Elements (NonMetals)
Responsible only for portion of notes discussed in class

Review Periodic Table and Periodic Trends

On periodic table:

Electronegativity (EN) increases going up and to right with max at F

Size of neutral atom increases going to left and down

Metals and Nonmetals (see e-notes on Solids)
Covalent bonds between nonmetals give molecules and network solids

Metallic bonds between metals give metallic solids

Ionic bonds between metals and nonmetals give ionic solids
Right side nonmetals form negative (-) ions (right receive electrons)
Left side metals form positive (+) ions (left lose electrons)
For acids in water H can act as positive ion (H+)

Hydrogen _H_

Lowest density of any chemical substance
Used in blimps in 1930s but flammable
Gas at room Temp B.P. –253°C (20K) and M.P.-259°C (14K)
Insoluble in water: 2mL gas/ 1L of water

Found in H₂O, organic and biological molecules
Most common element in universe

H₂ (H-H) isoelectronic with He
H has a small radius
Unique properties of both group 1 and 17
Bond energy 431kJ/mol – very strong bond
**Boron B**

Of group 13 elements only Boron is a nonmetal

Boron $B^{3+}$ - never formed because it requires too much energy to remove the three electrons and energy cannot be supplied by the lattice energy

Boron does not occur free in nature but found in a variety of different ores such as Borax $Na_2B_4O_7\cdot10H_2O$

Trigonal Planar, $sp^3$ hybrid - forms trigonal planar compounds

![Trigonal Planar Structure](http://www.nightingale.org/teachers/fuller/Chemistry%20II/Bonding/Lewis%20Worksheet%20Answers.htm)

**Group 14 (IVA)**

<table>
<thead>
<tr>
<th>Element</th>
<th>Symb.</th>
<th>Outer e-</th>
<th>M.P. ($^\circ$C)</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>C</td>
<td>$2s^22p^2$</td>
<td>3570</td>
<td>nonmetal</td>
</tr>
<tr>
<td>Silicon</td>
<td>Si</td>
<td>$3s^23p^2$</td>
<td>1420</td>
<td>metalloid</td>
</tr>
<tr>
<td>Germanium</td>
<td>Ge</td>
<td>$4s^24p^2$</td>
<td>959</td>
<td>metalloid</td>
</tr>
<tr>
<td>Tin</td>
<td>Sn</td>
<td>$5s^25p^2$</td>
<td>232</td>
<td>metal</td>
</tr>
<tr>
<td>Lead</td>
<td>Pb</td>
<td>$6s^26p^2$</td>
<td>327</td>
<td>metal</td>
</tr>
</tbody>
</table>

Properties

- C found in CO$_2$ of atmosphere all plants and animals contain
- Why are living organisms based on carbon molecules and not some other element to form backbone of complex biochemical molecules?

Carbon atoms have ability to form 4 bonds to form long chains or rings of like atoms and have other atoms attached to these chains and C-C bond is strong

Si found in SiO$_2$ silicon dioxide silica. SiO$_2$ found in sand, quartz, and other minerals as a 3 dimensional network. It has a M.P. of 1700$^\circ$C.

Pure Silicon made $SiO_2$ (l) + 2 C (s) $\rightarrow$ Si (l) + 2 CO (g)

Very pure silicon used in making semiconductors
Carbon monoxide- CO, gas at room temp.

\[
\text{C} \equiv \text{O}
\]


Carbon dioxide- CO\(_2\), gas at room temp.

![CO2 molecule](http://members.optushome.com.au/scottsoftc/chapter04/section4.html)

Silicon dioxide silica- SiO\(_2\), solid M.P. 1700°C, network crystal

![SiO2 network crystal](http://members.optushome.com.au/scottsoftc/chapter04/section4.html)
**Group 15 (VA)**

**List and properties**
5 outer electrons in orbitals $s^2p^3$

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>Appearance</th>
<th>State</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>N</td>
<td>colorless</td>
<td>Gas</td>
<td>Nonmetal</td>
</tr>
<tr>
<td>Phosphorous</td>
<td>P (P₄)</td>
<td>white, red, black</td>
<td>Solid</td>
<td>Nonmetal</td>
</tr>
<tr>
<td>Arsenic</td>
<td>As</td>
<td>gray metallic</td>
<td>Solid</td>
<td>Metalloid</td>
</tr>
<tr>
<td></td>
<td>As₄</td>
<td>yellow</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Antimony</td>
<td>Sb</td>
<td>gray metallic</td>
<td>Solid</td>
<td>Metalloid</td>
</tr>
<tr>
<td></td>
<td>Sb₄</td>
<td>yellow</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bismuth</td>
<td>Bi</td>
<td>gray metallic</td>
<td>Solid</td>
<td>Metal</td>
</tr>
</tbody>
</table>

