

## Lecture 32 - Group 17

- Group 17 - The Halogens
- The compounds
  - Oxides and Acids
  - Interhalogen Compounds
  - Sulfides

Group  
7B

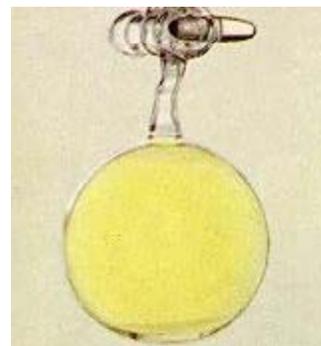
F <sup>9</sup>
Cl <sup>17</sup>
Br <sup>35</sup>
I <sup>53</sup>
At <sup>85</sup>

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## Group 17 - The Halogens "salt formers"

- The elements F, Cl, Br, I and At (Astatine) are known collectively as the halogens, meaning "salt-producers".
  - The name was first applied to Cl because of its ability to combine with metals to form salts.
  - Although there is the usual variation in group properties, the striking similarities among these elements are reminiscent of those of the alkali and alkaline earth metals.
  - F- latin fluere "to flow", Cl - greek chloros "green", Br greek bromos "stench", Iodine greek iodes "violet-like", At- astatine greek "astates" unstable (it is radioactive and there are no stable isotopes).
  - The most common compound is **sodium chloride** which is found from natural evaporation as huge deposits of 'rock salt' or the even more abundant 'sea salt' in the seas and oceans.
  - They lack only one electron to form a complete shell or subshell, and are extremely active chemically.
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- At room temperature, fluorine and chlorine are gases, bromine is liquid, and iodine is solid. They form diatomic molecules in the pure state. The halogens are poisonous, and chlorine gas and chlorine compounds have been used as chemical weapons. In small concentrations, chlorine is used to disinfect drinking water and to disinfect swimming pools.



### General Trends in Halogen Chemistry

There are several patterns in the chemistry of the halogens.

- Neither double nor triple bonds are needed to explain the chemistry of the halogens.
- The chemistry of fluorine is simplified by the fact it is the most electronegative element in the periodic table and by the fact that it has no  $d$  orbitals in its valence shell, so it can't expand its valence shell.
- Chlorine, bromine, and iodine have valence shell  $d$  orbitals and can expand their valence shells to hold as many as 14 valence electrons.
- The chemistry of the halogens is dominated by oxidation-reduction reactions

## Fluorine

- Name: derived from the Latin word "fleure," meaning to flow.
- Discovery: Fluorine was first prepared in 1886 by Henri Moissan after seventy-four years of effort by investigators including Davy, Gay-Lussac, Lavoisier, and Thenard.
- Description: It is a greenish pale yellow acidic gas and has a strong odor. Fluorine is the most reactive of the non-metals, and therefore will combine with most other elements.
- Source: Fluorine never occurs as a free element in nature. It most commonly occurs in the minerals cryolite, fluorspar, and fluorapatite. 0.06% of the Earth's crust is fluorine, which makes fluorine the 13th most common element in the crust.
- Uses: As an element, fluorine is used in rocket fuels and helps other materials burn. It was formally used in the production of CFC's until it was found that compounds in CFC's were damaging the Earth's ozone layer. A safer compound was substituted. Most fluorine is used in fluorine compounds. The element is used to make uranium hexafluoride, which is needed by the nuclear power industry. Fluoride is in toothpaste. It has been shown to reduce tooth decay. In a process called fluoridation, fluoride is added to a water supply to help prevent tooth decay. This is mostly beneficial to young children because their teeth are still developing. The average human body contains about a hundredth of an ounce of fluorine.
- Biological Role: The element fluorine is highly toxic. Too much of the fluoride ion can also be toxic.

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## Chlorine

- Name: derived from the Greek word "khlôros" meaning pale green.
  - Discovery: 1774 by C.W. Scheele in Uppsala, Sweden.
  - Description: a greenish yellow, dense gas with a sharp, pungent smell.
  - Source: Chlorine is not found free in nature, but combined chiefly with sodium chloride in common salt and the minerals carnallite and sodium chloride.
  - Uses: Chlorine is used to produce safe drinking water and many consumer products such as paper, dyestuffs, textiles, petroleum products, medicines, antiseptics, insecticides, foodstuffs, solvents, paints, and plastics. It is also used to produce chlorates, chloroform, carbon tetrachloride and bromine. A further substantial use for this element is in organic chemistry, both as an oxidizing agent and in substitution reactions.
  - Biological Role: The chloride ion is essential to life. Chlorine gas is a respiratory irritant, which can be fatal after a few deep breaths. It was used as a weapon in World War II. Chlorine liquid burns the skin.
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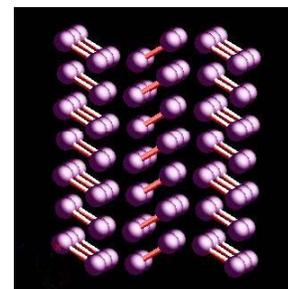
## Bromine

