Hydrogen

- Makes up <1% of the mass of the Earth's crust, but about 90% of the atoms in the Sun and outer space
- Can be formed via reactions that typically require high temperatures (1000 ^oC) and a catalyst
  - Water-gas reaction: $C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$
  - Water-gas shift reaction: $CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$
  - Reforming of methane (but in principle any hydrocarbon): $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$
    - Principal commercial source of hydrogen
  - Catalytic reforming: $C_6H_{14} \rightarrow C_6H_6 + 4H_2$

Uses for hydrogen

- About ½ of the H_2 manufactured is used to make NH_3 (Haber process), which can be used to fertilizers, plastics and explosives.
- A significant amount is also used in the petrochemical industry
  - Hydrogenation of unsaturated compounds: $C_6H_6 + H_2 \rightarrow C_6H_{12}$
  - Synthesis of methanol: $CO + H_2 \rightarrow CH_3OH$
- Metallurgy: $WO_3 + H_2 \rightarrow W + H_2O$

Carbon compounds (inorganic)

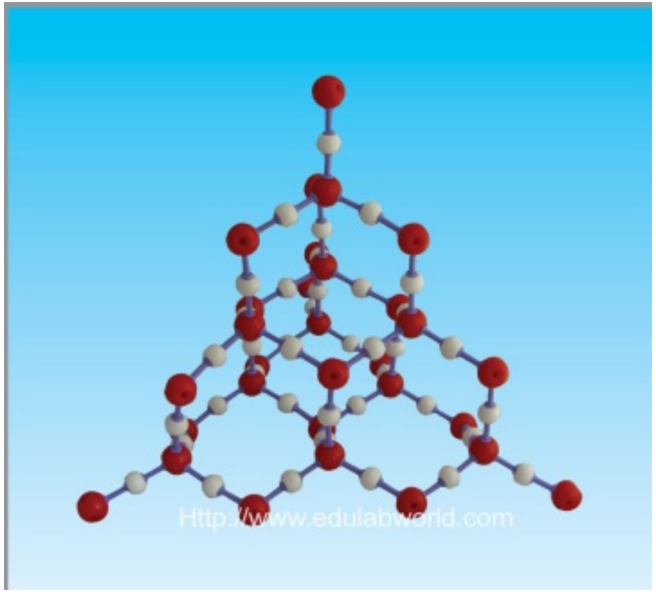
- Reaction with metals (oxides) to form carbides (acetylides) at high temperatures:
  - $CaO(s) + 3C(s) \rightarrow CaC_2(s) + CO(g)$
  - $CaC_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + C_2H_2(g)$
- Methane can be converted to inorganic compounds:
  - $CH_4 + 4S \rightarrow CS_2 + 2H_2S$
  - $CH_4 + 4Cl_2 \rightarrow CCl_4 + 4HCl$
- CN^- reacts much like a halide:
  - Dimerization to cyanogen $(CN)_2$
  - Disproportionation in basic solution: $(CN)_2 + 2OH^- \rightarrow CN^- + OCN^- + H_2O$

Silicon compounds

- Si is the 2nd most abundant element in the Earth's crust (after O)
- Si can make four bonds, but is incapable of making extended systems like C can
  - Si is significantly larger than C
  - Si-Si and Si-H bonds are relatively weak
- Si crystallizes in a cubic arrangement similar to diamond (tetrahedral, sp^3 hybridized)
  - Can't form π bonds so cannot form sheets the way graphite can (p orbitals are too large for efficient overlap)

Silica and silicates

- SiO_2 is really a network covalent solid where each Si atoms is bonded to 4 O atoms, and each O atom is bonded to 2 Si atoms
- SiO_4^{4-} and $Si_2O_7^{6-}$ can arrange tetrahedrally with cations to form minerals (ex. Th^{4+}, Zr^{4+}, Sc^{3+})



http://www.edulabworld.com/product/265-sio2-crystal-model-31046-1-d1a7/

Nitrogen compounds

- Ammonia can be synthesized by the Haber process: $N_2 + H_2 \rightarrow NH_3$
  - Generally used to make fertilizer:

$NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$

$NH_3 + H_3PO_4 \rightarrow NH_4H_2PO_4 + (NH_4)_2HPO_4$

  - Can be converted to NO using the Ostwald reaction, which can then form nitric acid:

$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

$2NO + O_2 \rightarrow 2NO_2$

$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$

Properties of oxygen

- Most abundant substance in Earth's crust
- Can form compounds with all elements except He, Ne and Ar
- Generally has an oxidation number of -2 in compounds (oxide), but it can also be -1 (O_2^{2-}, peroxide) or -1/2 (O_2^-, superoxide)
- Can exist as O_2 or O_3
- O_3 is a strong oxidizing agent (acidic solutions):

$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O \quad E^o = 2.075$ V

Synthesis of oxygen

- Generally made by decomposition reactions:

$HgO \rightarrow Hg + O_2$

$KClO_3 \rightarrow KCl + O_2$

$H_2O_2 \rightarrow H_2O + O_2$

- Reaction involving superoxide:

$KO_2 + CO_2 \rightarrow K_2CO_3 + O_2$

- Can also be made by electrolysis:

$H_2O \rightarrow H_2 + O_2$

Compounds with fluorine

- Fluorine reacts with every element except He and Ne
- Reaction with U allows for separation of U-235 and U-238 isotopes by gaseous diffusion:

$U + F_2 \rightarrow UF_6$

- Reaction with S forms a gaseous electrical insulator:

$S + F_2 \rightarrow SF_6$

- HF can be synthesized from a fluoride and concentrated sulfuric acid:

$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + HF$

- HF can be used for etching:

$SiO_2 + HF \rightarrow H_2O + SiF_4$

Compounds with chlorine

- Chlorine reacts with hydrocarbons:
  - Ex. $CH_4 + Cl_2 \rightarrow CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4$
- Chlorofluorocarbons (CFCs) are volatile liquids that are commonly used as refrigerants, although they are known to damage the ozone layer
  - Ex. $CFCl_3$ and CF_2Cl_2
- HCl can be synthesized from a chloride and concentrated sulfuric acid:

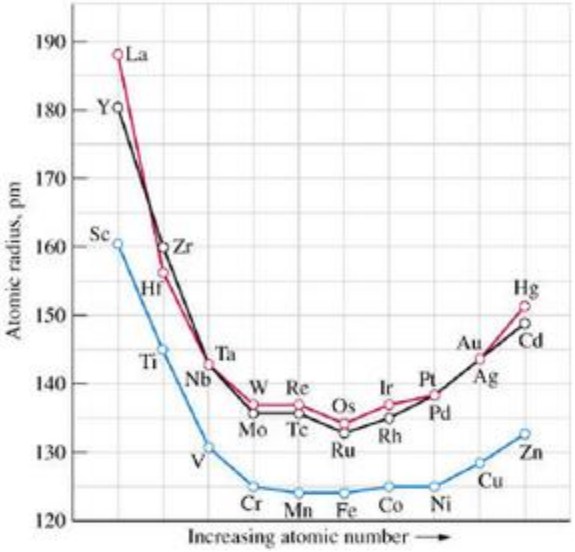
$NaCl + H_2SO_4 \rightarrow Na_2SO_4 + HCl$

Interesting facts about the d-block elements

- In the 4th period, Cu^{2+} is the only divalent cation that has a positive reduction potential
  - $Cu^{2+} + 2e^- \rightarrow Cu \; E^o = 0.340 \text{ V}$
- In the 4th period, Sc is the only metal reactive enough to react with water and displace hydrogen
  - $Sc + H_2O \rightarrow Sc^{3+} + H_2$
- Going from top to bottom, the number of oxidation states generally increases
  - As the oxidation number increases, the covalent nature of the compound also increases
- Sc and Cr hydoxides are amphoteric:
  - $Sc(OH)_3 + H^+ \rightarrow Sc^{3+}$ $Sc(OH)_3 + OH^- \rightarrow Sc(OH)_6^{3-}$
  - $Cr(OH)_3 + H^+ \rightarrow Cr(H_2O)_6^{3+}$ $Cr(OH)_3 + OH^- \rightarrow Cr(OH)_4^-$