Electronegativity increases going up - pull electrons toward atom
Ionization energies increase going up - harder to remove electrons from nonmetals

**Ions**
- Only nitride $N^{3-}$
- Only phosphide $P^{3-}$
- $Sb^{3+}$
- $Bi^{3+}$

Properties of nitrogen differ from other group 15 elements

: $\overset{3}{\overset{\text{N}}{\text{N}}}$:

http://courses.chem.psu.edu/chem38/mol-gallery/oxygen/oxygen.html

Diatomice molecule - very strong bond 941kJ/mol
very unreactive because of difficulty in breaking bond

Can form at most 4 covalent bonds (no d orbitals to make more) $NH_4^+$

For other group 15 elements can form up to 5 or 6 bonds using d orbitals, $PCl_6^-$
Oxidation state varies from 3- to 5+ for nitrogen

**Allotropes**

$P$
- Red phosphorous structure not known, intermediate reactive
- Black phosphorous layers, least reactive
- White phosphorous $P_4$, very reactive with $O_2$ at room temp.

$As$ and $Sb$
- Yellow nonmetal
- Gray metallic soft metal (More stable form)
- Yellow form easily converted to gray metallic form.

$Bi$
- Gray metallic soft metal
Group 16 (VIA)

List

O Oxygen
S Sulfur
Se Selenium
Te Tellurium
Po Polonium - product of radioactive decay

Properties

Group 16 elements are 2e- short of noble gas and either:
1. accept to 2e- to form ion       S^{2-}
2. or form two covalent bonds       -S-

<table>
<thead>
<tr>
<th>Symb.</th>
<th>Formula</th>
<th>State at room T</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>O_2</td>
<td>gas</td>
<td>colorless</td>
</tr>
<tr>
<td>S</td>
<td>S_8 ring, S chain</td>
<td>solid</td>
<td>yellow</td>
</tr>
<tr>
<td>Se</td>
<td>Se_8 ring, Se chain</td>
<td>solid</td>
<td>red to black</td>
</tr>
<tr>
<td>Te</td>
<td>Te chains</td>
<td>solid</td>
<td>silver to white</td>
</tr>
</tbody>
</table>

Size increases going down the group.
Electronegativity increases going up the group.

O stong oxidizing agent that reduces to gain electrons (removes from other atoms)

O 2^{nd} highest electronegativity, only F is stronger
Oxides of most metals are ionic

Free oxygen, 21% atmosphere O_2
Sand silica SiO_2 – silicon dioxide
Oxygen in many minerals (Fe_2O_3)
Water mostly oxygen
Body 60% oxygen by mass

Almost all O_2 produced from air
Liquefy and distill
O₂ B.P. = -183°C
N₂ B.P. = -196°C

As air warms N₂ bubbles off

Some very pure O₂ by electrolysis
2 H₂O → 2 H₂ (g) + O₂ (g)

O₂→ CO₂ cycle in nature:

Animals  C₆H₁₂O₆ + 6 O₂ → 6 CO₂ + 6 H₂O + energy
Plants  light energy + 6 CO₂ + 6 H₂O → C₆H₁₂O₆ + 6 O₂

Pollution

CO incomplete combustion binds with hemoglobin so no O₂ can be carried to body tissue

Atmosphere
2 SO₂ + O₂ → 2 SO₃

Burning coal or treating metal sulfides
Cu₂S + O₂ → 2 Cu + SO₂
Heat

Atmosphere
SO₃ + H₂O → H₂SO₄ + H⁺ + HSO₄⁻

SO₂ causes respiratory damage and damage to plant life

Acid rain in northeast and Canada

Copperhill 50 sq. miles of plant with no trees
1900s plant for producing sulfuric acid, 10% of country’s production
15 million trees planted to replace ones lost

Ozone  - Pale blue gas with punget odor

http://www.chm.bris.ac.uk/motm/ozone/CHEM.htm
S, Se, Te

allotropes- different structural forms of same

- $O_2$          $O_3$
- $S_8$ ring   long chains called plastic sulfur
- Yellow       red (rubbery)
- Vapor
- $S_8$, $S_6$, $S_4$, $S_2$

![Sulfur allotropes](http://www.molecules.org/experiments/Dunlavy/animation1.html)

Write in equations as S

Production of Sulfur:
Found as free element in underground deposits
Also in some minerals $Ca_2S$, $FeS_2$ pyrite (fools gold), $CaSO_4\cdot 2H_2O$ gypsum
Te, Se primarily found in copper deposits

![Frasch Process](http://cwx.prenhall.com/petrucci/medialib/media_portfolio/23.html)

99.5% pure sulfur obtained
Halogens Group 17 (VIIA)

Fluorine, Chlorine, Bromine, and Iodine

Halogens are Greek for salt former. They are found in nature as halide salts (NaCl) and as ions in water (Cl⁻).

