkeley by bombarding bismuth with alpha particles.

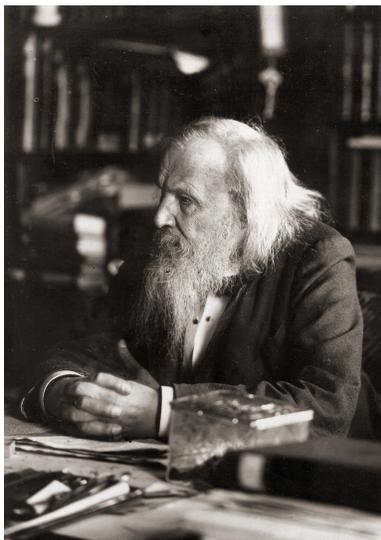


Figure 10.8: Russian chemist Dmitri Mendeleev (1834 - 1907).



Figure 10.9: Physicist and President of Cornell University, Dale R. Corson (1914 -).



Figure 10.10: Physicist Kenneth Ross MacKenzie (1912 - 2002).



Figure 10.11: Italian physicist Emilio Segrè (1905 - 1989).

10.1.1.2 Abundance

The abundance of the halogens is given in Table 10.2.

Element	Terrestrial abundance (ppm)
F	950 (Earth's crust), 330 (soil), 1.3 (sea water), 6×10^{-4} (atmosphere)
Cl	130 (Earth's crust), 50 – 2000 (soil), 1.8×10^4 (sea water)
Br	0.4 (Earth's crust), 5 – 40 (soil), 65 (sea water)
I	0.14 (Earth's crust), 3 (soil), 0.06 (sea water), 60×10^{-3} (atmosphere)
At	Trace in some minerals

Table 10.2: Abundance of the halogens.

10.1.1.3 Isotopes

The naturally abundant isotopes of the halogens are listed in Table 10.3. All 33 isotopes of astatine are radioactive.

Isotope	Natural abundance (%)
Fluorine-19	100
Chlorine-35	75.77
Chlorine-36	trace
Chlorine-37	24.23
Bromine-79	50.69
Bromine-81	49.31
Iodine-127	100%

Table 10.3: Abundance of the major isotopes of the halogens.

While ^{19}F is the only naturally abundant isotope of fluorine, the synthetic isotope, ^{18}F , has half life of about 110 minutes, and is commercially an important source of positrons for positron emission tomography (PET). PET is a nuclear medicine imaging technique that produces a 3-D image of processes within the body. The system detects pairs of γ -rays emitted indirectly by a positron-emitting radionuclide (tracer), which is introduced into the body on a biologically active molecule.

Trace amounts of radioactive ^{36}Cl exist in the environment at about $7 \times 10^{-11}\%$. ^{36}Cl is produced in the atmosphere by the interaction of cosmic rays with ^{36}Ar . In the ground ^{36}Cl is generated through neutron capture by ^{35}Cl or muon (an elemental particle similar to an electron) capture by ^{40}Ca . ^{36}Cl decays with a half-life of 308,000 years making it suitable for geologic dating in the range of 60,000 to 1 million years. However, due to the large amounts of ^{36}Cl produced by irradiation of seawater during atmospheric detonations of nuclear weapons between 1952 and 1958, it is also used as an event marker for 1950s water in soil and ground water.

Iodine has 37 isotopes of iodine, but only one, ^{127}I , is stable. Of the radioactive isotopes, ^{129}I (half-life 15.7 million years) is used for radiometric dating of the first 85 million years of solar system evolution. ^{129}I is also a product of uranium and plutonium fission, and as a consequence of nuclear fuel reprocessing and atmospheric nuclear weapons tests, the natural signal has been swamped. As a consequence it can now be used as a tracer of nuclear waste dispersion into the environment. ^{129}I was used in rainwater studies to track fission products following the Chernobyl disaster.

Due to preferential uptake of iodine by the thyroid, isotopes with short half lives such as ^{131}I can be used for thyroid ablation, a procedure in which radioactive iodine is administered intravenously or orally following a diagnostic scan. The lower energy isotopes ^{123}I and ^{125}I are used as tracers to evaluate the anatomic and physiologic function of the thyroid.

10.1.1.4 Industrial production.

Industrial production of fluorine involves the electrolysis of hydrogen fluoride (HF) in the presence of potassium fluoride (KF) during which fluorine gas is formed at the anode and hydrogen gas is formed at the cathode (Figure 10.12). The potassium fluoride (KF) is converted to potassium bifluoride (KHF₂), (10.2), which is the electrolyte and intermediate to the fluorine and hydrogen, (10.3).



Figure 10.12: The fluorine cell room at F2 Chemicals Ltd, Preston, UK.

The HF is formed as a byproduct of the production of phosphoric acid, since phosphate-containing minerals contain significant amounts of calcium fluorides, which upon treatment with sulfuric acid release hydrogen fluoride, (10.4).



