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: O₂ and O₃
- O₂ has two unpaired electrons and a triplet ground state that moderates its reactivity
Both $O_2$ and $O_3$ are powerful oxidants

\[ O_2 + 4H^+ + 4e^- \xrightleftharpoons{E^\circ=+1.23V} 2H_2O \]

\[ O_3 + 2H^+ + 2e^- \xrightleftharpoons{E^\circ=+2.08V} H_2O + O_2 \]

Partial reduction of $O_2$ gives hydrogen peroxide

\[ O_2 + 2H^+ + 2e^- \xrightleftharpoons{E^\circ=+0.70V} H_2O_2 \]

\[ H_2O_2 + 2H^+ + 2e^- \xrightleftharpoons{E^\circ=+1.76V} 2H_2O \]

Hydrogen peroxide synthesis is achieved with anthraquinone

\[ \text{H}_2/\text{Pd}^0 \]
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
  \[ CaO + H_2O \rightarrow Ca(OH)_2 \]
  \[ MgO + 2H^+ \rightarrow Mg^{2+} + H_2O \]

- **acidic oxides** are formed with p-block elements and give acid solutions when dissolved in water
  \[ N_2O_5 + H_2O \rightarrow 2HNO_3 \]
  \[ Sb_2O_5 + 2OH^- + 5H_2O \rightarrow 2Sb(OH)_6^- \]

- **amphoteric oxides** can act as either acids or bases
  \[ ZnO + 2H^+ \rightarrow Zn^{2+} + H_2O \]
  \[ ZnO + 2OH^- + H_2O \rightarrow Zn(OH)_4^{2-} \]
Sulfur

Sulfur has many allotropes

- $S_2$, $S_3$, $S_6$, $S_7$, $\alpha$-$S_8$, $\beta$-$S_8$, $\gamma$-$S_8$, ..., $S_{20}$

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

$\mu^2$-sulfide

$\mu^3$-sulfide

$\mu^4$-sulfide
Sulfur Halides

There are seven different sulfur fluorides...

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

$$S_8 + xsCl_2 \rightarrow S_2Cl_2 \xrightarrow{xsCl_2 \text{ FeCl}_3} SCl_2$$
Halogen

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

\[
K_2MnF_6 + 2SbF_5 \xrightarrow{150^\circ C} 2KSF_6 + [MnF_4] \rightarrow MnF_3 + \frac{1}{2} F_2
\]

Commercial uses

- preparation of aluminum and steel
- synthesis of Teflon

CFC-22

\[
CHClF_2 \xrightarrow{600-800^\circ C} HCl + CF_2 \rightarrow F_2CCF_2 \rightarrow PTFE
\]

- 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 $n = 3, 5, \text{ or } 7$

$$\text{F}^+ - \text{Cl}^- - \text{F}^- \quad \text{F}^- - \text{Cl}^- - \text{F}^- \quad \text{Cl}^{|+\text{II}} - \text{F}^-$$

- 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

$$2\text{Co}_2\text{O}_4 (s) + 6\text{ClF}_3 (g) \rightarrow 6\text{CoF}_3 (s) + 3\text{Cl}_2 (g) + 4\text{O}_2 (g)$$

- fluoride abstraction gives interhalogen cations

$$\text{ClF}_3 + \text{SbF}_5 \rightarrow [\text{ClF}_2]^+ + [\text{SbF}_6]^−$$
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

<table>
<thead>
<tr>
<th>Acid</th>
<th>$pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOCl</td>
<td>7.53</td>
</tr>
<tr>
<td>HOCIO</td>
<td>2.0</td>
</tr>
<tr>
<td>HOCIO$_2$</td>
<td>$-1.2$</td>
</tr>
<tr>
<td>HOCIO$_3$</td>
<td>$-10$</td>
</tr>
</tbody>
</table>

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

$$ClO_4^- < ClO_3^- < ClO_2^- \approx ClO^- \approx Cl_2$$
$$BrO_4^- < BrO_3^- \approx BrO^- \approx Br_2$$
$$IO_4^- < IO_3^- < I_2$$
$$ClO_4^- < BrO_4^- < IO_4^-$$

- 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

\[ \text{Xe} \xrightarrow{1 \text{ atm} F_2, 400^\circ C} \text{XeF}_2 \]

\[ \text{Xe} \xrightarrow{6 \text{ atm} F_2, 600^\circ C} \text{XeF}_4 \]

\[ \text{Xe} \xrightarrow{60 \text{ atm} F_2, 300^\circ C} \text{XeF}_6 \]

- once made, the xenon fluorides will do further chemistry

\[ \text{XeF}_6 + 3H_2O \rightarrow \text{XeO}_3 + 6HF \]

\[ 2\text{XeF}_6 + 3\text{SiO}_2 \rightarrow 2\text{XeO}_3 + 3\text{SiF}_4 \]

- XeO$_3$ is explosive but others are stable (XeO$_4$, XeO$_3$F$_2$, [XeO$_6$]$^{4-}$)
- VSEPR predicts the correct geometries for the noble gas fluorides and oxides