**Properties**

F 2s²2p⁵  
Cl 3s²3p⁵  
Br 4s²4p⁵  
I 5s²5p⁵

Valence electrons (above) and 1 short of noble gas so generally a single covalent bond or -1 ion

<table>
<thead>
<tr>
<th>Pure element</th>
<th>F₂</th>
<th>Cl₂</th>
<th>Br₂</th>
<th>I₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>pale yellow</td>
<td>yellow/ green</td>
<td>red</td>
<td>violet</td>
</tr>
<tr>
<td>M.P.</td>
<td>-218</td>
<td>-101</td>
<td>-7</td>
<td>+113</td>
</tr>
<tr>
<td>B.P.</td>
<td>-188</td>
<td>-35</td>
<td>+59</td>
<td>+183</td>
</tr>
<tr>
<td>State</td>
<td>gas</td>
<td>gas</td>
<td>liquid</td>
<td>solid</td>
</tr>
<tr>
<td>Bond energy</td>
<td>(155)</td>
<td>243</td>
<td>193</td>
<td>151</td>
</tr>
<tr>
<td></td>
<td>HF</td>
<td>HCl</td>
<td>HBr</td>
<td>HI</td>
</tr>
</tbody>
</table>

London forces hold together
Size increases going down the group
Electronegativity increases going up the group
 Ionic bond energies going up the group

F₂ has a weaker bond energy because of the repulsion of non-bonding electrons
**Group 18 Noble Gases (VIIIA)**

Until 1962 no compound of these elements was known not truly inert but still very low reactivity
No compound of He, Ne, Ar have been made

<table>
<thead>
<tr>
<th>Element</th>
<th>B.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>-269</td>
</tr>
<tr>
<td>Ne</td>
<td>-246</td>
</tr>
<tr>
<td>Ar</td>
<td>-186</td>
</tr>
<tr>
<td>Kr</td>
<td>-153</td>
</tr>
<tr>
<td>Xe</td>
<td>-107</td>
</tr>
<tr>
<td>Rn</td>
<td>-62</td>
</tr>
</tbody>
</table>

Size increases going down this group
Larger size, larger electron cloud, and larger London forces of attraction

Have the highest ionization energies so don’t tend to lose electrons and they have filled orbitals so don’t tend to gain electrons.

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td>XeF₂</td>
<td>129</td>
</tr>
<tr>
<td>XeF₄</td>
<td>117</td>
</tr>
<tr>
<td>XeF₆</td>
<td>50</td>
</tr>
<tr>
<td>XeO₄</td>
<td></td>
</tr>
</tbody>
</table>

About 30 compounds that have been made from noble gases
EXTRA MATERIAL – NOT COVERED IN CLASS

**Hydrogen**

**Production – Industry**

Steam reformer process:

\[
\text{CH}_4 (g) + 2 \text{H}_2\text{O} (g) \rightarrow \text{CO}_2 (g) + 4 \text{H}_2 (g) \text{ Ni (900°C)}
\]

Can remove CO2 by passing through cold water under pressure, CO2 is soluble in water

**Water Gas Reaction:**

\[
\text{C (s)} + \text{H}_2\text{O} (g) \rightarrow \text{CO (g)} + \text{H}_2 (g)
\]

Coke in pure carbon 1000°C water gas

Can separate liquefying CO
Both CO and H2 will burn water gas used as fuel

**Electrolysis of Water with Sulfuric acid added:**

\[
2 \text{H}_2\text{O} \rightarrow 2\text{H}_2 (g) + \text{O}_2 (g)
\]

Electrolysis
Very pure hydrogen

**Boron**

Found in several different crystal modifications in pure form
High mp, low electrical conductivity, brittleness, hardness

Reacts with halogens at high Temp.

BF₃, BCl₃ → gases
BBBr₃ → liquid
BI₃ → solid
Boric acid

H₃BO₃ pure form, white crystal

\[ \text{H₂O} + \text{B(OH)}₃ \text{(aq)} \rightleftharpoons \text{H}^+ \text{(aq)} + \text{B(OH)}₄^- \text{(aq)} \]

Other Compounds:

Diborane (gas under ordinary conditions)

Unusual three center bonds involve 2 electrons

2 (B 3e-) = 6e-
2 (H 1e-) = \( \frac{6e-}{12} \) e-

Group 14

Need atom that will form 4 bonds

http://msds.pcd.go.th/searchName.asp?vID=1406

nothing left over
Then why C and not Si or Ge?

