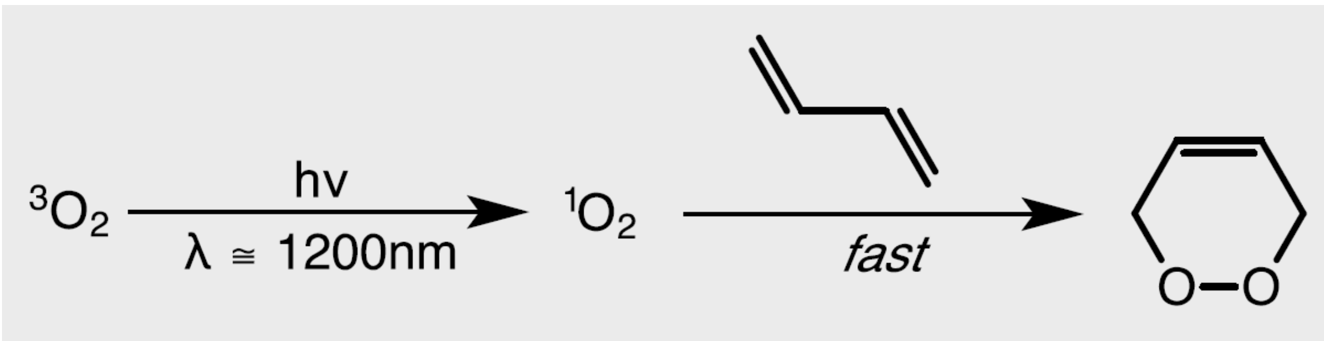
Chemistry of the Main Group Elements: Chalcogens through Noble Gases

Sections 8.7-8.10

Monday, November 9, 2015

Oxygen

- **Forms compounds with every element except He, Ne, and Ar**
- **Two naturally occurring allotropes: O_2 and O_3**
- **O_2 has two unpaired electrons and a triplet ground state that moderates its reactivity**



Oxygen

Both O_2 and O_3 are powerful oxidants

remember
$\Delta G = -nFE°$

$$O_2 + 4H^+ + 4e^- \xrightleftharpoons{E°=+1.23V} 2H_2O$$

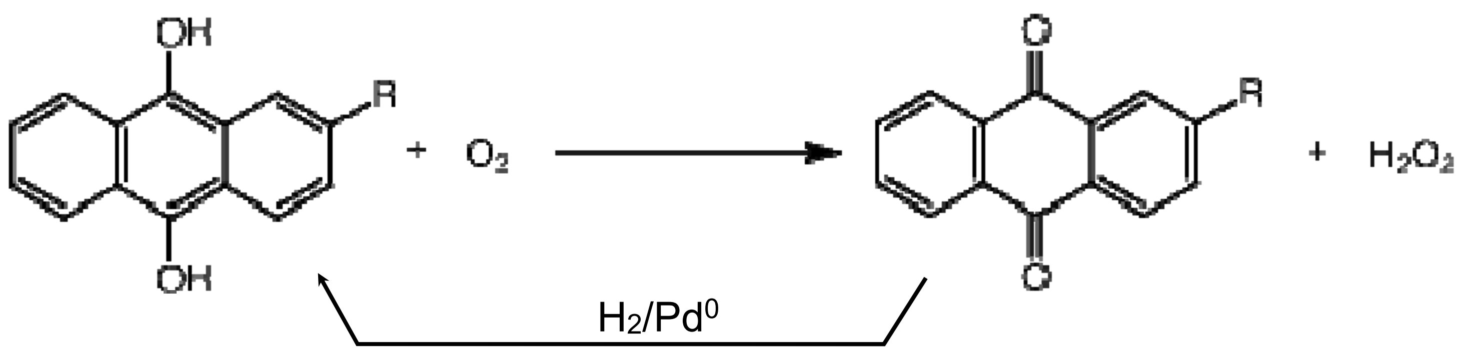
$$O_3 + 2H^+ + 2e^- \xrightleftharpoons{E°=+2.08V} H_2O + O_2$$