- Name: Derived from the Greek word "bromos" which means stench.
- Discovery: It was first isolated in pure form by a man named Antoine Jerome Balard in 1826, after being discovered by him in salt water.

Description: Bromine is a reddish-brown liquid that is very stinky and that fumes at room temperature. Bromine is the only non-metal that is a liquid at normal room conditions. Watch out! Once bromine contacts skin it causes painful burns that heal very slowly.

- Source: It does not occur uncombined in nature, but rather can be found combined with other elements and in salt water and springs. Bromine is produced by displacement from common sea water. Generally, chlorine is used to dislodge the bromine from other compounds in the water.
  - Uses: Bromine was used as an additive in leaded gasoline (when it was still on the market) to help prevent engine "knocking". Now it is used mostly in dyes, disinfectants, and photographic chemicals.
  - Biological Role: Bromine plays no biological role.
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## Iodine



- Name: Iodine, iodes means "violet" .
- Discovery: Iodine was discovered in 1811 by Bernard Courtois in France. Courtois often helped his father create sodium and potassium compounds. They would gather seaweed, burn it, and then soak it in water. Sulfuric acid would then be added in order to get the unwanted seaweed chemicals out of the mixture. After the water evaporated, they would be left with the compounds. Courtois discovered Iodine one day when he added too much sulfuric acid which created a beautiful release of violet vapor.
- Description: When solid it looks metallic and has a grayish- black or violet-dark gray color. As a gas (because of sublimation Iodine never exists as a liquid) it has a violet color and a harsh, unpleasant odor.
- Source: Salt mines contain some Iodine along with sea water but the main source is sea kelp. As kelp grows it takes Iodine out of the water. In order to collect the Iodine the sea kelp is harvested, dried and burned.

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- Uses: Iodine makes an excellent germ killer which links to its use in sanitation systems along with the creation of antiseptics and drugs. However it can also be used to make dyes, specialized soaps and photographic film. Chemists also use Iodine as a catalyst, a substance used to alter the speed of a chemical reaction.
  - Biological role: As mentioned before Iodine kills bacteria and other pathogens. It is also very crucial in maintaining a healthy life. Iodine is implicated with the production of the thyroid hormones.
  - People who do not maintain the proper level become ill with Goiter, the main symptom of which being the growth of a large lump in the base of the neck.
  - A lack of Iodine is also the leading cause of mental retardation, deafness, mutism and paralysis.
  - Because of this, many companies now support the manufacturing of iodized salt, when they add potassium iodide to the table salt.
  - In high doses the element can be just as harmful. It can irritate and burn the skin. If ingested it can be very poisonous.
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## Astatine

- Name: from the Greek word "astatos" meaning unstable.
  - Discovery: synthesized by bombarding Bismuth with alpha particles in 1940 by D.R. Corson, K. R. MacKenzie, and Emilio Segre
  - Description: Astatine is metallic in color. The longest lived isotope of astatine has a half-life of only 8.3 hours. There are only 20 isotopes, and astatine is radioactive.
  - Source: man-made.
  - Uses: sometimes used as a radioactive tracer.
  - Biological Role: Astatine is thought to accumulate in the thyroid gland like iodine, but this is probable. Some doctors believe if it behaves like iodine, astatine can be taken into the body and maybe used to kill cancer. However, not much information is known on astatine's role in the body.
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## Fundamental Properties and the Network

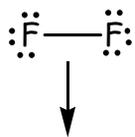
- The group is not divided by the metal-nonmetal line.
  - All halogens are non metals, although iodine and probably astatine do show some signs of metallic character. For example, solid iodine exhibits a metallic luster and, under some conditions, a complexed  $I^+$  cation.
  - At very high temps. Iodine is a conductor of electricity.
  - The above are exceptions and in general, the properties of these elements are consistent with their classification as nonmetals.
  - Fluorine is extremely reactive and observed to have properties so special that it cannot be classified as just another halogen, but rather should be called the "superhalogen".
  - It combines with all elements except helium, neon and argon.
  - Diatomic fluorine is so reactive that it will remove hydrogen from all of its compounds except HF.
  - Metals react violently when exposed to fluorine gas to produce salts.
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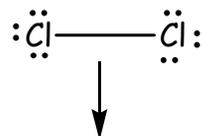
## Why should flourine be so much more reactive than its congeners?