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C</td>
<td>347</td>
</tr>
<tr>
<td>C-O</td>
<td>335</td>
</tr>
<tr>
<td>C-H</td>
<td>414</td>
</tr>
<tr>
<td>C-Cl</td>
<td>326</td>
</tr>
<tr>
<td>Si-Si</td>
<td>236</td>
</tr>
<tr>
<td>Si-O</td>
<td>368</td>
</tr>
<tr>
<td>Si-H</td>
<td>328</td>
</tr>
<tr>
<td>Si-Cl</td>
<td>391</td>
</tr>
</tbody>
</table>

Stronger bond strength means it is a more stable bond

Silicon has a tendency to bond to other elements rather than itself
Carbon is as likely to bond to itself as to other elements – strong C-C bond

http://cwx.prenhall.com/petrucci/medialib/media_portfolio/27.html
http://en.wikipedia.org/wiki/Thiocyanate

Only group 14 elements uses p orbitals to form pi bonds
Preparation

C found in CO₂ of atmosphere
all plants and animals contain
carbonates such as Ca(CO₃)₂ - limestone
hydrocarbons (CH) - oil
allotropes - diamond, graphite, and buckyballs
impure carbon – coal

90+ % of compounds (molecules) contain C atoms (20 million)

Pure Carbon

<table>
<thead>
<tr>
<th>Diamond</th>
<th>Graphite</th>
</tr>
</thead>
<tbody>
<tr>
<td>sp⁴ hybrid</td>
<td>sp³ hybrid</td>
</tr>
<tr>
<td>4 bonds for C</td>
<td>3 bonds in a plane</td>
</tr>
<tr>
<td>hard</td>
<td>soft black solid</td>
</tr>
<tr>
<td>high M.P. , stable</td>
<td>luster</td>
</tr>
<tr>
<td>bukyballs/ fullerenes</td>
<td>in plane of layers</td>
</tr>
<tr>
<td>(soccer ball shape)</td>
<td></td>
</tr>
<tr>
<td>3 dimensional network</td>
<td></td>
</tr>
</tbody>
</table>

C and Si compounds

Carbides- salt like anions of carbons alone

Calcium carbide

\[
\text{CaC}_2 (s) + 2 \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 (s) + \text{C}_2\text{H}_2 (g)
\]

acetylide (1) acetylene – burned for light and heat (2)

(2) http://www.oophda.com/hydrocarb/

Silicon carbide- SiC, diamond like tetrahedral structure
Silanes

\( \text{Si}_n\text{H}_{2n+2} \) like alkanes but only up to \( n = 6 \)

\( \text{Si}_2\text{H}_6 \)

Oxides

Carbonates

Calcium carbonate- \( \text{CaCO}_3 \), limestone

Glass fuse silicates and carbonates

\( \text{SiO}_2, \text{Na}_2\text{CO}_3, \text{CaCO}_3 \)

Cement is a mixture of limestone \( \text{CaCO}_3 \) and clay \( \text{H}_4\text{Al}_2\text{Si}_2\text{O}_9 \).
Group 15

Hydrogen Compounds

Gases at room temperature

\[
\begin{align*}
\text{NH}_3 & \quad \text{ammonia} \\
\text{PH}_3 & \quad \text{phosphine} \\
\text{AsH}_3 & \quad \text{arsine} \\
\text{SbH}_3 & \quad \text{stibine} \\
\text{BiH}_3 & \quad \text{bismuthine}
\end{align*}
\]

Arsine, stibine, and bismuthine are very poisonous gases.

Pyramidal molecule

http://www.elmhurst.edu/~chm/onlcourt/chm110/outlines/topic5.html

Most important compound ammonia prepared by the Haber process

\[
\text{N}_2 (g) + 3 \text{H}_2 (g) \rightleftharpoons 2 \text{NH}_3 (g)
\]

\begin{align*}
\text{Fe} \\
\text{Process performed at 500 atm and 500°C with a catalyst (Fe, Fe}_3\text{O}_4, \text{K}_2\text{O, Al}_2\text{O)}
\end{align*}

NH\textsubscript{3} has hydrogen bonding in liquid state

Hydrazine

http://en.wikipedia.org/wiki/Hydrazine

Strong reducing agent used in some rocket fuels.
### Production

<table>
<thead>
<tr>
<th>Source</th>
<th>Production</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>in the air distillation of liquefied air</td>
</tr>
<tr>
<td>Ca₃(PO₄)₂ (+2)(-3)₂, phosphate rock</td>
<td>heat with sand SiO₂ and coke (carbon)</td>
</tr>
<tr>
<td>As As₂S₃</td>
<td>heat with O₂ to produce oxide, then heat oxide with coke (carbon) to produce metal and CO</td>
</tr>
<tr>
<td>Sb Sb₂S₃ sulfide ores in Cu₂S</td>
<td>“ “ “</td>
</tr>
<tr>
<td>Bi Bi₂S₃</td>
<td>“ “ “</td>
</tr>
</tbody>
</table>