Periodic trends – atomic radius

- Going from left to right, atomic radius decreases, then increases
  - greater attraction between nucleus and inner e^-s then greater repulsion between inner e^-s
- Going from top to bottom, atomic radius increases then stays approximately constant (or even decreases slightly)
  - Greater number of energy levels (shells), but then lanthanide contraction occurs since the 6th period contains 4f orbitals, which are not very good at screening (shielding) valence e^-s from the nucleus



http://gwapchem.wikispaces.com/23.7+Transition+Metals

Lanthanide (rare-earth) metals

- f-block elements
- Inserted between d-block elements
- Very similar properties to each other and to 3B metals
  - Difficult to separate and isolate
- $Ce^{4+} + e^{-} \rightarrow Ce^{3+}$ has a greater E^{o} than for reductions involving $Cr_2O_7^{2-}$ or MnO_4^{-}

Magnetic properties of metals

- Most d-block metals are paramagnetic because they have unpaired d electrons
  - Individual magnetic moments that can (temporarily) align in the presence of an external field
- Fe, Co and Ni are also ferromagnetic
  - Domains that can (permanently) align in the presence of an external field, even after the field is removed!
  - Requires certain interatomic distances
  - Can also occur in alloys (Al-Cu-Mn, Ag-Al-Mn, and Bi-Mn)

Properties of Fe, Co and Ni

- Fe can form +2 or +3 ions with $[Ar]3d^6$ and $[Ar]3d^5$ electron configurations (particularly stable)
- Co and Ni form primarily +2 ions ($[Ar]3d^7$ and $[Ar]3d^8$, respectively)
  - Co can have an oxidation number of +3 in complex ions such as $[Co(NH_3)_6]^{3+}$

Properties of Cu, Ag and Au

- Relatively unreactive (filled d orbitals)
  - Do not displace H_2 from H^+ solutions (but can react to form SO_2 or NO_x by reacting with H_2SO_4 or HNO_3)
- Highest electrical and thermal conductivities of all the metals
- Au does not react with any single acid to form H^+, but it does with *aqua regia* (1:3 HNO_3:HCl):

$$Au + 4H^+ + NO_3^- + 4Cl^- \rightarrow [AuCl_4]^- + 2H_2O + NO$$

- Au is resistant to oxidation, while Ag can tarnish (Ag_2S) and Cu can corrode ($Cu_2(OH)_2CO_3$)

Organic compounds

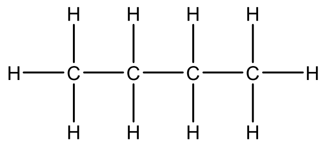
- C, H, N, O – about 95% of Earth's living things
- C, H, N, O, P, S – about 99%
- Carbon is king!
  - 4 covalent bonds (with itself or other elements)
  - Optimum size and valence
- Functional group
  - Collection of certain atoms that confer characteristic chemical (and biological) activities

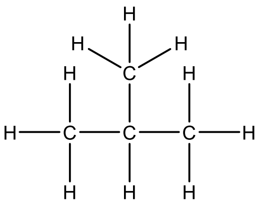
Hydrocarbons - alkanes

- Simplest organic molecules
- Saturated
- General formula C_nH_{2n+2}

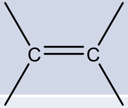
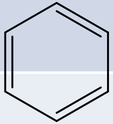
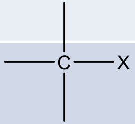
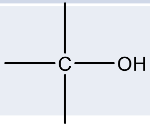
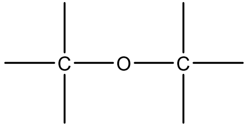
Constitutional Isomers

- Same chemical formula, different structural formula
- Leads to ENORMOUS diversity

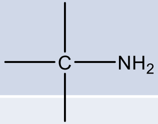
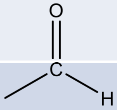
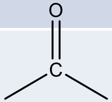
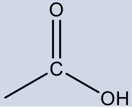
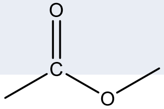




Functional Groups

Functional Group	Structure
Alkene	
Alkyne	
Aromatic Ring (arene)	
Halide (X = F, Cl, Br, I)	
Alcohol	
Ether	

Functional Groups

Functional Group	Structure
Amine	
Aldehyde	
Ketone	
Carboxylic Acid	
Ester	
Amide