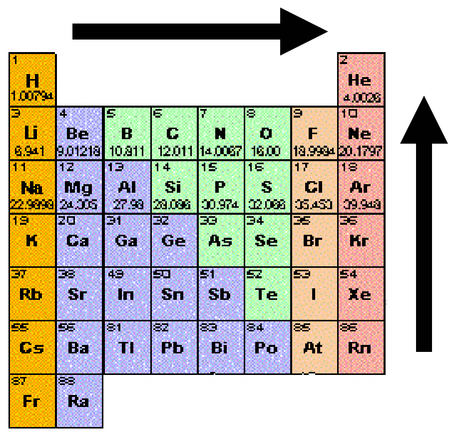
Chapter 14 - The Elements: The First Four Main Groups

- Periodic Trends
- Hydrogen
- Group 1/I: Alkali Metals
- Group 2/II: The Alkaline Earth Metals
- Group 13/III: The Boron Family
- Group 14/IV: The Carbon Family

Periodic Trends

Atomic Properties (Effective Nuclear Charge)

Effective Nuclear Charge: (Z_{eff}) The net nuclear charge after taking into account the shielding caused by other electrons in the atom.



Why: Going across the periodic table does not add more orbital's it only allows for electrons to enter into a preexisting orbital. The electrons in an orbital are spread out due to electron electron repulsion therefore the electrons that enter into the orbital do not shield the nucleus adequately and the effective nuclear charge goes up across a row. However going down a group adds more electron orbits which shield the nucleus more effectively and the effective nuclear charge goes down.

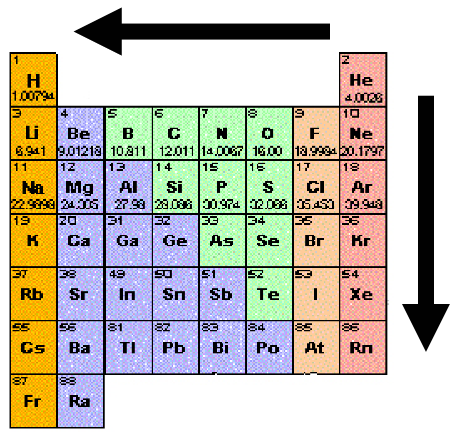
Example:

Which has the bigger effective nuclear charge? Li or F F or I

Periodic Trends

Atomic Properties (Atomic Radii)

Atomic Radii: Half the distance between the centers of neighboring atoms in a solid or a homonuclear molecule.



Why: Going across a period the effective nuclear charge increases therefore the pull on the electrons increases and the atomic radii decrease. Going down a group the effective nuclear charge decreases therefore the atomic radii increases.

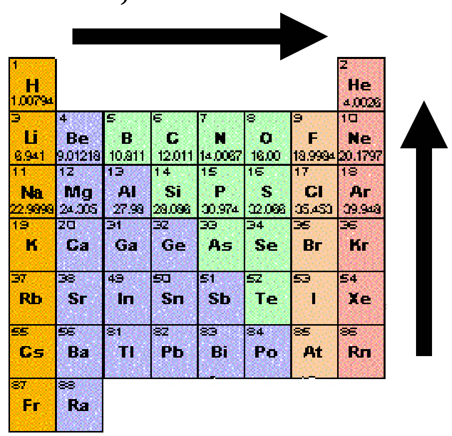
Example:

Which has the bigger atomic radii? Li or F F or I

Periodic Trends

Atomic Properties (First Ionization Energy)

First Ionization Energy: The minimum energy required to remove the first electron from the ground state of a gaseous atom, molecule, or ion.



Why: Going across a period the effective nuclear charge increases therefore it is harder to remove an electron and the first ionization energy increases. However, going down a group the effective nuclear charge decreases causing the first ionization energy to also decrease.

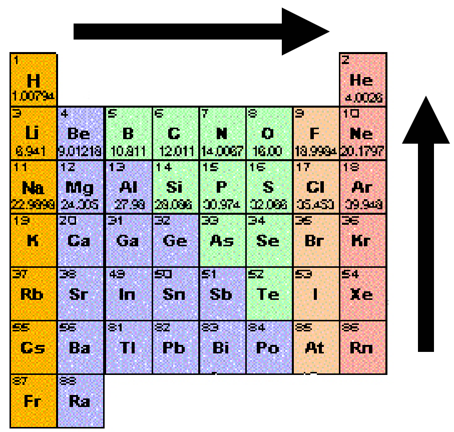
Example:

Which has the bigger first ionization energy? Li or F F or I

Periodic Trends

Atomic Properties (Electron Affinity)

Electron Affinity: (E_{ea}) The energy released when an electron is added to a gas-phase atom.



Why: Going across a period the effective nuclear charge increases therefore the atom has a larger positive charge and releases more energy when an electron is added to the atom. Going down a group the effective nuclear charge decreases and therefore the atom has a smaller positive charge and the electron affinity decreases.