**Example 1:**

Heat

\[
\text{Ca}_3\text{(PO}_4\text{)}_2 \text{(s)} + 6 \text{SiO}_2 \text{(s)} \rightarrow \text{6 CaSiO}_3 \text{(l)} + \text{P}_4\text{O}_{10} \text{(g)}
\]

Heat

\[
\text{P}_4\text{O}_{10} \text{(g)} + 10 \text{C} \text{(s)} \rightarrow \text{P}_4 \text{(g)} + 10 \text{CO} \text{(g)}
\]

**Example 2:**

\[
2 \text{Sb}_2\text{S}_3 \text{(s)} + 9 \text{O}_2 \text{(g)} \rightarrow \text{SbO}_6 \text{(g)} + 6 \text{SO}_2 \text{(g)}
\]

**Example 3:**

\[
2 \text{As}_2\text{S}_3 \text{(s)} + 9 \text{O}_2 \text{(g)} \rightarrow \text{As}_4\text{O}_6 \text{(g)} + 6 \text{SO}_2 \text{(g)}
\]

\[
\text{As}_4\text{O}_6 \text{(s)} + 6 \text{C} \text{(s)} \rightarrow \text{As}_4 \text{(g)} + 6 \text{CO}
\]

### Nitrides and Phosphides

- N³⁻, P³⁻

At high temp
- Ionic Nitrides: Mg₃N₂, magnesium nitride
  - Will react with a number of metals at high temp.
  - High M.P., white, crystalline solids

- Covalent nitrides: BN, boron nitride
  - Network crystal
  - Others are molecules

Metal with white phosphorous to form metal phosphides
- Ca₃P₂
Halogen Compounds

Trihalides and pentahalides (not N) are most important halogen compounds.

Tri compounds have been made with F, Cl, Br, and I.
All trihalides are covalent compounds except BiF$_3$ which is ionic.

P, As, Sb, and Bi compounds can be prepared by direct combination of the elements.

N trihalide from halogenation of ammonia.

Structure of PCl$_n$

<table>
<thead>
<tr>
<th>PCl$_3$</th>
<th>PCl$_5$</th>
<th>PCl$_4^+$</th>
<th>PCl$_6^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyramidal</td>
<td>Trigonal</td>
<td>Tetrahedral</td>
<td>Octahedral</td>
</tr>
<tr>
<td>(1)</td>
<td>(2)</td>
<td>(2)</td>
<td></td>
</tr>
</tbody>
</table>

(1) [http://www.inchm.bris.ac.uk/schools/vsepr/examples/pcl3.htm](http://www.inchm.bris.ac.uk/schools/vsepr/examples/pcl3.htm)
(2) [http://www.chm.bris.ac.uk/motm/ascl5/ascl5h.htm](http://www.chm.bris.ac.uk/motm/ascl5/ascl5h.htm)

Sulfides, selenides, tellurides only with group 1 and 2 metals are truly ionic.

Usually oxygen has negative oxidation number except F, S, Se, and Te have +4, +6 with O and Halogens.

Oxygen Compounds

<table>
<thead>
<tr>
<th></th>
<th>Oxidation Number</th>
<th>Formula</th>
<th>Compound Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$O</td>
<td>+1</td>
<td>dinitrogen oxide</td>
<td>(nitrous oxide)</td>
</tr>
<tr>
<td>NO</td>
<td>+2</td>
<td>nitrogen oxide</td>
<td></td>
</tr>
<tr>
<td>N$_2$O$_3$</td>
<td>+3</td>
<td>dinitrogen trioxide</td>
<td>N=O (nitric oxide)</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>+4</td>
<td>nitrogen dioxide</td>
<td></td>
</tr>
<tr>
<td>N$_2$O$_5$</td>
<td>+5</td>
<td>dinitrogen pentoxide</td>
<td></td>
</tr>
</tbody>
</table>

N$_2$O – laughing gas, general anesthetic, gas in whipped cream aerosol cans.
\[ \text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{NO}(\text{g}) \]

3000°C

Atmospheric nitrogen converted to NO by lightning

\[ 2 \text{NO}_2 \leftrightarrow \text{N}_2\text{O}_4 \text{ equilibrium} \]

Brown Colorless

Smog

Oxyacid of nitrogen

Nitric acid

\[ \text{H}_2\text{NO}_3 \rightarrow \text{H}^+ (\text{aq}) + \text{NO}_3^- (\text{aq}) \]

Nitrate

\[ \begin{array}{c}
\cdot \cdot \\
\cdot - \cdot \\
\cdot \cdot \\
\end{array} \]

http://members.tripod.com/~EppE/chembond.htm

\[ \text{P}_4\text{O}_6 \text{ phosphorous (III) oxide} \]