Chlorine is generally manufactured by electrolysis of a sodium chloride solution (brine). The production of chlorine results in the co-products caustic soda (sodium hydroxide, NaOH) and hydrogen gas (H₂). Chlorine can also be produced by the electrolysis of a solution of potassium chloride, in which case the co-products are hydrogen and caustic potash (potassium hydroxide). There are three industrial methods for the extraction of chlorine by electrolysis of chloride solutions, all proceeding by the same reaction at the cathode, (10.5), and anode, (10.6), which lead to the overall reaction, (10.7), where M = Na or K.





Bromine exists exclusively as bromide salts in the Earth's crust, however, due to leaching, bromide salts have accumulated in sea water, but at a lower concentration than chloride. The majority of bromine is isolated from bromine-rich brines, which are treated with chlorine gas, flushing through with air. In this treatment, bromide anions are oxidized to bromine by the chlorine gas, (10.8).



Two major sources of iodine are used for commercial production: the caliche (a hardened sedimentary deposit of calcium carbonate found in Chile) and the iodine containing brines of gas and oil fields in Japan and the United States. The caliche contains sodium nitrate (NaNO_3); in which traces of sodium iodate (NaIO_3) and sodium iodide (NaI) are found. During the production of sodium nitrate the sodium iodate and iodide is extracted. Iodine sourced from brine involves the acidification with sulfuric acid to form hydrogen iodide (HI), which is then oxidized to iodine with chlorine, (10.9). The aqueous iodine solution is concentrated by passing air through the solution causing the iodine to evaporate. The iodine solution is then re-reduced with sulfur dioxide, (10.10). The dry hydrogen iodide (HI) is reacted with chlorine to precipitate the iodine, (10.11).



10.1.1.5 Physical properties

The physical properties of the halogens (Table 10.4) encompasses gases (F_2 and Cl_2), a liquid (Br_2), a non-metallic solid (I_2), and a metallic metal (At).

Element	Mp (°C)	Bp (°C)	Density (g/cm ³)
F	-219.62	-188.12	1.7×10^{-3} @ 0 °C, 101 kPa
Cl	-101.5	-34.04	3.2×10^{-3} @ 0 °C, 101 kPa
Br	-7.2	58.8	3.1028 (liquid)
I	113.7	184.3	4.933
At	302	337	ca. 7

Table 10.4: Selected physical properties of the halogens.

10.1.1.6 Reactivity

All the halogens are highly reactive and are as a consequence of the stability of the X^- ion are strong oxidizing agents (Table 10.5).

Reduction	Reduction potential (V)
$F_2 + 2 e^- \rightarrow 2 F^-$	2.87
$Cl_2 + 2 e^- \rightarrow 2 Cl^-$	1.36
$Br_2 + 2 e^- \rightarrow 2 Br^-$	1.07
$I_2 + 2 e^- \rightarrow 2 I^-$	0.53

Table 10.5: Electrochemical reduction potential for halogens.

WARNING: Elemental fluorine (fluorine gas) is a highly toxic, corrosive oxidant, which can cause ignition of organic material. Fluorine gas has a characteristic pungent odor that is detectable in concentrations as low as 20 ppb. As it is so reactive, all materials of construction must be carefully selected and metal surfaces must be passivated. In high concentrations, soluble fluoride salts are also toxic and skin or eye contact with high concentrations of many fluoride salts is dangerous.

10.1.1.6.1 Use of chlorine as a weapon

Chlorine gas, also known as *bertholite*, was first used as a weapon in World War I by Germany on April 22, 1915 in the Second Battle of Ypres. At around 5:00 pm on April 22, 1915, the German Army released one hundred and sixty eight tons of chlorine gas over a 4 mile front against French and colonial Moroccan and Algerian troops of the French 45th and 78th divisions (Figure 10.13). The attack involved a massive logistical effort, as German troops hauled 5730 cylinders of chlorine gas, weighing ninety pounds each, to the front by hand. The German soldiers also opened the cylinders by hand, relying on the prevailing winds to carry the gas towards enemy lines. Because of this method of dispersal, a large number of German soldiers were injured or killed in the process of carrying out the attack. Approximately 6,000 French and colonial troops died within ten minutes at Ypres, primarily from asphyxiation and subsequent tissue damage in the lungs. Many more were blinded. Chlorine gas forms hydrochloric acid when combined with water, destroying moist tissues such as lungs and eyes. The chlorine gas, being denser than air, quickly filled the trenches, forcing the troops to climb out into heavy enemy fire.



Figure 10.13: The gas attack of the Second Battle of Ypres.

As described by the soldiers it had a distinctive smell of a mixture between pepper and pineapple. It also tasted metallic and stung the back of the throat and chest. The damage done by chlorine gas can be prevented by a gas mask, or other filtration method, making the fatalities from a chlorine gas attack much lower than

those of other chemical weapons. The use as a weapon was pioneered by Fritz Haber (Figure 10.14) of the Kaiser Wilhelm Institute in Berlin, in collaboration with the German chemical conglomerate IG Farben, who developed methods for discharging chlorine gas against an entrenched enemy. It is alleged that Haber's role in the use of chlorine as a deadly weapon drove his wife, Clara Immerwahr, to suicide. After its first use, chlorine was used by both sides as a chemical weapon (Figure 10.15), but it was soon replaced by the more deadly gases phosgene and mustard gas.



