Elements – (Metals)

Only responsible for portion of notes discussed in class
not responsible for extra topics listed in second part of these notes below

Properties of Metals

Properties:
1) Electrical and thermal conduction
2) Luster
3) Deform under stress without cleaving
4) Form positive ions

Why:
1) Electrical and thermal conduction
Electrical and thermal conduction because of movement of free electrons while metals cations remain fixed

2) Luster
Electrons are excited to higher energy state by light all wavelengths.
Electrons fall back to lower levels and re-emit light so metals have shiny surface.

3) Deform under stress without cleaving
Held together by mobile electrons
Ductile – drawn into wire
Malleable – pounded into plate

4) Form positive ions
Metals readily lose one or more electrons since electron configuration is such that many inner electrons shield full charge of nucleus and so outer electrons are not as strongly held. For example K forms K^+ but Cl is apt to gain electron to become Cl^-. Notice that both K^+ and Cl^- are isoelectronic (same electronic configuration as) with noble gas Ar.

High Density because of close packed arrangement and many metals have 12 nearest neighbors

Group 1 and group 2 metals are exceptions to above in that they are soft metals
They have largest radii and smallest masses

Most metals have high M.P. and B.P. which shows the strength of the metallic bond

Occurence

Some pure metals – native metals	example - gold (not reactive)
Most metals obtain from oxides	example iron oxide
or from carbonates or sulfides converted to oxides	

Group 1 (IA) metals- alkali metals

List		Outermost e
Li	Lithium	$2s^1$
Na	Sodium	$3s^1$
K	Potassium	$4s^1$
Rb	Rubidium	$5s^1$
Cs	Cesium	$6s^1$
Fr	Francium (rare)	$7s^1$

Properties

Compared to other metals

Low density

Low melting point, low boiling point (Cs M.P. = 29 ^oC)

Soft (can cut with steel knife)

Have one electron beyond noble gas so form +1 ions

easy to get off first electron, difficult to get off 2nd electron

Good reducing agents because they will undergo oxidation

$Li \rightarrow Li^+ + e^-$ occurs readily

Reaction examples

With chlorine gas

$2K(s) + Cl_2(g) \rightarrow 2\ KCl\ (s)$ where made of K^+ cations and Cl^- anions

Can have explosive reaction with water - more reactive as go down group

$$2K + 2\ H_2O \rightarrow 2\ KOH\ (aq) + H_2(g) + \text{energy}$$

Metals have strong tendency to oxidize $+E^o_{ox}$

The larger the $+E^o_{ox}$ the more the energetic the reaction

$Na \rightarrow Na^+ + e^-$ +2.71V more reactive than Zn

$Zn \rightarrow Zn^{2+} + 2\ e^-$ +.76 V

Less reactive metals will react with acid in water

$Zn\ (s) + 2\ H^+\ (aq) \rightarrow Zn^{2+}\ (aq) + H_2\ (g)$

Group 2 (IIA) Metals – alkaline earth metals

List

Be	Beryllium	$2s^2$
Mg	Magnesium	$3s^2$
Ca	Calcium	$4s^2$
Sr	Strontium	$5s^2$
Ba	Barium	$6s^2$

Properties and Reactions

Second most reactive metals
Not found free in nature
Produced by electrolysis of molten chlorides

M.P. much greater than Group 1 metals (Sr M.P. = 800°C, Cs M.P. = 29°C)

Tend to form +2 ions

Reaction examples

Mg	+	X_2 →	MgX_2	X = halogen F, Cl, Br, I
2 Ca	+	O_2 →	2 CaO	

Group 13 (IIIA) Metals

List

Al	Aluminum
Ga	Gallium
In	Indium
Tl	Thallium

Properties
Al is most abundant metal of earth's crust (8%)
other Group 13 metals found in trace amounts

Al important in containers and light weight parts

Al tends to form 3+ ions

Group 14 (IVA) metals

List

Ge	Germanium
Sn	Tin
Pb	Lead

Properties
Form +4, +2 oxidations states
But not +4 ions, +4 ox nu is associated with covalent compounds

Generally form covalent compounds rather than ions - example $PbCl_4$ is actually covalent and not ionic because metal is more like nonmetal and less like metal in some ways.

Group 3 – 12 (IIIB – IIB)- Transition Metals

Properties

High M.P. and B.P. (Group 3 exception Zn, Cd, Hg)
Extreme example Hg liquid at room temp.

Good conductors of electricity and heat
(Group 11 are outstanding conductors Cu, Ag, Au)

Electronic configuration:
Filling of d orbitals
Variety of oxidation states possible for transition metals
Be aware of range of possibilities

+1 important only for Cu^+, Ag^+, Au^+, Hg_2^{2+}
+2 important for 4th period (s orbital e^- come off first)
Maximum ox. nu. in middle of d period

Unpaired electrons cause many transition metal compounds to be:
colored solids (most pure organic compounds are white solids)
and paramagnetic (attracted to a magnetic field –
unpaired electrons are like tiny magnets in atoms)

Relative Reactivity

Observe that gold does not react in hydrochloric or nitric acid (a classic test for gold) while zinc reacts with both and copper with only nitric.