(+3)(-2)

http://www.chemguide.co.uk/inorganic/period3/oxidesphys.html

\[ \text{P}_4\text{O}_{10} \text{ phosphorous (V) oxide, used as drying agent} \]

(5)(-2)

http://www.chemguide.co.uk/inorganic/period3/oxidesphys.html
PO₄ phosphate

Ca₃(PO₄)₂ (s) + 4 HNO₃ (l) → Ca(H₂PO₄)₂ (s) + 2 Ca(NO₃)₂ (s)
Too insoluble to be used directly
Phosphates and nitrates are important in fertilizers

Group 16

Production – Lab

Thermal decomposition of oxygen compounds

2 KClO₃ → 2 KCl (s) + 3 O₂ (g)
MnO₂ (catalyst)
Potassium chlorate
Potassium chloride

2 HgO → 2 Hg + O₂ (g)

Reactions

Strong bond energy 494 kJ/mol \( \text{O=O} \)
Broken at high temp.

Many reactions give off energy exothermic so self sustaining but still at high temp.

Form ionic compounds with metals and form covalent compound with nonmentals

With Metals:

Ions of oxygen

\( \text{O}_2^- \) superoxide (large group 1 metals Cs, Rb, K, O₂)
\( \text{O}_2^{2-} \) peroxide
\( O^{2-} \) oxide (normally produced and at high temp. favored)
\[ 4 \text{ Mg (s)} + \text{ O}_2 \text{(g)} \rightarrow 2 \text{ MgO (s)} \]
\[ 4 \text{ Al (s)} + 3 \text{ O}_2 \text{(g)} \rightarrow 2 \text{ Al}_2\text{O}_3 \text{(s)} \]
\[ 2 \text{ Hg (l)} + \text{ O}_2 \text{(g)} \rightleftharpoons 2 \text{ HgO (s)} \]

Many metals can have more than one oxidation state and so different oxides form:

FeO  \[ \text{ low pressure } T > 600 \]
\[ (+2)(-2) \]

Fe\(_2\)O\(_4\)  \[ T = 300 \text{ in air} \]
\[ (+3) \]

Fe\(_2\)O\(_3\)  \[ T > 300 \]
\[ (+3)(-2) \]

With Nonmetals:

Except for noble gases and group 17 elements, all nonmetals in elemental state react with \( \text{O}_2 \).

\[ 2 \text{ H}_2 \text{(g)} + \text{ O}_2 \text{(g)} \rightarrow 2 \text{ H}_2\text{O (g)} \]
\[ 2 \text{ C (s)} + \text{ O}_2 \text{(g)} \rightarrow 2 \text{ CO (g)} \text{ Incomplete combustion} \]
\[ \text{C (s)} + \text{ O}_2 \text{(g)} \rightarrow \text{ CO}_2 \]
\[ \text{S (s)} + \text{ O}_2 \text{(g)} \rightarrow \text{ SO}_2 \text{(g)} \]
\[ \text{N}_2 \text{(g)} + \text{ O}_2 \text{(g)} \rightarrow 2 \text{ NO (g)} \text{ Very high } T, \text{ electric arc} \]

Other oxides prepared by other than direct combination of elements.

Most compounds produce same products as if individual elements were used.

\[ 2 \text{ H}_2\text{S} + 3 \text{ O}_2 \rightarrow 2 \text{ H}_2\text{O (g)} + 2 \text{ SO}_2 \text{(g)} \]
\[ \text{CH}_4 \text{(g)} + 2 \text{ O}_2 \rightarrow \text{ CO}_2 \text{(g)} + 2 \text{ H}_2\text{O (g)} \]

\[ 3 \text{ O}_2 \text{(g)} \rightarrow 2 \text{ O}_3 \text{(g)} \]

Electrical
Discharge

Ozone can decompose to oxygen at room temperature
Ozone can rapidly oxidize metal
More reactive than oxygen

Ozone in upper atmosphere prevents ultraviolet rays (UV – shorter wavelength than visible)
\[ O_3 \rightarrow O_2 + O \]

UV radiation

Converts radiant energy into heat energy

\[ O + O_2 + M \rightarrow O_3 + M \]

\( M = \text{absorb energy} \)

\[ E = h \nu \cdot c = \lambda \nu \]

\[ E = \frac{hc}{\lambda} \]

Hydrogen Peroxide

\[ \begin{array}{cc}
\text{H} & \text{O} \\
\text{O} & \overset{\rightarrow}{\text{H}}
\end{array} \]

Peroxide unstable

http://www.chemistry.ohio-state.edu/~grandinetti/teaching/Chem121/lectures/chemical%20bonds/bonds.html

May explode in pure form

Save in solution with water

\[ \text{BaO}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{BaSO}_4 + \text{H}_2\text{O}_2 \]

Participates in oxidation reaction at temperature where \( O_2 \) slow

\[ \text{PbS} + 4 \text{H}_2\text{O}_2 \rightarrow \text{PbSO}_4 + 4 \text{H}_2\text{O} \]

\[ O_2 \rightarrow \text{slow} \]

Oxygen

\(-1 \rightarrow -2\)

Oxidizing agent, it is reduced

Hydrogen Compounds:

Not direct combination because \( \text{H}_2\text{S}, \text{H}_2\text{Se}, \text{H}_2\text{Te} \) are unstable at high temperature.