Figure 10.14: German scientist and Nobel Prize winner Fritz Haber (1868 - 1934).



Figure 10.15: A poison gas attack, in World War I.

10.1.1.7 Vapor phase

All the halogens form X_2 dimers in the vapor phase in an analogous manner to hydrogen. Unlike dihydrogen, however, the bonding is associated with the molecular orbital combination of the two p-orbitals (Figure 10.16). The bond lengths and energies are given in Table 10.6.

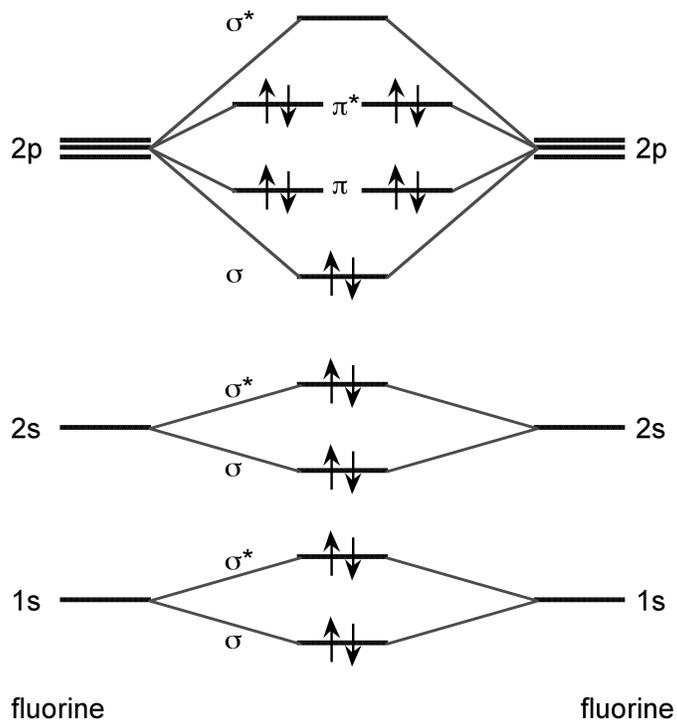


Figure 10.16: Molecular orbital diagram for the formation of F_2 .

Element	Bond length (\AA)	Energy (kJ/mol)
F_2	1.42	158
Cl_2	1.99	243
Br_2	2.29	193
I_2	2.66	151

Table 10.6: Bond lengths and energies for halogens.

10.1.1.8 Solid state

Iodine crystallizes in the orthorhombic space group $Cmca$ (Figure 10.17). In the solid state, I_2 molecules still contain short I-I bond (2.70 \AA).

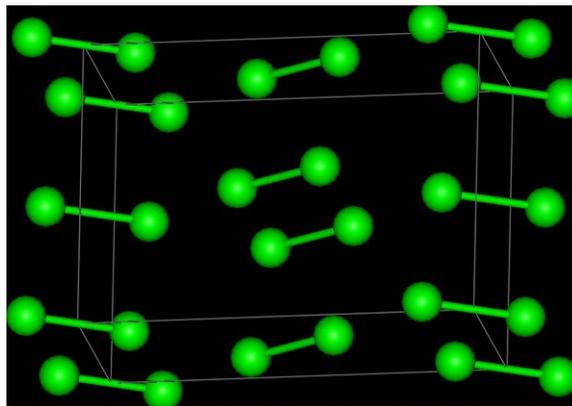


Figure 10.17: The solid state structure of I_2 .

10.1.2 Compounds of the halogens.

The chemistry of the halogens is dominated by the stability of the -1 oxidation state and the noble gas configuration of the X^- anion.

10.1.2.1 Oxidation state

The use of oxidation state for fluorine is almost meaningless since as the most electronegative element, fluorine exists in the oxidation state of -1 in all its compounds, except elemental fluorine (F_2) where the oxidation state is zero by definition. Despite the general acceptance that the halogen elements form the associated halide anion (X^-), compounds with oxidation states of +1, +3, +4, +5, and +7 are common for chlorine, bromine, and iodine (Table 10.7).

Element	-1	+1	+3	+4	+5	+7
Cl	HCl	ClF	ClF ₃ , HClO ₂	ClO ₂	ClF ₅ , ClO ₃ ⁻	HClO ₄
Br	HBr	BrCl	BrF ₃	Br ₂ O ₄	BrF ₅ , BrO ₃ ⁻	BrO ₄ ⁻
I	HI	ICl	IF ₃ , ICl ₃	I ₂ O ₄	IO ₃ ⁻	IO ₄ ⁻

Table 10.7: Examples of multiple oxidation states for the halogens.

10.1.3 Bibliography

- G. Agricola, *De Re Metallica*, Dover Publications, UK (1950)
- K. Christe, *Inorg. Chem.*, 1986, **25**, 3721.

10.2 Compounds of Fluorine²

Elemental fluorine (F₂) is the most reactive element. Fluorine combines directly with all other elements, except nitrogen and the lighter noble gases. It also reacts with many compounds forming fluorides, and many organic compounds inflame and burn in the gas. The highly reactive nature is due to the weak F-F bond (thermodynamically unstable), which provides a low activation energy to reactions (kinetically unstable). The ΔG for reactions is often large due to the strength of the resulting X-F bonds. The weak F-F bond (158 kJ/mol) is due to the small size (0.5 Å) and high nuclear charge of fluorine that result in a small overlap of the bonding orbitals and a repulsion between the non-bonding orbitals (lone pairs) on the two fluorine atoms.