Example:

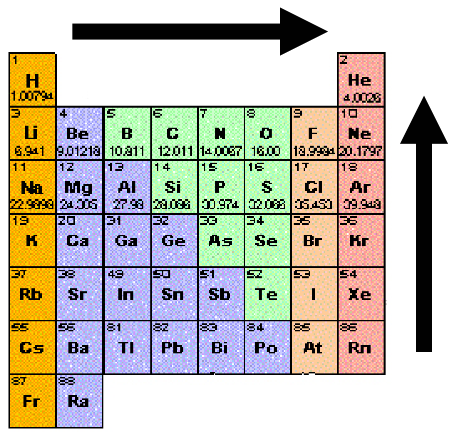
Which has the bigger electron affinity? Li or F F or I

Note: This trend has the most atoms that do not obey the trend

Periodic Trends

Atomic Properties (Electronegativity)

Electronegativity: (χ) The ability of an atom to attract electrons to itself when it is part of a compound.



Why: Going across a period the effective nuclear charge increases therefore the atom has a larger positive charge and attracts more electrons to itself in a compound causing the electronegativity to increase. Going down a group the effective nuclear charge decreases and therefore the atom has a smaller positive charge causing the electronegativity to decrease.

Example:

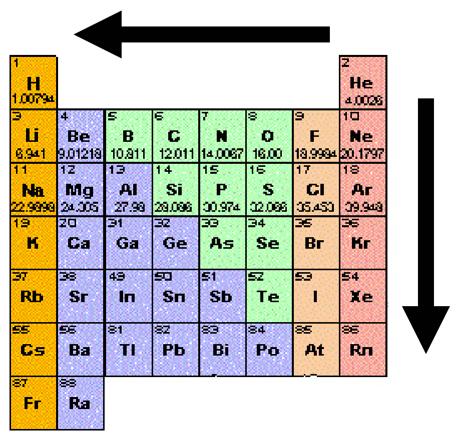
Which has the bigger electronegativity? Li or F F or I

Note: Bonds between things of similar electronegativities tend to be covalent

Periodic Trends

Atomic Properties (Polarizability)

Polarizability: (α) The ease with which the electron cloud of a molecule can be distorted.



Why: Going across a period the effective nuclear charge increases therefore the electrons are held tighter to the nucleus and are unable to deform when bonded with other atoms. However, going down a group the effective nuclear charge decreases and the electrons are not held as tightly to the nucleus and therefore, deform more easily when bonding with other atoms.

Example:

Which is easier to polarize? Li or F F or I

Periodic Trends

Atomic Properties

Student Question:

Which atom is larger?

A) Thallium (Tl) B) Lead (Pb)

Which atom is more electropositive?

A) Potassium (K) B) Rubidium (Rb)

Which atom has the greatest electron affinity?

A) Arsenic (As) B) Fluorine (F)

C) Sulfur (S)

Periodic Trends

Bonding Trends (Number of Bonds)

Most main group elements form the same number of bonds as the |oxidation number|.

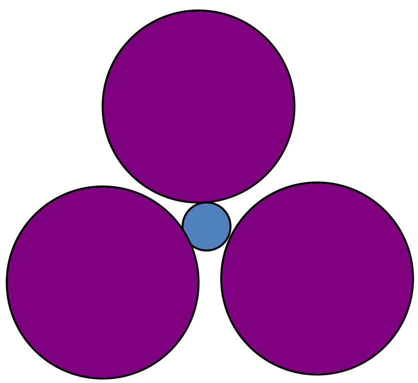
Element	Number of Valence e^-	Typical Oxidation Number	Typical Number of Bonds Formed	Example
Na	1	+1	1	NaCl(s)
O	6	-2	2	H_2O(l)
F	7	-1	1	HF(l)

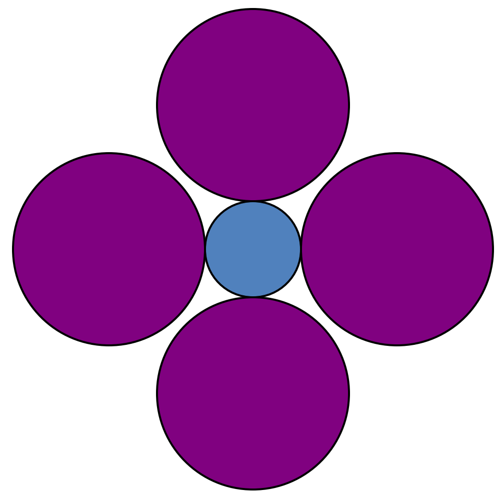
Elements in period three and higher have access to the empty *d* orbitals and can use them to expand their valence shells past the usual octet of e^- and there for do not always follow this rule.

Periodic Trends

Bonding Trends (Size)

The smaller the size of the atom the fewer the other atoms that can bond with it.





In general only period 2 elements form multiple bonds with themselves or other elements in the same period because only they are small enough for their p orbitals to have substantial π overlap.

Periodic Trends

Bonding Trends (Hydrides)

Hydrides: Compounds that contain hydrogen.