Partial reduction of O_2 gives hydrogen peroxide

$$O_2 + 2H^+ + 2e^- \xrightleftharpoons{E°=+0.70V} H_2O_2$$

$$H_2O_2 + 2H^+ + 2e^- \xrightleftharpoons{E°=+1.76V} 2H_2O$$

Hydrogen peroxide synthesis is achieved with anthraquinone



Oxides

An oxide is any compound with an oxygen in the 2– oxidation state; there are three types,

- *basic oxides* **are formed with metals and give basic solutions when dissolved in water**

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

$$MgO + 2H^+ \longrightarrow Mg^{2+} + H_2O$$

- *acidic oxides* **are formed with *p*-block elements and give acid solutions when dissolved in water**

$$N_2O_5 + H_2O \longrightarrow 2HNO_3$$

$$Sb_2O_5 + 2OH^- + 5H_2O \longrightarrow 2Sb(OH)_6^-$$

- *amphoteric oxides* **can act as either acids or bases**

$$ZnO + 2H^+ \longrightarrow Zn^{2+} + H_2O$$

$$ZnO + 2OH^- + H_2O \longrightarrow Zn(OH)_4^{2-}$$

Sulfur

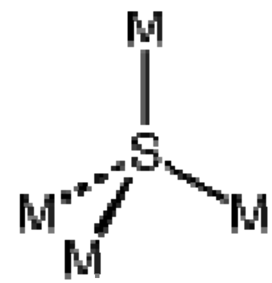
Sulfur has many allotropes

- **S_2, S_3, S_6, S_7, <u>α-S_8</u>, β-S_8, γ-S_8, ... , S_{20}**

Considered ‘soft’ compared to oxygen, it bonds strongly to most transition metals

***μ^2*-sulfide**

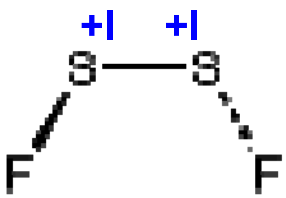
***μ^3*-sulfide**



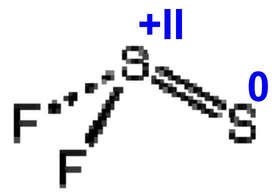
***μ^4*-sulfide**

Sulfur Halides

There are seven different sulfur fluorides...

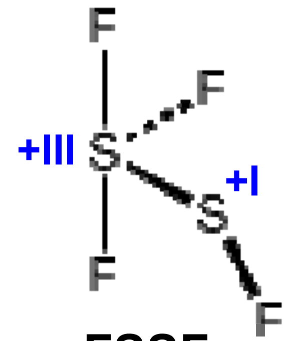


S_2F_2

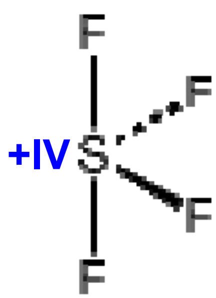


SSF_2

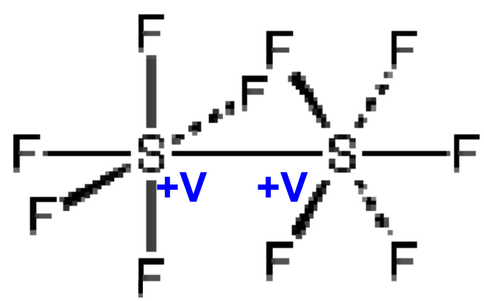
SF_2



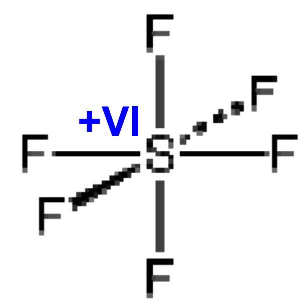
$FSSF_3$



SF_4



S_2F_{10}



SF_6

...but for the other halogens only S_2X_2 and SX_2 complexes are known

$$S_8 + xsCl_2 \longrightarrow S_2Cl_2 \xrightarrow[FeCl_3]{xsCl_2} SCl_2$$

Halogens

Chemistry of the halogens is dominated by the drive to complete the octet.