10.2.1 Ionic salts

The ease of formation of F⁻ anion is due to the high electron affinity of fluorine (-322 kJ/mol). Since the fluoride ion is small (1.33 Å) and the least polarizable anion (i.e., *hard*) it is stable in ionic lattices with metal cations in a high oxidation state (high charge), e.g., MnF₄ and CrF₅. In general the highest oxidation states for any metal are found with the fluoride salts. The large ionization energies needed to produce the cations are recovered by the high lattice energies.

10.2.2 Covalent compounds

The high electronegativity of fluorine means that it forms a single electron pair bond polar bond with a high ionic character. The polar nature of the bond means that there is a large inductive effect within a molecule. For example, perfluoroethanol (CF₃CF₂OH) has an acidity comparable to acetic acid.

The high strength of X-F bonds (Table 10.8) is also due to the high ionic character (up to 50%) that results in a high activation energy for bond breaking. In contrast, the low polarizability of the fluorine means that the inter-molecular van der Waals bonds are very weak. Thus, even with very high molecular weights the boiling point can be very low, e.g, WF₆, Bp = 17 °C, Mw = 297.84 g/mol.

Bond	Bond energy (kJ/mol)
C-F	486
N-F	272
P-F	490

Table 10.8: Typical bond energies for X-F bonds.

A wide range of fluoride complexes may be prepared from both metal (FeF₆³⁻, RuF₆⁻, PtF₆²⁻, and SnF₆²⁻) and non-metal (BF₄⁻, SiF₆²⁻, and PF₆⁻) fluorides. While many fluorides are salts, when the metal is in its higher oxidation states (e.g., OsF₆ and WF₆), the formation of an ionic lattice with the appropriate cation (i.e., Os⁶⁺ and W⁶⁺ respectively) is energetically unfavorable.

10.2.2.1 Hydrogen fluoride

WARNING: Hydrogen fluoride (HF) is converted to highly corrosive hydrofluoric acid upon contact with moisture. Pure hydrogen fluoride must be handled in metal or polythene vessels, while aqueous solutions will readily etch and dissolve standard laboratory glassware requiring the use of fluorinated polymer (e.g., Teflon) containers.

²This content is available online at <<http://cnx.org/content/m33815/1.1/>>.

Hydrogen fluoride is synthesized by the reaction of a fluoride salt with a concentrated acid, (10.12). The HF vapor may be condensed, and then subsequently purified by distillation.



The H-F bonding in hydrogen fluoride involves an electron pair bond with a high degree of ionic character. This results in a very polar H-F bond and a large dipole moment (1.86 D).

In the vapor phase, hydrogen fluoride is monomeric above 80 °C, but at lower temperatures it associates into oligomers and small polymers, e.g., cyclic (HF)₆, as a consequence of strong intermolecular hydrogen bonds. As a pure liquid (Mp = -83 °C, Bp = 19.5 °C) hydrogen fluoride is extensively associated by strong hydrogen bonding to form zig-zag polymers (Figure 10.18).

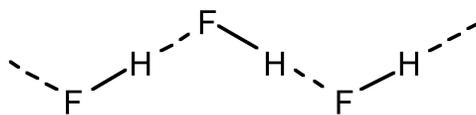
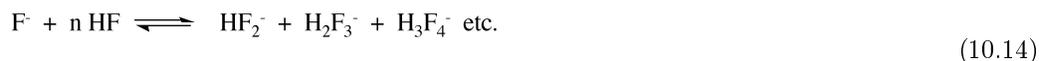


Figure 10.18: The hydrogen bonding in HF.

Hydrogen fluoride has a high dielectric constant (84.2) and as such is a good solvent for polar molecules. However, it is not a good solvent for salts (even fluorides) because it does not solvate cations too well. Despite this, it is useful as a solvent because it is non-oxidizing and easy to evaporate off products.

In a similar manner to water, hydrogen fluoride self-ionizes, (10.13). Salts of H₂F⁺ are known and the F⁻ anion is further solvated by the HF to form a series of salts, (10.14). The complex anion HF₂⁻ is also formed in aqueous solutions of hydrogen fluoride (pK = 0.7).



Hydrogen fluoride is actually a weak acid in aqueous solution with a low pK = 3.5. In fact, HF is a weaker acid than the other halogen analogs:



This trend is despite the fluorine being more electronegative than the other halogens, but is consistent with the strength of the H-F bond (568 kJ/mol).

Hydrogen fluoride is used as a non-oxidizing acid for the hydrolysis of proteins and acid catalyzed condensation reaction. The stability of its salt (HF₂⁻) allow for the study of very strong acids, (10.16) and (10.17).



The acidity of HF may be increased sufficiently by the addition of a fluoride acceptor (e.g., SbF_5) to facilitate the reaction with a weak base such as benzene, (10.18).