Most elements in the main group form binary compounds with hydrogen that reflect their location on the periodic table.

NH_3 CH_4 H_2O HF

The nature of the binary hydride is related to the characteristics of the element bonded to the hydrogen.

Three different classifications of binary hydrides:

- Saline Hydrides
- Metallic Hydrides
- Molecular Hydrides

Periodic Trends

Bonding Trends (Saline Hydrides)

Saline hydrides are formed by the members of the *s* block when they are heated the in the presence of $H_2(g)$

Example:

$$2K(s) + H_2(g) \xrightarrow{\Delta} 2KH(s)$$

Properties:

White

High melting point

Crystal structure similar to halides (rock salt structure)

Ionic Bonds

Periodic Trends

Bonding Trends (Metallic Hydrides)

Metallic hydrides are formed by heating certain *d* block metals in the presence of $H_2(g)$

Example:

$$2Cu(s) + H_2(g) \xrightarrow{\Delta} 2CuH(s)$$

Properties:

Black

Powdery

Electrically conductive solids

Metal hydrides release their H when heated or treated with acid therefore they are being investigated for storing and transporting hydrogen

Periodic Trends

Bonding Trends (Molecular Hydrides)

Molecular hydrides are formed when nonmetals form covalent bonds with hydrogen.

Example:

HF, HCl, HBr

Properties:

Volatile

Many are Bronstead acids

Periodic Trends

Bonding Trends (Oxides)

All main group element except for the noble gasses react with oxygen to form oxides.

Oxides formed from atoms on the…		
Left side of the periodic table (*s* and most of the *d* block)	Left side of the *p* block	Right side of the periodic table
▪Soluble in $H_2O(l)$ ▪Ionic ▪Tend to be strong bases	▪Insoluble ▪High melting points ▪Tend to be amphoteric	▪Low melting point ▪Often gaseous (NO(g)) ▪Tend to be Lewis acids

Periodic Trends

Bonding Trends (Anhydrides)

Acid Anhydrides: A compound that forms an oxoacid (an acid that contains oxygen) when it reacts with water

Example:

$N_2O_5(l) + H_2O(l) \rightarrow 2HNO_3(l)$ — $N_2O_5(l)$ is the anhydride

$SO_3(l) + H_2O(l) \rightarrow H_2SO_4(l)$ — $SO_3(l)$ is the anhydride

Formula Anhydrides: A compound that has the formula of an acid minus the elements of water but does not react with water to produce the acid.

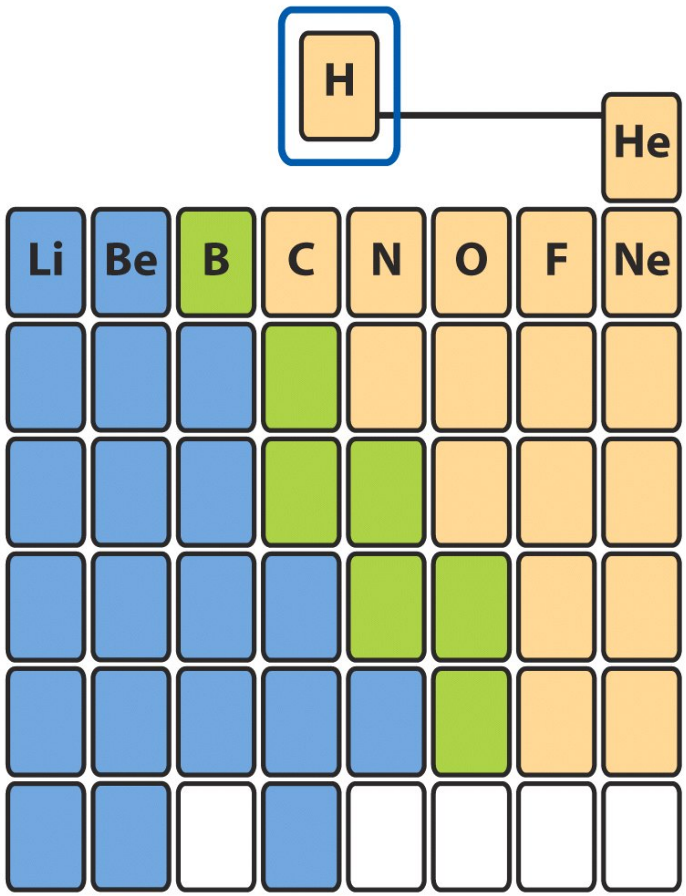
Example:

$CO(g) + H_2O(l)$ does not go to $HCOOH(l)$

$CO(g)$ is the formula anhydride

Hydrogen

The Element



Properties:

Colorless

Odorless

Tasteless

- Electron configuration is $1s^1$(similar to the electron configurations of group 1 elements)
- Classified as a non metal
- Therefore it doesn't fit into any group

Hydrogen

The Element

The elemental form of H is H_2

H_2 is small and nonpolar so the H atoms can only attract each other through weak London forces.