- The first factor is the weakness of the F-F bond (155 KJ/mol) in the diatomic molecule.
  - The F-F internuclear distance is so small that the lone pairs on each atom are thought to significantly repel each other.
  - The high electronegativity of flourine gives a large polar or ionic component to all E-F bonds in addition to the normal covalent bond strength.
  - The H-F bond has a particularly high bond energy (568 KJ/mol), making it among the strongest single bonds known.
  - For these reasons, the reactions of flourine with nonmetals (producing covalent E-F bonds) are most favorable.
  - When diatomic F reacts with metals, ionic flourides are formed. These too are exceptionally stable, and the reactions that produce them are correspondingly favorable.
  - The stability of ionic flourides can be traced to the exceptionally small size of the F<sup>-</sup> ion, leading to a high charge density compared with other anions.
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Compare F<sub>2</sub> with Cl<sub>2</sub>



smaller bond  
short bond  
the lone pairs repel  
each other, this leads  
to a weakening of the bond

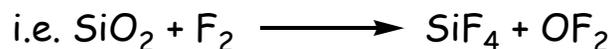


larger bond  
increasing bond length from Cl<sub>2</sub> - At<sub>2</sub> which  
leads to weaker bonds

Bond Energies KJ/mol

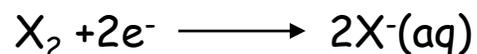
F	155
Cl	240
Br	190
I	149
At	116

F<sub>2</sub> is more reactive than the other halogens due to the weak F-F bond.  
It reacts with metals, metal oxides and non metal oxides

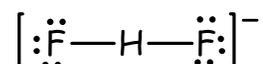


Since it is so reactive it is difficult to isolate

- A high charge density corresponds to a high value of the lattice energy, the energy released when an ionic lattice is formed from its constituent gaseous ions.
- The trends in standard reduction potentials of the halogens are closely related to the uniqueness of fluorine.
- F has the highest  $E^\circ$  (2.87 V) of the group and that chlorine is a distant second (1.36 V), with the rest of the values steadily decreasing from 1.07 to 0.3 V.
- The more positive the value of the standard reduction potential, the more spontaneous the reduction half-reaction tends to be and the stronger the oxidizing properties of the halogen.
- F is by far the strongest oxidizing agent of the halogens, and the oxidizing abilities steadily decrease as you go down the group.
- F is the strongest oxidizing agent since the exceptionally low F-F bond energy makes the bond easy to break and greatly favors the generation of  $2F^\cdot$ , so does the charge density of the small fluoride ion, leading to a large exothermic hydration energy (the energy released when a gaseous ion is surrounded by polar water molecules).



- The primary reason for the decrease in oxidizing power of the heavier halogens is the decreasing hydration energy (as the ions get larger) and the decreasing electron affinity.
- The F<sup>-</sup> ion undergoes strong H-bonding  
The HF<sub>2</sub><sup>-</sup> ion exists



equal in length  
there is strong H bonding

### HydroAcids - Hydrides

- HF - weak acid  $K_a = 6.7 \times 10^{-5}$
- HCl, HBr, HI are all strong acids they dissociate completely in water.
- HF is more dangerous than HCl inspite of it being weak.
- It exists as undissociated molecules than can be absorbed through the skin and work its way to the bones.

Hydrofluoric Acid (HF) is one of the strongest and most corrosive of the inorganic acids. Therefore, special safety precautions are necessary when using this chemical. HF is used in a variety of industrial and research applications including glass etching, pickling of stainless steel, removal of sand and scale from foundry castings and as a laboratory reagent. Exposure usually is accidental and most likely due to inadequate use of protective measures (face shields, safety goggles, acid gloves and acid aprons). In the US, more than 1000 cases of HF exposure are reported annually. Actual incidence rate is unknown.