Finally, hydrogen fluoride can be used in the synthesis of other fluorine-containing compounds:



10.2.2.2 Organic fluorine compounds

Organic compounds in which some or all of the hydrogen atoms are replaced by fluorine have unique (and often important) properties. The high stability of fluorocarbon compounds is a consequence of the C-F bond energy (486 kJ/mol) in comparison with that of C-H (415 kJ/mol); however, while kinetically stable, fluorocarbons are not necessarily particularly thermodynamically stable.

Replacement of hydrogen with fluorine results in an increased density; since the small size of fluorine means that the minimal distortion or structural change occurs as a result of the substitution. As with metal salts, the weak inter-molecular forces means that completely fluorinated organic compounds have low boiling points. One attribute of the low inter-molecular forces is the low coefficient of friction for fluoropolymers such as polytetrafluoroethylene, commonly known as Teflon (Figure 10.19).

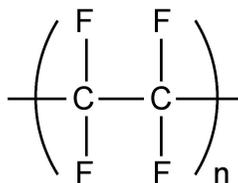
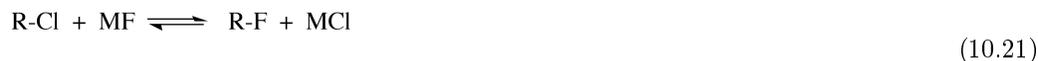


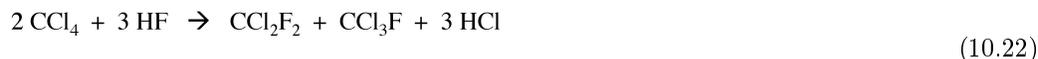
Figure 10.19: The structure of polytetrafluoroethylene (Teflon).

10.2.2.2.1 Synthetic routes to fluorocarbon compounds

The simplest route to a fluorocarbon compounds involves the direct replacement of another halogen by a metal fluoride, (10.21). The driving force for this reaction depends on the free-energy difference of MF and MCl, which is related to the difference in lattice energies. Thus, the larger the metal cation, the more favored the reaction. In this regard, AgF and CsF are the most effective fluorination agent.



Anhydrous hydrogen fluoride (HF) reacts with chlorocarbon compounds in the presence of a catalyst such as SbCl_5 or CrF_4 , (10.22). However, elevated temperatures ($50 - 150^\circ\text{C}$) and high pressures ($50 - 500$ psi) are required.



The direct replacement of hydrogen with fluorine is possible if the reaction is carried out under dilute conditions in the presence of a catalyst, (10.23).



Sulfur tetrafluoride (SF_4) is a particularly selective fluorination agent. It can be used to convert ketones to difluoro compounds, (10.24).



10.3 Compounds of Chlorine³

10.3.1 Comparison to fluorine

To appreciate the chemistry of chlorine in comparison to that of fluorine it is necessary to appreciate the differences and trends between the elements. As may be seen in Table 10.9, chloride is significantly larger than fluorine. In addition while chlorine is an electronegative element its electronegativity is significantly less than that of fluorine, resulting in less polar bonding.

Element	Ionic radius (Å)	Covalent radius (Å)	van der Waal radius (Å)	Electronegativity
Fluorine	1.33	0.64	1.47	-4.1
Chlorine	1.81	0.99	1.75	-2.9

Table 10.9: Comparison of physical characteristics for fluorine and chlorine.

The X-Cl bond is an electron pair covalent bond with a highly polar nature. In this regard, chlorine is similar to fluorine. However, there are two key features with regard to chlorine's bonding that differentiates it from fluorine.

1. Unlike fluorine, chlorine can form multiple covalent bonds, e.g., ClO_4^- and ClF_3 .
2. Unlike fluorine, chlorine can form π -bonds with oxygen, i.e., $\text{Cl}=\text{O}$.

The chloride ion (Cl^-) forms salts with ionic lattices (e.g., NaCl) but also forms a wide range of complexes, e.g., $[\text{Fe}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ and $[\text{RhCl}_6]^{3-}$. Chloride also acts as a bridging ligand in which one, two or three chlorides can bridge two metal centers (Figure 10.20).

³This content is available online at <http://cnx.org/content/m34967/1.1/>.

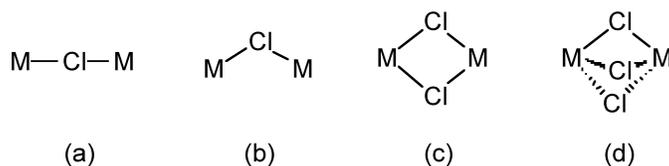


Figure 10.20: Structures of common halide bridging moieties.

Chloride (and bromide) bridges are usually bent, whereas fluoride bridges can be either linear or bent. As an example, BeF_2 and BeCl_2 are isostructural, consisting of infinite chains with bent bridges (Figure 10.21). In contrast, transition metal pentahalides show different structures depending on the identity of the halide. This, TaCl_5 dimerizes with bent bridges (Figure 10.22a), while TaF_5 forms a cyclic tetramer with linear fluoride bridges (Figure 10.22b).

