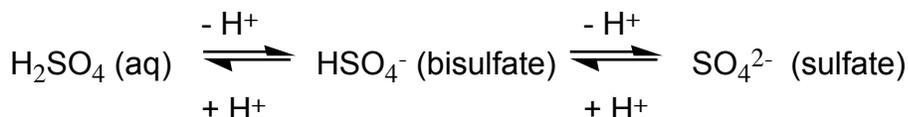


Also get solid polymers.

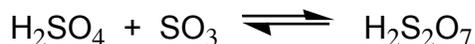
SO₃ is a powerful oxidant, with water, gives sulfuric acid – H₂SO₄.

A viscous, hydrogen bonded liquid; which is a good strongly acidic solvent. In dilute solutions in water it is a dibasic acid.



Many salts known for both anions. Sulfate can be monodentate or bidentate ligand.

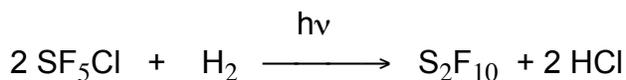
SO₃ dissolves in concentrated H₂SO₄ to give “fuming” sulfuric acid which contains some pyrosulfuric acid – VERY CORROSIVE



Halides of Sulfur

Sulfur hexafluoride (SF₆) is a gas at stp. Octahedral structure. Formed from the reaction of S with excess F₂; a very violent reaction. SF₆ is very inert and has a high dielectric constant so is used as an insulator. Kinetically inert due to (a) coordinate saturated S, and (b) high S-F bond strength. Thermodynamically should react with water but rates are too slow.

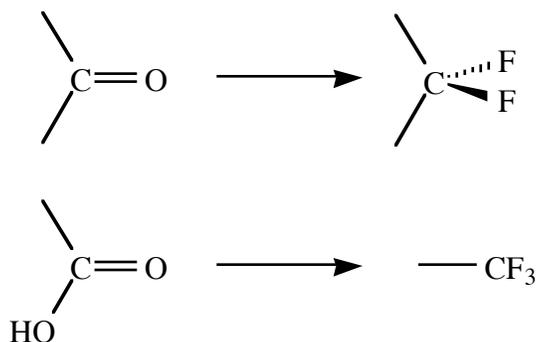
S₂F₁₀ contains a weak S-S bond with octahedral coordination. It is unreactive at room temperature, but at high temperature is a powerful oxidant.



Sulfur tetrafluoride has a trigonal bipyramidal structure with the lone pair in an equatorial position. .



Useful fluorinating agent



Chlorides are less stable and not so useful for synthesis. Don't get SCl_6 , but can make SCl_2 and SCl_4 (unstable).

Summary

1. Variation in properties: like Group 15, the elements of Group 16 cover the spectrum of properties from non-metallic oxygen to metallic polonium.
2. Oxidation states: oxygen is confined to a maximum possible OS of 2+ (in OF_2). The other elements form hypervalent compounds up to the group oxidation state maximum of 6+. The 2- state (which provides an octet of electrons) occurs for all elements.
3. Catenation: the ability of an element to form chains, is a commonly occurring theme in sulfur chemistry, second only to carbon.
4. Strong $p\pi$ bonding occurs between oxygen and many other elements. The oxides of the non-metallic elements are acidic, while those of metals are typically basic.

The Group 17 (Halogen) Elements

Aims

1. Unique features of fluorine
2. Decrease in electronegativity and increase in metallic character going down the Group.

Fluorine

2 types of compounds

- a) ionic F⁻: easy to form fluoride ion, fairly small non-polarizable (hard), stable in ionic lattices with metal cations with a large charge (MnF₄, CrF₅).
- b) Covalent bonding X-F.
 - i. polar – high ionic character, big inductive effect, (CF₃CF₂OH is acidic as acetic acid)
 - ii. Strong bonds due to fact that can have 80% ionic character, need high activation to break. Stabilize high oxidation states.
 - iii. Very weak van der Waal forces (due to low polarizability). Even with large molecular weight (WF₆ bp = 17 °C)

F₂ gas very reactive, due to weak F-F bond and strong X-F bond; activation energy is small.

Hydrogen Fluoride



Condense the vapor to get liquid HF, purify by distillation.

Bonding has a lot of ionic character, very polar (molecule has a large dipole moment).

In the gaseous state it is monomeric above 80 °C, at lower temperatures, associated into small polymers (cyclic [HF]₆) by strong intermolecular hydrogen bonds.

The pure liquid (bp = 19.5 °C, mp = -83 °C) has extensive association through strong hydrogen bonding (zig-zag chains). It has a high dielectric constant. Good solvent for polar molecules (not very good for salts because does not solvate well). Useful because (a) non-oxidizing, (b) easy to evaporate. Handle in metal or polyethylene vessels. TOXIC and CORROSIVE (very bad burns). Slightly self ionized.