London Forces: The force of attraction that arises from the interaction between instantaneous electric dipoles on neighboring molecules.

Hydrogen

The Element

TABLE 14.1 Physical Properties of Hydrogen

Valence configuration: $1s^1$
*Normal form**: colorless, odorless gas

Z	Name	Symbol	Molar mass ($g \cdot mol^{-1}$)	Abundance (%)	Melting point (°C)	Boiling point (°C)	Density ($g \cdot L^{-1}$)†
1	hydrogen	H	1.008	99.98	−259 (14 K)	−253 (20 K)	0.089
1	deuterium	^2H or D	2.014	0.02	−254 (19 K)	−249 (24 K)	0.18
1	tritium	^3H or T	3.016	radioactive	−252 (21 K)	−248 (25 K)	0.27

**Normal form* means the state and appearance of the element at 25°C and 1 atm.
†The density refers to the same conditions.

- Most H is made up of only two particles (an electron and a proton)
- H is the most abundant element in the universe and accounts for 89% of all atoms.
- Little free H on earth
- H_2 gas is so light that it moves very fast and can escape the earths gravitational pull
- Need heavier planets to confine H_2

Hydrogen

The Element

Most commercial $H_2(g)$ is obtained as a by product of petroleum refining

Example:

$CH_4(g) + H_2O(g) \xrightarrow{Ni\,Catalyst} CO(g) + H_2(g)$

Can't Separate CO from H_2

$CO(g) + H_2O(g) \xrightarrow{Fe/Cu\,Catalyst} CO_2(g) + H_2(g)$

Membranes that can separate CO_2 from H_2

Hydrocarbon: Compounds that contain H and C

1/3 of the H produced is used for hydrometallurgical extractions of copper and other materials since H is a strong reducing agent.

Hydrogen

The Element

Hydrogen as a fuel source

- Light (low density)
- Clean Burning
- Plenty of abundant H in H_2O

Example:

$2H_2O(l) \xrightarrow{light} O_2(g) + 2H_2(g)$ (electrolysis of water)

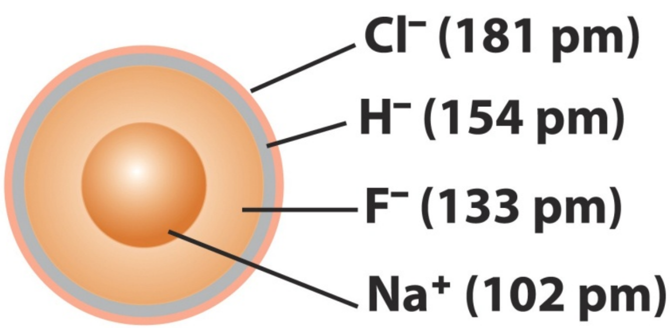
Problem: The electrolysis of water requires a lot of energy in the form of electricity

Hydrogen

Compounds of H

- Hydrogen can form both cations (H^+) and anions (H^-)
- Hydrogen has an intermediate electronegativity
- Forms covalent bonds with both nonmetals and metalloids

Anion



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The hydride ion is very large

The large radius makes it highly polarizable in compounds since it is hard for the single proton to control the two electrons.

Hydrogen

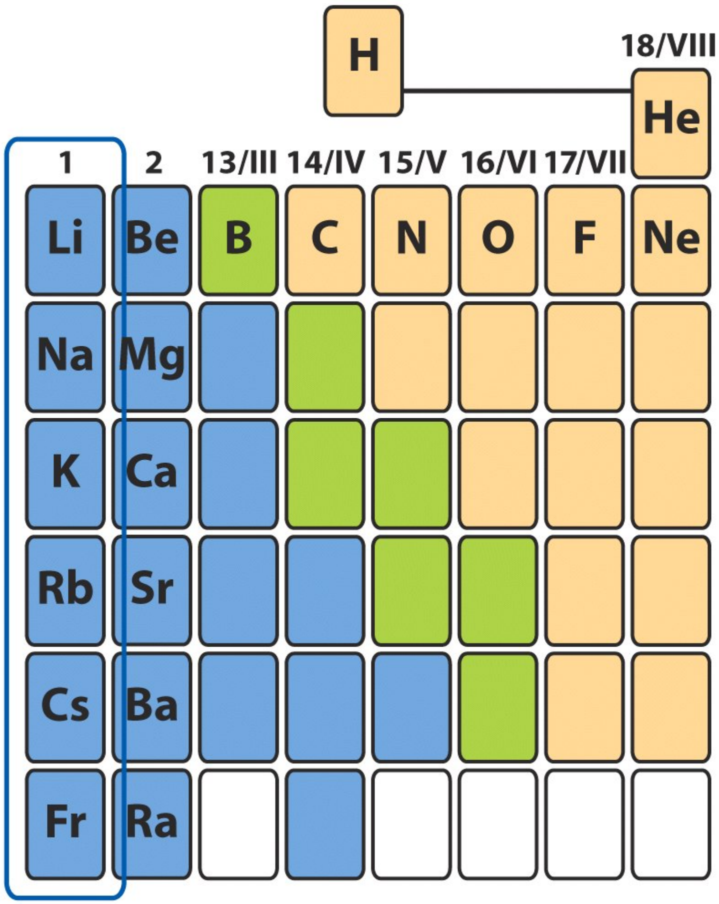
Compounds of H (Hydrogen Bonding)