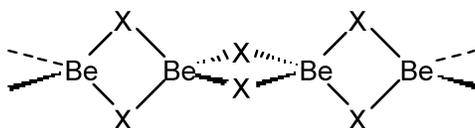


Figure 10.21: The solid state structure of BeX_2 ($X = \text{F}$ or Cl).

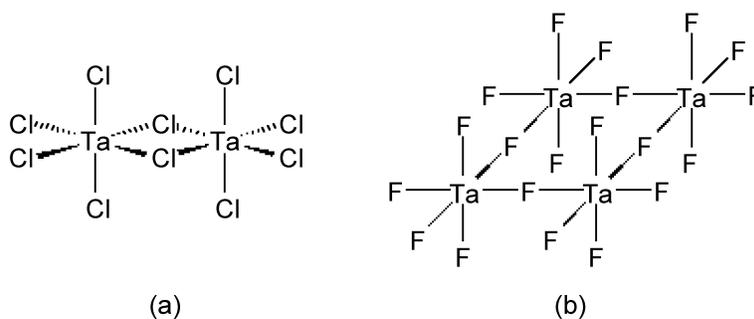


Figure 10.22: The solid state structure of (a) TaCl_5 and (b) TaF_5 .

10.3.1.1 The halide bridge

The bridging halide bonds can be described by both Lewis and molecular orbital (MO) theory. In a simple picture, the lone pair of a terminal halide can be thought to act as a Lewis base donor ligand to the second Lewis acidic metal center. Indeed some bridging halides are asymmetric consistent with this view; however, the symmetrical ones can be described by a resonance form. From a molecular orbital point of view, the bridging halide is represented by a combination of two metal centered orbitals with two halogen orbitals.

10.3.2 Hydrogen chloride

Hydrogen chloride (HCl) is prepared by the reaction of concentrated sulfuric acid (H₂SO₄) with either NaCl or concentrated HCl solution.

Hydrogen chloride is a polar molecule with a dipole of 1.08 D. However, the lower polarity as compared to that of hydrogen fluoride (1.91 D) is consistent with the physical and chemical properties. Hydrogen chloride is a gas at room temperature (Mp = -114.25 °C, Bp = -85.09 °C), and its low boiling point is consistent with weak hydrogen bonding in the liquid state. While self-ionization, (10.25), is very small, liquid HCl dissolves some inorganic compounds to give conducting solutions, (10.26).



Hydrogen chloride is soluble (and reacts) in water, (10.27). The pK_a of the reaction (-7.0) is larger than observed for fluorine (3.2) and as such HCl is a stronger acid than HF.



10.3.3 Oxides of chlorine

Chlorine forms a series of oxides (Table 10.10) in which the chlorine has the formal oxidation states +1, +4, +6, and +7. The physical properties of the oxides are summarized in Table 10.10. While, the oxides of chlorine are not very stable (in fact several are shock sensitive and are prone to explode) the conjugate oxyacids are stable.

Compound	Mp (°C)	Bp (°C)
Cl ₂ O	-116	4
ClO ₂	-5.9	10
Cl ₂ O ₄	-117	44.5
Cl ₂ O ₆	3.5	unstable
Cl ₂ O ₇	-91.5	82

Table 10.10: Physical properties of the oxides of chlorine.

Dichlorine monoxide (Cl₂O, Figure 10.23a) is a yellowish-red gas that is prepared by the reaction of chlorine with mercury oxide, (10.28), or with a solution of chlorine in CCl₄.



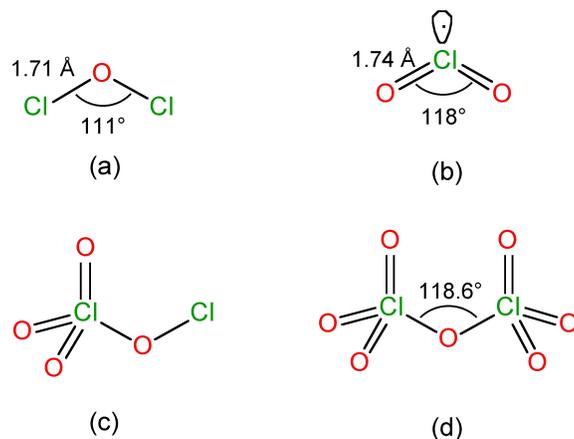


Figure 10.23: The structure of (a) Cl_2O , (b) ClO_2 , (c) Cl_2O_4 , and (d) Cl_2O_7 .

When heated or subject to a spark, Cl_2O explodes to Cl_2 and O_2 . Dichlorine monoxide reacts with water to form an orange-yellow solution of hypochlorous acid, (10.29).



Chlorine dioxide (ClO_2) is a yellowish gas at room temperature and is commonly used in industry as an oxidizing agent. The best synthesis of ClO_2 involves the reduction of potassium chlorate (KClO_3) by oxalic acid at 90°C , since the CO_2 formed acts as a diluent for the highly explosive ClO_2 . On an industrial scale ClO_2 is made by the exothermic reaction of sodium chlorate with SO_2 in sulfuric acid, (10.30). The photolysis of ClO_2 yields a dark brown solid with the formula Cl_2O_3 ; however, its facile explosive decomposition precludes study.