- one allotrope for the elemental forms – X_2
- HF is extremely toxic – it will leach Ca^{2+} from tissue and bone

Fluorine is the most reactive non-metal and most powerful oxidant

- discovered in 1886 during HF electrolysis
- first chemical synthesis in 1986 by Karl Christie at USC

$$K_2MnF_6 + 2SbF_5 \xrightarrow{150°C} 2KSbF_6 + [MnF_4] \longrightarrow MnF_3 + \frac{1}{2}F_2$$

Commercial uses

- preparation of aluminum and steel
- synthesis of Teflon

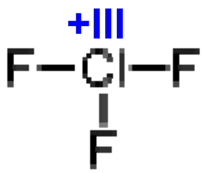
CFC-22 $$CHClF_2 \xrightarrow{600-800°C} HCl + CF_2 \longrightarrow F_2CCF_2 \longrightarrow PTFE$$

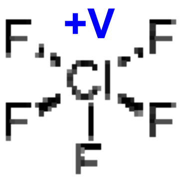
- water fluorination (as NaF)
- toothpaste (as NaF, SnF_6^-, or other salt)

Interhalogens

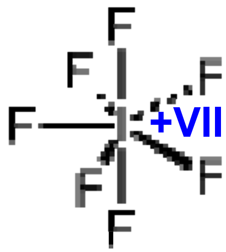
Halogen-halogen bonding occurs readily

- **Diatomics: ClF, ICl, IBr**
- **Higher species follow the formula XY_n where X is the heavier halogen, Y is the lighter (i.e., more electronegative) halogen and n = 3, 5, or 7**





- **same combinations for BrF_n and IF_n, but for iodine n = 7 is also accessible**



- **all interhalogens are strong oxidants and fluorinating agents**
- **interhalogens can cause O_2 evolution from metal oxides**

$$2Co_2O_4(s) + 6ClF_3(g) \longrightarrow 6CoF_3(s) + 3Cl_2(g) + 4O_2(g)$$

- **fluoride abstraction gives interhalogen cations**

$$ClF_3 + SbF_5 \longrightarrow [ClF_2]^+ + [SbF_6]^-$$

Halogen Oxo-Anions

Known for all halogens except fluorine, with halogen oxidation states of +1, +3, +5, and +7

- **acidity increases with increasing number of oxygens**

Acid	*pK*a
HOCl	7.53
HOClO	2.0
$HOClO_2$	–1.2
$HOClO_3$	–10

- **all oxo-anions are thermodynamically strong oxidants, but they are kinetically stabilized:**

slow

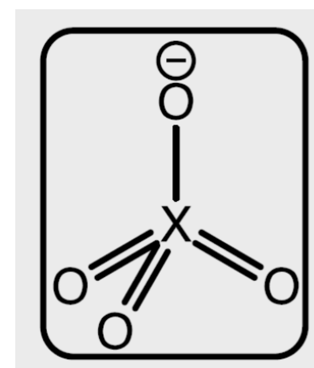
$$ClO_4^- < ClO_3^- < ClO_2^- \cong ClO^- \cong Cl_2$$

$$BrO_4^- < BrO_3^- \cong BrO^- \cong Br_2$$

$$IO_4^- < IO_3^- < I_2$$

$$ClO_4^- < BrO_4^- < IO_4^-$$

fast



- **some oxo-anions do not exist because they disproportionate**

$$2HBrO_2 \longrightarrow BrO_3^- + HOBr + H^+$$

Noble Gases

Naturally-occurring, closed valence shell gases

- **elements exist as monomeric gases with low boiling points**
- **inert to reduction, but heavier members can be oxidized**

$$Xe \xrightarrow[400^\circ C]{1\,atm F_2} XeF_2$$

$$Xe \xrightarrow[600^\circ C]{6\,atm F_2} XeF_4$$

$$Xe \xrightarrow[300^\circ C]{60\,atm F_2} XeF_6$$

- **once made, the xenon fluorides will do further chemistry**

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

$$2XeF_6 + 3SiO_2 \longrightarrow 2XeO_3 + 3SiF_4$$

- **XeO_3 is explosive but others are stable (XeO_4, XeO_3F_2, $[XeO_6]^{4-}$)**
- **VSEPR predicts the correct geometries for the nobel gas fluorides and oxides**