- Small elements
- Between H and highly electronegative atoms (ex: N, O, and F)
- 5% as strong as covalent bonds (between the same atoms)
- Coulombic interactions between the partially positive charge on a hydrogen atom and the partially negative charge of another atom form the H bond

$$O^{\delta -}---{}^{\delta +}H-O$$

Group 1: The Alkali Metals

The Elements



Properties:

Soft

Lustrous metals

- Electron configuration is ns^1(n is the period number)
- Classified as metals

Group 1: The Alkali Metals

The Elements

- Properties are dominated by the fact that they lose their e^- easily
- Most Violently reactive of all the metals
- React strongly with $H_2O(l)$ the vigor of the reaction increase down the group
  (ex: $2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$)
- The alkali metals are all too easily oxidized to be found in their free state in nature
- Great reducing agents

Group 1: The Alkali Metals

The Elements

- Not easily extracted from their ores. Have to use electrolysis of their molten salts (ex. Na in the Downs process)
- Low melting points
- Low boiling points
- Low densities
- Most form ionic compounds in nature
- Alkali metals react directly with almost all nonmetals (except the noble gasses)

Example:

$$6Li(s) + N_2(g) \rightarrow 2Li_3N(s)$$

Group 1: The Alkali Metals

Compounds of Lithium

Lithium differs slightly from the other element in the group

- Small size if the Li^+ cation
  - Strong polarizing power
  - Forms bonds with highly covalent character

Uses:

Ceramics

Lubricants

Medicine (lithium carbonate (treatment for bipolar disorder))

Group 1: The Alkali Metals

Compounds of Sodium

Importance of Sodium compound:

Low cost

High solubility in water

NaCl (Sodium Chloride commonly know as table salt)

Methods of Obtaining NaCl

- Mined as rock salt which is a deposit of sodium chloride left as ancient oceans evaporated
- Obtained from the evaporation of brine (sea water)

Properties:

White

Solid salt

Uses:

Electrolytic production of chlorine and sodium hydroxide from brine

$$2Na^+(aq) + 2Cl^-(aq) + 2H_2O(l) \rightarrow Cl_2(g) + 2OH^-(aq) + H_2(g) + 2Na^+(aq)$$

Group 1: The Alkali Metals

Compounds of Sodium

NaOH (Sodium Hydroxide commonly know as lye)

Properties:

Soft

Waxy

White

Corrosive solid

Methods of Obtaining NaOH

- Electrolysis of brine

Uses:

Inexpensive starting material for the production of other sodium salts

Group 1: The Alkali Metals

Compounds of Sodium

$NaHCO_3$ (Sodium Hydrogen Carbonate (Sodium Bicarbonate) commonly called baking soda)

How baking soda works

The hydrogen carbonate reacts with a weak acid (HA) that is present in the batter (sour milk, buttermilk, lemon juice, vinegar…..)

$$HCO_3^-(aq) + HA(aq) \rightarrow A^-(g) + H_2O(l) + CO_2(g)$$

The $CO_2(g)$ produced causes the batter to rise

Baking powder contains a solid weak acid as well as the hydrogen carbonate therefore $CO_2(g)$ is released when water is added

Group 1: The Alkali Metals

Common Reactions

Reaction with Halogens

$2M + X_2 \rightarrow 2MX$ X_2 is any group 9 molecule

Reactions with Oxygen

$4Li + O_2 \rightarrow 2Li_2O$ Need excess Oxygen

$2Na + O_2 \rightarrow Na_2O_2$

$M + O_2 \rightarrow MO_2$ M = K, Rb, or Cs

Reaction with H

$2M + H_2 \rightarrow 2MH$

Reaction with N

$6Li + N_2 \rightarrow 2Li_3N$ Li only

Reaction with Water

$2M + 2H_2O \rightarrow 2MOH + H_2$

Reaction with Ions

$2M + 2H^+ \rightarrow 2M^+ + H_2$

Group 1: The Alkali Metals

Compounds of Potassium

- More expensive than Na compounds
- Similar properties to Na compounds
- Less hygroscopic (water absorbing than corresponding Na compounds)
- Principle mineral source of K is $KCl \cdot MgCl_2 \cdot 6H_2O$ and KCl