The structure of ClO_2 (Figure 10.23b) is equivalent to SO_2 with one extra electron, resulting in a paramagnetic unpaired electron species. Unusually, despite the unpaired electron configuration, ClO_2 shows no tendency to dimerize. This is unlike the analogous NO_2 molecule.

Dichlorine tetraoxide (Cl_2O_4) is commonly called chlorine perchlorate as a consequence of its structure (Figure 10.23c). Dichlorine hexaoxide (Cl_2O_6) is an unstable red oil that has the ionic structure in the solid state: $[\text{ClO}_2]^+[\text{ClO}_4]^-$.

Dichlorine heptoxide (Cl_2O_7) is a relatively stable oil, that is prepared by the dehydration of perchloric acid at -10°C , (10.31), followed by vacuum distillation. The structure of Cl_2O_7 (Figure 10.23d) has been determined by gas phase electron diffraction.



The reaction of Cl_2O_7 with alcohols and amines yields alkyl perchlorates (ROClO_3) and amine perchlorates (R_2NClO_3), respectively.

10.3.4 Fluorides of chlorine

Given the isolobal relationship between the halogens it is not surprising that the mixed dihalogens can be prepared, e.g., ClF, ICl, and BrCl. Chlorine fluoride is a highly reactive gas (Bp = -100.1 °C) that is a powerful fluorinating agent, and is prepared by the oxidation of chlorine by chlorine trifluoride, (10.32).



The higher electronegativity of fluorine as compared to chlorine (Table 10.9), and the ability of chlorine to form more than one bond, means that higher fluorides of chlorine are also known, i.e., ClF₃ and ClF₅. Chlorine trifluoride (ClF₃, Bp = 11.75 °C) is a useful fluorinating agent, that is prepared by the high temperature reaction of elemental chlorine and fluorine, is a useful fluorinating agent. The gaseous pentafluoride (ClF₅, Bp = -31.1 °C) is prepared by the reaction of potassium chloride with fluorine, (10.34).



The structure of ClF₃ is T-shaped with two lone pairs on chlorine (Figure 10.24a), while that of ClF₅ is square pyramidal with a single lone pair on chlorine (Figure 10.24b).

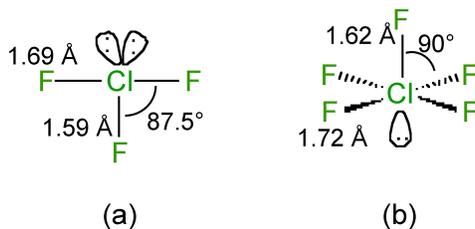


Figure 10.24: The structures of (a) ClF₃ and (b) ClF₅.

In general the halogen fluorides are very reactive; explosive reactions occur with organic compounds. They are all powerful fluorinating agents when diluted with nitrogen, and the order of reactivity follows:



Like most halogen fluorides, ClF, ClF₃ and ClF₅ all react with strong bases (e.g., alkali metal fluorides) to form anions, (10.36) and (10.37), and strong acids (e.g., AsF₅ and SbF₅) to form cations, (10.38), (10.39), and (10.40).





10.4 Oxyacids of Chlorine⁴

Table 10.11 lists the various oxyacids of chlorine. The relative strengths increase with the number of oxygen atoms since the more there are, the greater is the extent to which the negative charge on the resulting anion can be delocalized.

Oxyacid	Formula	pK _a
Hypochlorous	HOCl	7.5
Chlorous	HClO ₂	1.9
Chloric	HClO ₃	-2
Perchloric	HClO ₄	-10

Table 10.11: Relative acidity of oxyacids of chlorine.

10.4.1 Hypochlorous acid

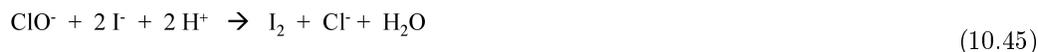
Hypochlorous acid (HOCl) can be made pure in the gas phase, (10.41), while strong acid solutions can be made from Cl₂O. In contrast, dilute aqueous solutions are obtained with a suspension of mercury oxide to remove the chloride, (10.42).



Solutions of the anion, OCl⁻, are obtained by electrolysis of brine solution; allowing the products to mix at low temperature, (10.43).



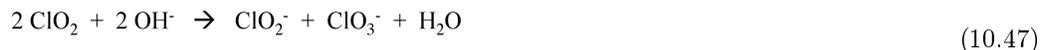
The anion (hypochlorite) is a good oxidant, (10.44) and (10.45), but can undergo disproportionation, (10.46); slowly at 25 °C, but fast above 80 °C.



⁴This content is available online at <<http://cnx.org/content/m34842/1.2/>>.

10.4.2 Chlorous acid

Chlorous acid (HOClO) is prepared by the reaction of ClO_2 with base, (10.47), followed by the precipitation of the ClO_2^- salt with barium chloride, (10.48). The barium salt is dried and then reacted with a calculated amount of H_2SO_4 , (10.49).



The pure acid is unknown since it is too unstable, however, salts can be prepared directly, e.g., (10.50).



