Introduction

- All elements except helium, neon and krypton form some sort of halogen compound.
- The structures vary from ionic to covalent.
- Halides are often the source materials for the synthesis of other substances.
- The halides are often the "generic" compounds used to illustrate the range of oxidation states for the other elements.
- The class of fluorocarbons is an important group of organic chemicals which often have unique properties.

Occurrence and Isolation, and Properties of the Elements

Fluorine

- Occurs in fluorspar, CaF₂, cryolite, Na₃AlF₆ and fluorapatite, 3Ca₃(PO₄)₂.Ca(F,Cl)₂. It is actually more abundant than chlorine.
- It is made by electrolysis, for example, of a mixture of 2 to 3 parts of HF with KF which melts at 70 - 100 °C. It is a pale yellow gas, bp -118 °C.
- It is the most reactive of all the elements and attacks all the others except He, Ne and Ar so it has to be handled in special apparatus: stainless steel and copper because they become coated with a protective fluoride layer and are the materials of choice. (If all traces of HF are removed, fluorine can be handled in glass apparatus also, but this is nearly impossible.)
- Fluorine will also attack many compounds yielding fluorides.
- The reason for its great reactivity seems to be connected with the weak F-F bond probably due to strong repulsion between the non-bonding (lone-pair) electrons. (In this respect it is similar to hydrazine and hydrogen peroxide.)

Chlorine

- Occurs mainly as rock salt, NaCl, potassium chloride and magnesium chloride.
- Chlorine is manufactured by the electrolysis of brine. At one time this was done using a mercury cathode, which also produced sodium amalgam, hence sodium hydroxide by hydrolysis. The sodium hydroxide was often recombined with the chlorine to form sodium hypochlorite (bleach) for use in the paper industry. The mercury is now recognized as a major pollutant. Now "membrane" cells are used to prevent the electrolytes around the two electrodes from mixing.
- Chlorine is a green gas bp -34.6 °C.
Bromine

- It occurs with chlorine and can be obtained by displacement from bromides with chlorine.
- Bromine is a brown liquid, mp -7.2, bp 58.8 °C.

Iodine

- Iodine is found in brines, and as IO₃⁻ with deposits of NaNO₃.
- It is black solid with a metallic sheen. It sublime at room temperature and its vapour is purple. It also forms purple solution in non-polar solvents.
- The brown solution obtained by dissolving iodine in potassium iodide contains the linear I₃⁻ ion.

  The intense blue complex with starch used in iodometric titrations contains the I₅⁻ ion.

Halides

They can be made by:

1. Direct reaction. In the case of fluorine, particularly, high oxidation states can be reached.
2. Reaction with an oxide.
3. Halogen exchange reactions.
4. By dehydration of hydrated halides.

Molecular Halides

As a class of compounds, the halides illustrate the distinction between ionic solids, network solids and molecular compounds (which can be solids liquids or gases). This section deals with all three, its heading notwithstanding!

- Broadly, the more covalent the halide, the more likely it is to be truly molecular. Examples would be BCl₃ or IF₃.
- As the compounds become less covalent, halogen bridges are found, leading first to dimers such as Al₂Cl₆.
- As the covalency continues to decrease, the amount of bridging increases and network solids can be found. An example is (AlF₃)ₙ in which all the aluminum is 6-coordinated and all the fluorines are bridging (2-coordinate). The bonding remains quite covalent.
- At the ionic limit one finds salts such as sodium chloride, where the forces between sodium and chloride ions are almost entirely electrostatic. Both ions are 6-coordinate in NaCl.
- The position along the above progression is influenced by factors such as the electronegativity of the components, their size, and the possibility of multiple bonding which might stabilize a monomeric molecular compound such as BF₃ (pp - pp) or SF₆ (dp - pp).

The particularly high electronegativity of fluorine leads to some special properties in its compounds:

- CF₃COOH is a strong acid unlike CH₃COOH.
- NF₃ and N(CF₃)₃ are not at all basic, unlike ammonia.
Halogen Oxides

**Fluorine** forms two oxygen compounds:

1. Oxygen Fluoride, OF₂ a yellow gas produced by:

   \[ \text{F}_2 + \text{NaOH(aq)} \rightarrow \text{OF}_2 \]

2. Dioxygen difluoride, O₂F₂ a yellow-orange solid produced by:

   \[ \text{F}_2(g) + \text{O}_2(g) \rightarrow \text{O}_2\text{F}_2 \text{ (Electric discharge through the reactants)} \]

**Chlorine** does not react directly with oxygen, but forms a dangerously explosive paramagnetic oxide ClO₂ in the following reaction:

\[ \text{NaClO}_3 + \text{SO}_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{ClO}_2 + 2\text{NaHSO}_4 \]

It is used as a chlorinating agent in organic synthesis well diluted with air!

**Iodine** forms one important oxide, I₂O₅, by dehydration of HIO₃:

\[ \text{HIO}_3 \rightarrow \text{I}_2\text{O}_5 + \text{H}_2\text{O} \text{ (240 °C)} \]

Its use is as a reagent for quantitative analysis for carbon monoxide:

\[ 5\text{CO} + \text{I}_2\text{O}_5 \rightarrow \text{I}_2 + 5\text{CO}_2 \]

then the iodine is titrated as triiodide with thiosulphate:

\[ \text{I}_2 + \Gamma \rightarrow \text{I}_3^- \]
Oxo Acids

• The reaction of the halogens with water produces hypohalous acids, HOX, and halide ion in solution:

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

The pure compounds are unknown except HOF which is none too stable itself.

The solutions can be used to obtain the salts e.g. sodium hypochloride, bleach. The XO\(^-\) ions disproportionate further in basic solution, (IO\(^-\) very rapidly even in neutral solution):

\[ 3\text{ XO}^- \rightarrow 2\text{ X}^- + \text{ XO}_3^- \]

• For chlorine the following reactions are important:
  ◦ Production of chlorite, ClO\(_2^-\), and chlorate, ClO\(_3^-\):

\[ \text{ClO}_2 + 2\text{OH}^- \rightarrow \text{ClO}_2^- + \text{ClO}_3^- + \text{H}_2\text{O} \]

  ◦ Perchlorate is produced by electrolytic oxidation of chlorate:

\[ \text{ClO}_3^- + \text{H}_2\text{O} \rightarrow \text{ClO}_4^- + 2\text{H}^+ + 2\text{e}^- \]

• Periodate species are unlike the others due to the large size and low electronegativity of iodine. The following equilibria are important:

\[ \text{H}_5\text{IO}_5 \]

\[ \text{H}^+ + \text{H}_4\text{IO}_5^- \ K = 10^{-3} \]

\[ \text{H}_4\text{IO}_6^- \]

\[ \text{IO}_4^- + 2\text{H}_2\text{O} \ k = 29 \]
Periodate is used as an oxidizing agent in organic synthesis.

Interhalogens

- The species are molecules or molecule ions, for example, BrCl, IF₅, Br₃⁺, I₃⁻.
- The neutral species will be XX'ₙ where n is odd and 7 or less and X' will be the lighter halogen. The range of isolable compounds is governed by steric effects.
- Most are made by direct reactions.

Organic Compounds of Fluorine

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