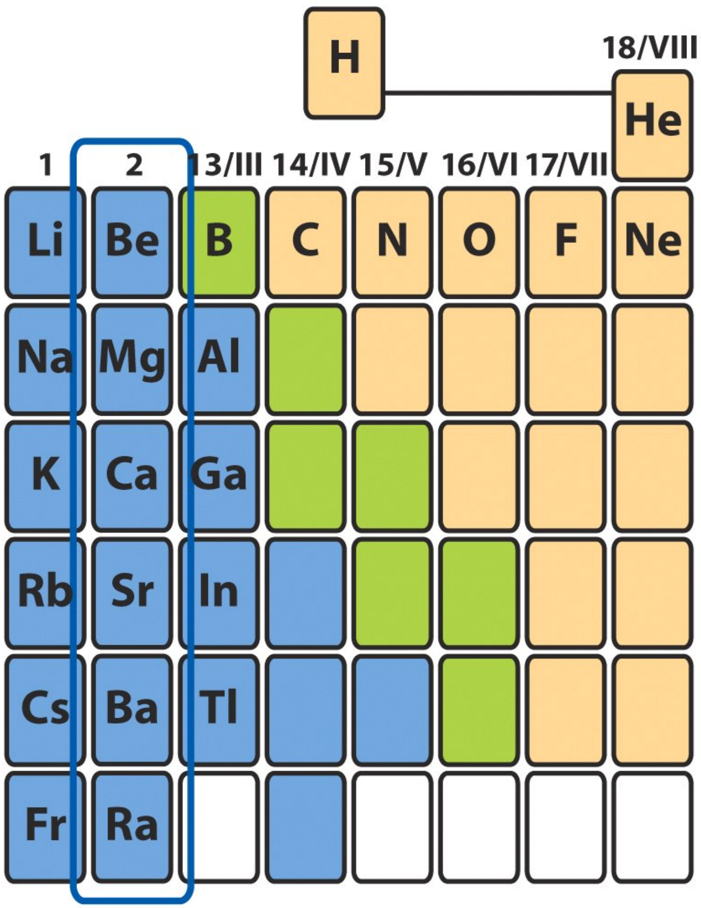
KNO_3 (Potassium Nitrate)

Used to facilitate the ignition of matches by releasing O_2 when heated

$$2KNO_3(s) \xrightarrow{\Delta} 2KNO_2(s) + O_2(g)$$

Group 2: The Alkali Earth Metals

The Elements



- Electron configuration is ns^2(n is the period number)
- Classified as metals
- All group 2 element are too reactive to occur in the uncombined state in nature
- Usually found as doubly charged cations
- All group 2 elements except for beryllium react with water and the vigor of the reaction increases going down the group

Group 2: The Alkali Earth Metals

The Elements (Beryllium)

beryllium

- Has some non metal tendencies
- Mainly found in the form $3BeO{\cdot}Al_2O_3{\cdot}6SiO_2$ (these crystals can weigh several tons)
- The gemstone emerald contains Be but its green color is caused by Cr^{3+} ions
- Used as windows for x-ray tubes (thin sheets of the metal are transparent to x-rays)
- Obtained by the electrolytic reduction of molten beryllium chloride

Group 2: The Alkali Earth Metals

The Elements (Magnesium)

magnesium

- Occurs in sea water as the mineral dolomite $CaCO_3 \cdot MgCO_3$
- Mg is present in the chlorophyll molecule therefore enables photosynthesis
- Protective oxide forms which protects Mg from extensive oxidation from air
- Used in the manufacturing of airplanes due to the fact that it is a light and tough
- Obtained by either chemical or electrolytic reduction of its compounds

Group 2: The Alkali Earth Metals

The Elements (Calcium)

calcium

- Also found in sea water
- Ca is the element of rigidity and construction (bones, shells, concrete, mortar, limestone (buildings)…)
- Obtained by electrolysis or by reduction with aluminum in a version of the thermite process (same for strontium and barium)

$$3CaO(s) + 2Al(s) \xrightarrow{\Delta} Al_2O_3(s) + 3Ca(s)$$

Group 2: The Alkali Earth Metals

The Elements

Alkali earth metals can often be identified by the color they give off in a flame

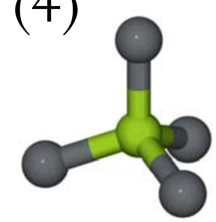
Group 2 Element	Flame Color
Calcium	Orange-Red
Strontium	Crimson
Barium	Yellow-Green

Due to there colors salts of these elements are often time used in fireworks

Group 2: The Alkali Earth Metals

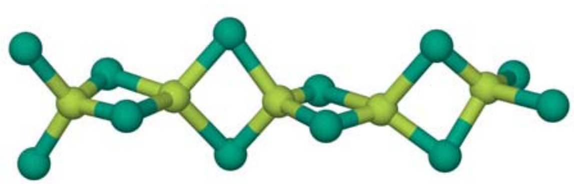
Compound of Beryllium

- Beryllium compounds are very toxic
- Dominated by the highly polarizing character of the Be^{2+} ion and small size
- Highly polarizing character causes the formation of bonds that have strong covalent character
- Small size limits the number of groups that can attach to it (4)
- The structural unit is commonly tetrahedral



2 BeX_4 unit

$$BeO(s) + C(s) + Cl_2(s) \xrightarrow{600\text{–}800°C} BeCl_2(g) + CO(g)$$



3 Beryllium chloride, $BeCl_2$

The Be atom in the $BeCl_2$ act as Lewis acids and accept electrons pairs form the Cl atoms of the neighboring $BeCl_2$ groups forming a chain of tetrahedral $BeCl_4$ units in the solid

Group 2: The Alkali Earth Metals

Compound of Magnesium

- Compounds primarily have ionic bonds but still have some covalent character

$Mg(OH)_2$ (Magnesium Hydroxide commonly called Milk of Magnesia)

Because $Mg(OH)_2$ is relatively insoluble in water. It is not absorbed into the stomach and stays in the stomach a long time to react with whatever acid is present.