The anion (ClO_2^-) is stable in alkaline solutions but in acid solutions decomposition occurs, (10.51).



As with hypochlorite, the chlorite anion is a strong oxidant, (10.52).



10.4.3 Chloric acid

The chloric anion (ClO_3^-) is made from the reaction of chlorine gas with hot alkali (80°C) or by the electrolysis of hot NaCl solution.



To obtain a solution of the acid, ClO_3^- is precipitated as the barium salt, (10.54), which is removed, dried, and suspended in water and treated with a calculated amount of H_2SO_4 , (10.55). The free acid cannot be isolated and a maximum concentration of only 40% can be obtained in water.



The ClO_3^- anion is pyramidal both in solid salts and in solution, and many salts are known; however, those with organic cations are explosive. The anion is a strong oxidizing agent, (10.56) and (10.57), and it disproportionates slowly in solution, (10.58).



10.4.4 Perchloric acid

The perchlorate anion (ClO_4^-) is best made by electrolytic oxidation of chlorate in aqueous solution, (10.59). Fractional distillation can concentrate the solution to 72.5% which is a constant boiling mixture. This concentration is moderately safe to use, however, 100% perchloric acid may be obtained by dehydration with H_2SO_4 .



WARNING: Perchloric acid is a very dangerous liquid that will explode if traces of metal ions are present. It is also a very strong oxidizing agent that will convert organic compounds to CO_2 and H_2O .

Perchloric acid is a very strong acid that is fully ionized in aqueous solution, such that the salt $[\text{H}_3\text{O}][\text{ClO}_4]$ can be isolated. Many other perchlorate salts are known, but those with organic cations are explosive. Perchlorate salts of metals are often used when studying complex formation in aqueous solution, because ClO_4^- is a very weak ligand (PF_6^- is better) and unlikely to form complexes itself. However, perchlorate does complex with +3 and +4 cations.

10.5 Bromine Trifluoride as a Solvent⁵

WARNING: Bromine trifluoride is a toxic, colorless, and corrosive liquid with a pungent choking smell that is soluble in sulfuric acid but explodes on contact with water and organic compounds. Vapors severely irritate and may burn the eyes, skin, and respiratory system. The liquid burns all human tissue and causes severe damage.

Bromine trifluoride (BrF_3) has a liquid range similar to water (Mp = 8.8 °C and Bp = 127 °C), and like water it auto ionizes, (10.60).



The products, like those of water's self-ionization, are an acid (BrF_2^+) and a base (BrF_4^-). However, unlike water, BrF_3 reacts with fluoride acids and bases not proton acids and bases. Thus, in BrF_3 a base is a salt that provides F^- , i.e., potassium fluoride (KF) is a base in BrF_3 solution in the same manner as potassium hydroxide (KOH) is a base in water. The product from the reaction of a fluoride donor salt with BrF_3 is the formation of the conjugate base, BrF_4^- , (10.61).



Other examples of this type of reaction include:



By analogy, an acid in BrF_3 solution is a compound that acts as a fluoride (F^-) acceptor, i.e., a Lewis acid, (10.64).



⁵This content is available online at <<http://cnx.org/content/m33061/1.3/>>.

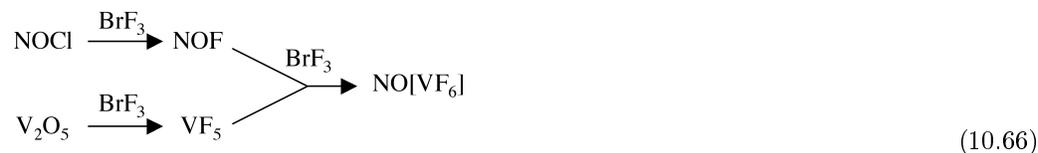
Exercise 10.5.1**(Solution on p. 485.)**What are the products from the reaction of HF with BrF₃?**10.5.1 Bromine trifluoride as a fluorinating agent**

Bromine trifluoride is a strong fluorinating agent that is able to convert a metal (e.g., vanadium) to its associated fluoride compound, (i.e., VF₅). A wide range of salts and oxides may be converted to fluorides with the metal in a high oxidation state. However, it should be noted that BeO, MgO, and Al₂O₃ form oxo fluorides rather than the fluoride.

The reaction of silver with BrF₃ yields the monofluoride, while the same reaction with gold yields the trifluoride, Eq. If the reactions are combined in BrF₃ solution a mixed metal fluoride salt is formed, (10.65).



A similar reaction occurs with NOCl and V₂O₅, (10.66).

**Exercise 10.5.2****(Solution on p. 485.)**

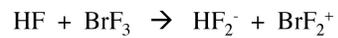
What are the products from the reaction of BrF₃ with (a) Sb₂O₅, (b) KCl, and (c) a mixture of Sb₂O₅ and KCl?

10.5.2 Bibliography

- J. H. Simons, *Inorg. Synth.*, 1950, **3**, 184.

Solutions to Exercises in Chapter 10

Solution to Exercise 10.5.1 (p. 484)



Solution to Exercise 10.5.2 (p. 484)

(a) SbF_5 , (b) KF , and (c) $\text{K}[\text{SbF}_6]$.