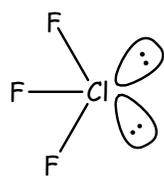
- HF acid burns are a unique medical problem. Dilute solutions deeply penetrate before dissociating, thus causing delayed injury and symptoms. Burns to the fingers and nail beds may leave the overlying nails intact. Severe burns occur after exposure of concentrated (ie, 50% or stronger solution) HF acid to 1% or more body surface area (BSA), exposure to HF acid of any concentration to 5% or more body surface area (BSA), or inhalation of HF acid fumes from a 60% or stronger solution. The vast majority of cases involve only small areas of exposure, usually on the hands and fingers.
- The 2 mechanisms that cause tissue damage are corrosive burn from the free hydrogen ions and chemical burn from tissue penetration of the fluoride ions.
- Fluoride ions penetrate and form insoluble salts with calcium and magnesium.
- Soluble salts also are formed with other cations but dissociate rapidly. Consequently, fluoride ions release, and further tissue destruction occurs.
- Mortality/Morbidity:
- Local effects include tissue destruction and necrosis. Burns may involve underlying bone.
- Systemic fluoride ion poisoning from severe burns is associated with hypocalcemia (low Calcium levels), hyperkalemia (low Potassium levels), hypomagnesemia (low magnesium levels), and sudden death.
- Deaths have been reported from concentrated acid burns to as little as 2.5% Body Surface Area (BSA).

## Oxides, Oxo Acids

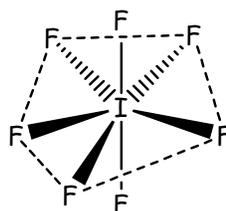
- They are obnoxious smelling highly unstable oxidizing agents with the disconcerting tendency to explode.
- The major chlorine oxides are:  
 $\text{Cl}_2\text{O}$ ,  $\text{ClO}$ ,  $\text{ClO}_2$  (used in bleaching pulp for paper making, it is kept well diluted to decrease the chances of explosion) and  $\text{Cl}_2\text{O}_7$ .
- All are strong oxidants, as well as being unpleasant explosive substances.
- $\text{Cl}_2\text{O} + \text{CaO} \longrightarrow \text{Ca}(\text{OCl})_2$  this is household bleaching powder. ( $\text{NaOCl}$  - liquid bleach).
- Dichlorine heptoxide  $\text{Cl}_2\text{O}_7$  is a shock-sensitive oily liquid. It is formally the anhydride of perchloric acid.
- There are no stable bromine oxides at room. temp.
- Of the iodine oxides, diiodine pentoxide,  $\text{I}_2\text{O}_5$  is the most important. It is used to quantitatively determine  $\text{CO}$  concentrations.

## Interhalogens

- The interhalogens are generally considered to be compounds composed of two or more different halogen atoms.
- The neutral binary interhalogens, of formula  $XX'_n$  where X is the less electronegative and X' is the more electronegative atom. Examples of these are given in Table 18.3  
e.g. ClF, ClF<sub>3</sub>, ClF<sub>5</sub>, BrCl, BrF, BrF<sub>2</sub> etc..
- As a general rule, the larger, less electronegative atom is in the centre surrounded by one, three, five or seven smaller, more electronegative atoms.



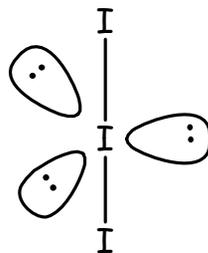
Chlorine trifluoride



Iodine heptafluoride

- The most common of the polyatomic monohalogen anions is the triiodide ion  $I_3^-$ .
- The solubility of solid iodine  $I_2$  in water is greatly enhanced by the addition of an alkali-metal iodide, most often KI.
- The increased solubility is due to the formation of the aqueous  $I_3^-$  ion.
- $I_2(aq) + I^- \longrightarrow I_3^-(aq)$

- The linear structure of the triiodide anion is in accord with VSEPR theory ideas.
- Other  $I_n^{m-}$  ions can be thought of as combinations of  $I^-$ ,  $I_2$  and  $I_3^-$  groups held together by intermolecular forces
- Refer to Figure 18.4, Rogers.



The structure of triiodide  $I_3^-$

## Sulfur Halides

$SF_6$  - gas that is used as an electrical insulator or in a transformer (it is an octahedral molecule).

$S_2Cl_2$  and  $S_2Cl_2$  are used in the vulcanization of rubber for the production of tires.  $S_2Cl_2$  is shipped in railway tank cars, it is shipped as a liquid, 50 tons per car to the tire companies.