Properties:

Not very soluble in H_2O

Liquid

Collide suspension

When $Mg(OH)_2$ neutralizes stomach acid it produces $MgCl_2$ which is a laxative therefore $Mg(OH)_2$ should be used sparingly

Group 2: The Alkali Earth Metals

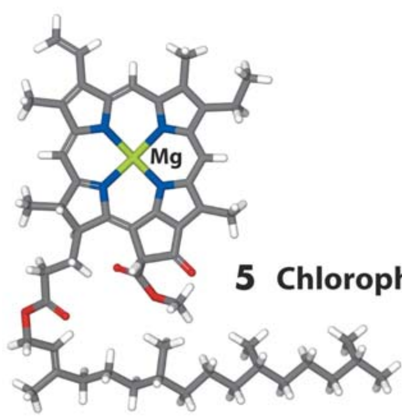
Compound of Magnesium

$MgSO_4$ (Magnesium Sulfate commonly called Epsom Salts)

Is another laxative. The magnesium ions inhibit the absorption of water in the intestines thereby increasing the flow of water through the intestines.

Chlorophyll

- Captures light from the sun and channels its energy into photosynthesis
- The role of the Mg^{2+} ion is to keep the ring rigid thereby insuring that the photon is not lost as heat before the chemical reaction occurs



5 Chlorophyll

Group 2: The Alkali Earth Metals

Compound of Calcium

$CaCO_3$ (Calcium Carbonate)

- Most common calcium compound
- Occurs naturally in chalk and limestone

$CaCO_3(s)$ decomposes into $CaO(s)$ (lime or quicklime) when heated

$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$$

CaO is called quicklime because the reaction with water is fast and extremely exothermic.

$$CaO(s) + H_2O(l) \rightarrow Ca^{2+}(aq) + 2OH^{-}(g)$$

$Ca(OH)_2$ is known as slacked lime because the thirst of lime for water has been quenched or slacked

Group 2: The Alkali Earth Metals

Compound of Calcium

Uses of CaO:

Used in iron making. CaO is an Lewis base and reacts with silica in the iron ore to transform it into liquid slag

$$CaO(s) + SiO_2(s) \xrightarrow{\Delta} CaSiO_3(l)$$

About 50 kg of lime is needed to produce 1 ton of iron

Uses of $Ca(OH)_2$:

Used as an inexpensive base in industry as well as to adjust the pH of soils in agriculture and to remove Ca^{2+} from hard water containing $Ca(HCO_3)_2$

$$HCO_3^-(aq) + OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(l)$$

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$$

Group 2: The Alkali Earth Metals

Compound of Calcium

Concrete

Strong building material made from bonder and a filler

Filler:

Usually gravel and sand

Bonder:

Made by heating calcium oxide, calcium silicates, and calcium aluminum silicates.

The pellets are ground together with gypsum ($CaSO_4 \cdot 2H_2O$)

When the filler, bonder, and water are mixed together the water reacts to form hydrates (compounds containing H_2O) and hydroxides (compounds containing OH^-) which bind the salts together in a three dimensional network