Use dilute acid on sulfides

\[ \begin{array}{cc}
\text{S}^{2-} & \text{Se}^{2-} \\
\text{tellurides} & \text{Te}^{2-}
\end{array} \]
Fe (s) + 2 H⁺ (aq) \rightarrow Fe^{2+} (aq) + H₂S (g)

H₂S, H₂Se, H₂Te are all unpleasant smelling poisonous gases. are bent molecules like water water is liquid due to hydrogen bonding

Hydrogen compounds dissolve in water to give weak acids

H₂S (aq) \rightleftharpoons H⁺ (aq) + HS⁻ (aq)

Stronger acid and lower electronegativity as go down periodic table and hence gives up H more readily.

<table>
<thead>
<tr>
<th>Forms of Sulfur</th>
<th>Ox. # of Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen sulfide</td>
<td>H₂S</td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>SO₂</td>
</tr>
<tr>
<td>Sulfur trioxide</td>
<td>SO₃</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>Pyrosulfuric acid</td>
<td>H₂S₂O₇</td>
</tr>
</tbody>
</table>

Production of Sulfuric Acid

(4+ oxidation state of S)

(6+ preparation of H₂SO₄, sulfuric acid)

Sulfur dioxide SO₂

Burn sulfur S (s) + O₂ \rightarrow SO₂ (g)

Roasting sulfides Ca₂S + O₂ \rightarrow 2 Cu + SO₂ (g)

SO₂ colorless gas with sharp irritating odor and poisonous (+4)(-2)₂

Sulfur Trioxide

2 SO₂ (g) + O₂ (g) \rightarrow 2 SO₃ (g)

Pt catalyst 600°C

\[ 
\begin{array}{c}
\text{O}::\text{S}=\text{O}::
\end{array}
\]

\[ 
\begin{array}{c}
\text{O}::\text{S}=\text{O}::
\end{array}
\]

\[ 
\begin{array}{c}
\text{O}::\text{S}=\text{O}::
\end{array}
\]

Very reactive and strong oxidizing agent

$$\text{SO}_3 \ (g) \ + \ \text{H}_2\text{SO}_4 \ (l) \ \rightarrow \ \text{H}_2\text{S}_2\text{O}_7 \ (l)$$

Pyrosulfuric acid

$$\text{H}_2\text{S}_2\text{O}_7 \ + \ \text{H}_2\text{O} \ \rightarrow \ 2 \ \text{H}_2\text{SO}_4 \ (l)$$

Add enough pyrosulfuric acid to make desired concentration of sulfuric acid

Sulfuric acid is colorless, oily, liquid,

[Tetrahedral shape diagram]

[Tetrahedral shape diagram]

http://www.eou.edu/webshack/404_error.html

Tetrahedral shape

Sulfuric acid – about 40 million tons in U.S., SO₂ ad air through tube with Pt metal and vanadium catalyst
1831 patent to make sulfur trioxide

Suggested SO₃ + H₂O
Used to make fertilizers, chemical,

Pyrosulfuric acid (H₂S₂O₇)

[Pyrosulfuric acid (H₂S₂O₇) diagram]

http://ja.wikipedia.org/wiki/%E3%83%81%E3%82%AA%E7%A1%AB%E9%85%B8
Group 17

Production - Industry

Sources
F  CaF_{2} fluorospar mineral deposits
Cl  Cl^{-} seawater
Br  Br^{-} seawater
I  I^{-} oil well brines

F_{2}:

CaF_{2} (s) + H_{2}SO_{4} (l) \rightarrow CaSO_{4} (s) + 2 HF (g)

K^{+} HF_{2}^{2-} ions

No chemical agent can be used to oxidize F since it is strongest oxidizing agent
Cannot be in water since F^- electrolyze water

Cl_{2}:

2 Na^{+} (aq) + 2 Cl^{-} (aq) + 2H_{2}O \rightarrow H_{2} (g) + Cl_{2} (g) + 2 Na^{+} (aq) + 2OH^{-} (aq)
electrolysis

Br_{2}:

Cl_{2} (g) + 2 Br^{-} (aq) \rightarrow 2 Cl^{-} (aq) + Br_{2} (l)
Use Cl2 as oxidizing agent

I_{2}:

Cl_{2} (g) + 2 I^{-} (aq) \rightarrow 2 Cl^{-} (aq) + I_{2} (s)

Production - Lab

F_{2} only by electrolysis
Others need oxidizing agent that will take electron from halide

MnO_{2} (s) + 4 H^{+} (aq) + 2 Cl^{-} (aq) \rightarrow Mn^{2+} (aq) + Cl_{2} (g) + 2 H_{2}O
Reduction  Oxidation
Manganese dioxide
## Compounds

<table>
<thead>
<tr>
<th>Type</th>
<th>Reaction</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interhalogen</td>
<td>$X_2 + X'_2 \rightarrow 2XX'$</td>
<td></td>
</tr>
<tr>
<td>Hydrogen Halides</td>
<td>$X_2 + H_2 \rightarrow 2HX$</td>
<td></td>
</tr>
<tr>
<td>Metal Halides</td>
<td>$nX_2 + 2M \rightarrow 2MX_n$</td>
<td></td>
</tr>
</tbody>
</table>

Oxyacids of the Halogens

### Interhalogen Compounds:

Examples (some combination have not been made)

- All $XX'$: BrCl, ICl, .... Except IF
- $XX_3'$: IF$_3$
- $XX_5'$: IF$_5$, Cl$_5$, BrF$_5$
- $XX_7'$: only IF$_7$ (need to have room around central atom)

### Valence Electrons

<table>
<thead>
<tr>
<th>Central</th>
<th>Outer</th>
<th>Pairs Bond</th>
<th>Pairs Nonbond</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 +</td>
<td>3</td>
<td>XX$_3'$</td>
<td>IF$_3$</td>
</tr>
<tr>
<td>7 +</td>
<td>4</td>
<td>XX$_5'$</td>
<td>IF$_5$</td>
</tr>
<tr>
<td>7 +</td>
<td>7</td>
<td>XX$_7'$</td>
<td>IF$_7$</td>
</tr>
</tbody>
</table>

More fluorine atoms around central atom

### Hydrogen Halides:

$$H_2 + X_2 \rightarrow 2HX$$

Reactivity: $F_2 > Cl_2 > Br_2 > I_2$

- Hydrogen fluoride: HF
- Hydrochloride: HCl
- Hydrobromide: HBr
- Hydroiodide: HI

All gases at room temperature

Weak acid – Hydrofluoric acid, Hydrochloric acid (stored in plastic, etch glass)
Strong acid - Hydrobromic acid, Hydroiodic acid
Hydrofluoric acid will react with glass

\[ \text{SiO}_2 (\text{s}) + 6 \text{HF (aq)} \rightarrow 2 \text{H}^+ + \text{SiF}_6^{2-} \text{ (aq)} + 2 \text{H}_2\text{O} \]

Metal Halides:

Made by direct reaction of elements

(Group 1, Group 2, Metal) + Halides = Ionic Bond

(Transition, other metals) + Halides = Somewhat covalent Bond

Ionic character decreases in order F > Cl > Br > I

AlF: Completely ionic
AlCl: Semicovalent – layer held together by London forces
Al\(_2\)Br\(_6\): Covalent – form molecules in crystal
Al\(_2\)I\(_6\):

Oxyacids of chlorine:

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Ox #</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hypochlorous</td>
<td>HO-Cl</td>
<td>+1</td>
<td>hypochloride</td>
</tr>
<tr>
<td>Chlorous</td>
<td>HO-ClO</td>
<td>+3</td>
<td>chlorite</td>
</tr>
<tr>
<td>Chloric</td>
<td>HO-ClO(_2)</td>
<td>+5</td>
<td>chlorate</td>
</tr>
<tr>
<td>Perchloric</td>
<td>HO-ClO(_3)</td>
<td>+7</td>
<td>perchlorite</td>
</tr>
</tbody>
</table>

Acid strength increases with the higher oxidation number for Cl

**Industrial Uses of Halogens**

(are used to make other compounds)

**F**

Freon CCL2F2 fluorochlorocarbons in refrigeration
Teflon
F₂ → UF₆ separate ²³⁵U and ²³⁸U
NaF  prevent tooth decay

Cl

Many organic compounds contain Cl
Pharmaceuticals
Solvents      carbon tetrachloride
Pesticides
Dyes
Bleaching     chlorox
Polymers      PVC plastic

Br

Fumigants    (EDB Carcinogen, ethylene dibromide)

http://www.inchem.org/documents/jmpr/jmpmono/v65apr06.htm

Fire proofing agents
AgI photography
Some pharmaceuticals