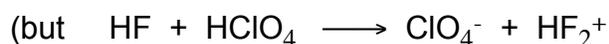
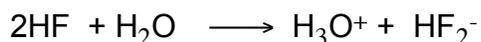
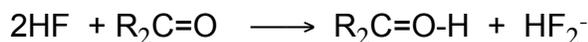


F⁻ is also solvated by HF

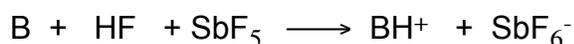


Uses of HF

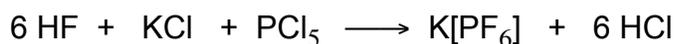
1. As a strong oxidizing agent – hydrolyse proteins, acid catalyzed condensation reactions
2. Study protonation reactions (strongly acidic)



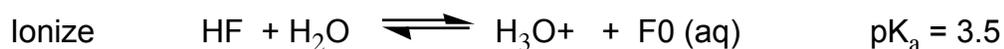
3. Acidity increased by adding fluoride acceptors (SbF₅)



4. To synthesize other fluorine-containing compounds.



Aqueous solutions (commercially, 40 % solutions available: CAUTION painful burns)



The pK is fairly low; HF is a weaker acid than HCl < HBr < HI; even though F is more electronegative than the other halogens. The weak acidity occurs because of strong H-F bond.

Many fluoride salts are formed (NaF, CaF₂) with ionic lattices. Since F⁻ is the smallest and least polarizable anion, it can occur with metal ions in high oxidation states (the ionization energies needed are recovered by the high lattice energy).

Fluoride complexes [Fe(III)F₆³⁻, Ru(V)F₆⁻, Pt(IV)F₆²⁻, Sn(IV)F₆²⁻] may be made isolated. In each case the metals are in their highest oxidation states.

Chlorine (a comparison with fluorine)

1. larger species; covalent radii 0.99 Å (Cl) versus 0.64 Å (F)
2. electronegativity: 2.9 (Cl) versus 4.1 (F)
3. Bonds (a) X-Cl similar to X-F; (b) can give greater than 1 bond (ClO_4^-)

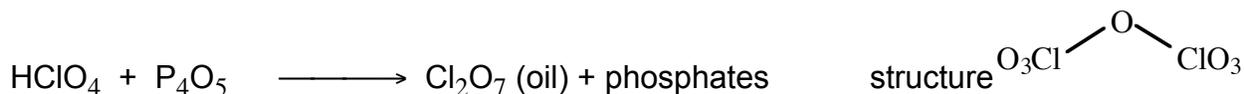
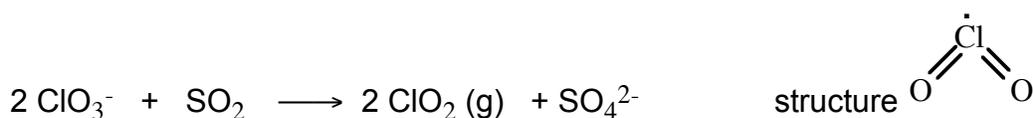
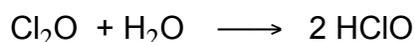
Cl_2 gas is very toxic and very reactive through direct combination with other elements.

Hydrogen Chloride

HCl gas is less polar than HF; in the liquid phase there is little H-bonding and it makes a poor solvent. Strong acid in aqueous solution.

Oxides of Chlorine

Oxides are not very stable (Cl_2O , ClO_2 , Cl_2O_7)



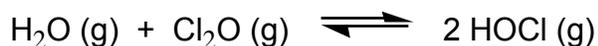
Oxyacids of Chlorine

The relative strength increases with the number of oxygen atoms, since the more the negative charge is delocalized.

Hypochlorous	HOCl	$\text{pK} = 7.5$
Chlorous	HOClO	$\text{pK} = 1.9$

Chloric	HOClO ₂	pK = -2
Perchloric	HOClO ₃	pK = -10

Hypochlorous acid: this acid can be made pure in the gas state



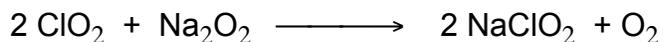
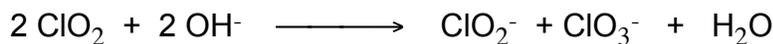
Strong aqueous solutions can be made from Cl₂O, but dilute aqueous solutions are made from dissolution of Cl₂.



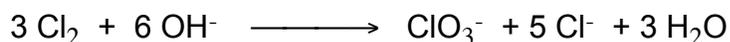
An improved yield is obtained by using a suspension of HgO to remove the chloride.



Chlorous acid: is not known as a pure acid, but made in solution or as a salt.

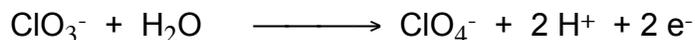


Chloric acid: the anion is made from Cl₂ in hot alkali (> 80 °C) or by electrolysis of hot NaCl solutions.



The free acid is not isolated a maximum concentration in water is 40 %, but salts are isolated. SALTS WITH ORGANIC CATIONS ARE EXPLOSIVE

Perchloric acid: The anion is best made by electrolytic oxidation of chlorate in aqueous solution.



By fractional distillation it can be concentrated to 72.5% (constant boiling mixture); this is modestly safe to use. The 100% perchloric acid can be made by distilling from a dehydrating agent (conc. H₂SO₄). It is a dangerous liquid that EXPLODES if traces of metal ions are present. It is a powerful oxidizing agent (organic compounds → CO₂ +

H₂O). A very strong acid; many salts known (those with organic cations are EXPLOSIVE); very weak ligand.

Fluorides