Group 2: The Alkali Earth Metals

Common Reactions

Reaction with Halogens

$M + X_2 \rightarrow MX_2$ X_2 is any group 9 molecule

Reaction with Oxygen

$2M + O_2 \rightarrow 2MO$

Reaction with H

$M + H_2 \rightarrow MH_2$

Reaction with N

$3M + N_2 \rightarrow M_3N_2$ High temperatures

Reaction with Water

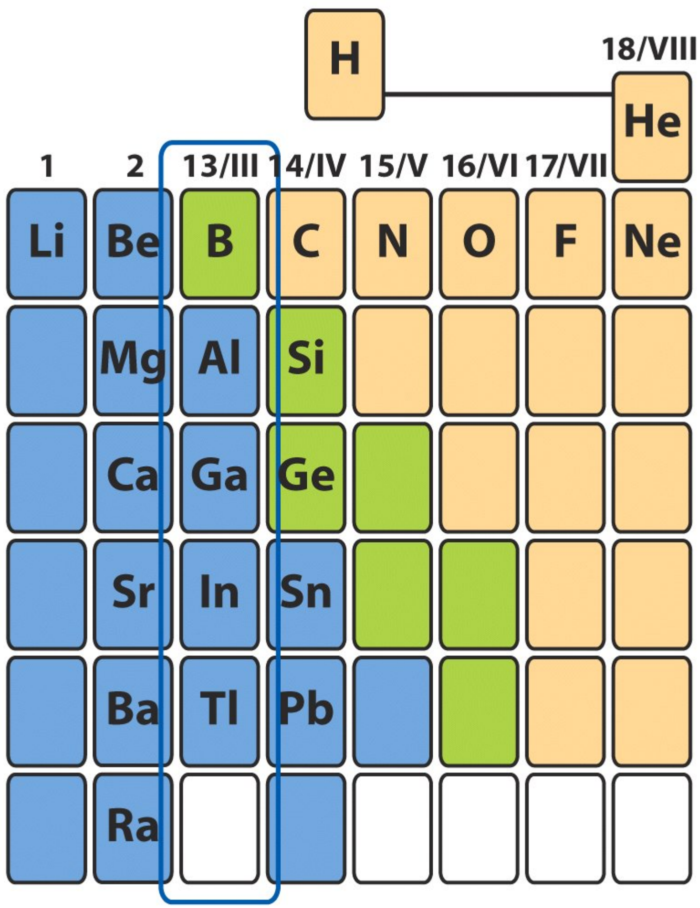
$M + 2H_2O \rightarrow M(OH)_2 + H_2$

Reaction with Ions

$M + 2H^+ \rightarrow M^{2+} + H_2$

Group 13: The Boron Family

Elements



- Electron configuration is ns^2np^1 (n is the period number)
- Boron and aluminum almost always have an oxidation number of +3
- The heavier elements of the group are more likely to keep their *s* electrons and can have oxidation numbers of +1 or +3

Group 13: The Boron Family

Elements (Boron)

- High ionization energy
- Metalloid
- Forms covalent bonds
- Small atomic radius
- Tends to form compounds that have incomplete octets or are electron deficient
- Mined as borax and kernite ($Na_2B_4O_7 \cdot xH_2O$ x = 10 or 4)
- Elemental boron exists in variety of different structures, one of the more common ones being B_{12}
- Because of the three dimensional network formed by the bonds, boron is very hard and when incorporated in plastics, forms a material that is stiffer than steel yet lighter than aluminum

6 B_{12}

Group 13: The Boron Family

Elements (Aluminum)

- Most abundant metallic element in the Earth's crust
- Low density
- Strong metal
- Amphoteric
- Excellent electrical conductor
- Commercial source of aluminum is bauxite ($Al_2O_3 \cdot xH_2O$ where x ranges from 1 to 3)
- Bauxite ore is turned into alumina (Al_2O_3) using the Bayer process

Group 13: The Boron Family

Elements (Aluminum)

- Hall discovered that if you add Na_3AlF_6 to alumina (Al_2O_3) that the melting temperature decreased from 2050°C to 950°C
- An electrochemical cell can then be used to extract the Al(s)

  Cathode Reaction: Al^{3+}(melt) + 3e^- → Al(l)

  Anode Reaction: 2O^{2-}(melt) + C(gr) → CO_2(g) + 4e^-

  Overall: 4Al^{3+}(melt) + 6O^{2-}(melt) + 3C(gr)→ 4Al(l) + 3CO_2(g)
- A current of 1 A must flow for 80 h to produce 27 g of Al about enough for 2 soft drink cans
- If recycled Al is used then the energy consumption drops to less than 5% of the original energy need to extract Al from bauxite
- The energy that we are throwing away when we discard an aluminum can is equivalent to burning the amount of gasoline that would fill half the can

Group 13: The Boron Family

Compounds of Boron

$B(OH)_3$ (Boronic Acid)

Properties:
- White
- Solid
- Melts at 171°C
- Lewis Acid

- Toxic to bacteria, insects, and humans
- Used as an mild antiseptic and pesticide
- Has an incomplete octet so forms bonds by accepting lone pairs of electrons
- Forms an acid anhydride with water
  $(OH)_3B + :OH_2 \rightarrow (OH)_3B\text{-}OH_2$

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Compounds of Aluminum

Al_2O_3 (Aluminum oxide commonly know as alumina)

- Variety of crystal structures
- Many forms are important ceramic materials
- Some impure forms of alumina are ruby (Cr^{3+}), sapphire (Fe^{3+} and Ti^{4+}), and topaz (Fe^{3+})
- Amphoteric

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Common Reactions

Reaction with Halogens

$2M + 3X_2 \rightarrow 2MX_3$ X_2 is group 9 molecule, Tl gives TlX as well but no TlI_3

Reactions with O

$4M + 3O_2 \rightarrow 2M_2O_3$

Reactions with N

$2M + N_2 \rightarrow 2MN$

Reactions with the ions

$2M + 6H^+ \rightarrow 2M^{3+} + 3H_2$

$2M + 2OH^- + 6H_2O \rightarrow 2M(OH)_4^- + 3H_2$