	HCl(aq)	HNO_3(aq)
Zn	Yes	Yes
Cu	No	Yes
Au	No	No

So therefore the relative reactivity is: Zn > Cu > Au

Air oxidation of metals causes corrosion that destroys metal and changes properties
Rust costs billions of dollars a year. Gold is prized for jewelry because it doe not react.

Lanthanides (inner transition elements)

List

Elements number 51 through 71 (see Periodic Table)
Filling of 4f orbitals

Properties and Reactions

Lanthanide contraction- atomic ionic radii decrease with increasing atomic number because 4f orbitals are not outermost

Also because 4f are not outermost, addition of electrons does not cause much variation in properties

Chemistry of lanthanides are all very similar

All form +3 oxidation state through loss of 2 s e^- and 1 f e^-

Elements are very difficult to separate and are frequently found as mixtures of lanthanide elements in nature

Very Reactive:

$$2\ M + 3\ X_2 \rightarrow 2\ MX_3$$
$$2\ M + 3\ O_2 \rightarrow 2\ M_2O_3$$

Extra Topics in Chemistry 1120 Metals given below (will not cover)

Metallic Bond and Conduction

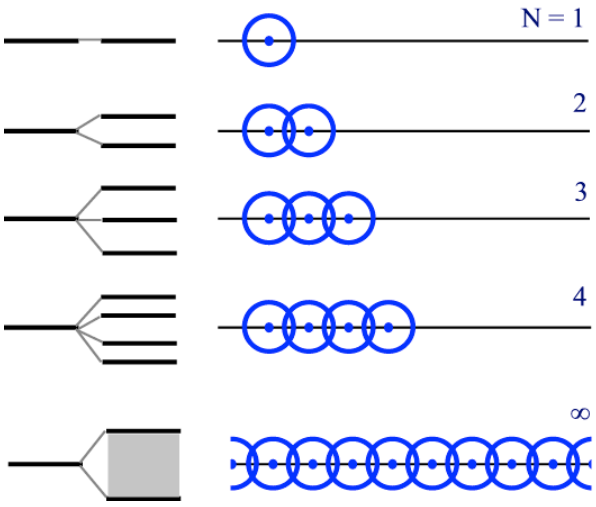
Array of positive ions surrounded by outer electrons

Because low electronegativities, ionization energies of outer e- are loosely held and free to move

Energy band within crystal

Each atom brings to the crystal certain orbitals and the orbitals may be partially or completely filled

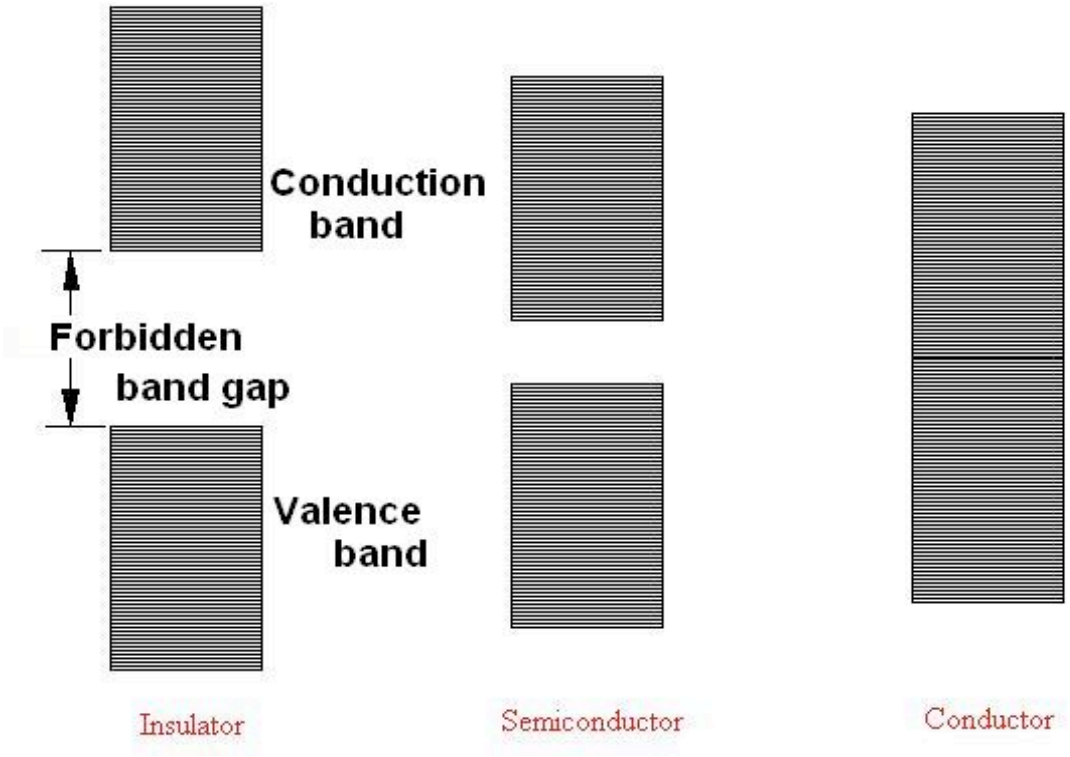
Bands energy level (in diagram below energy increases going down usually higher energy level as you go up in diagram)



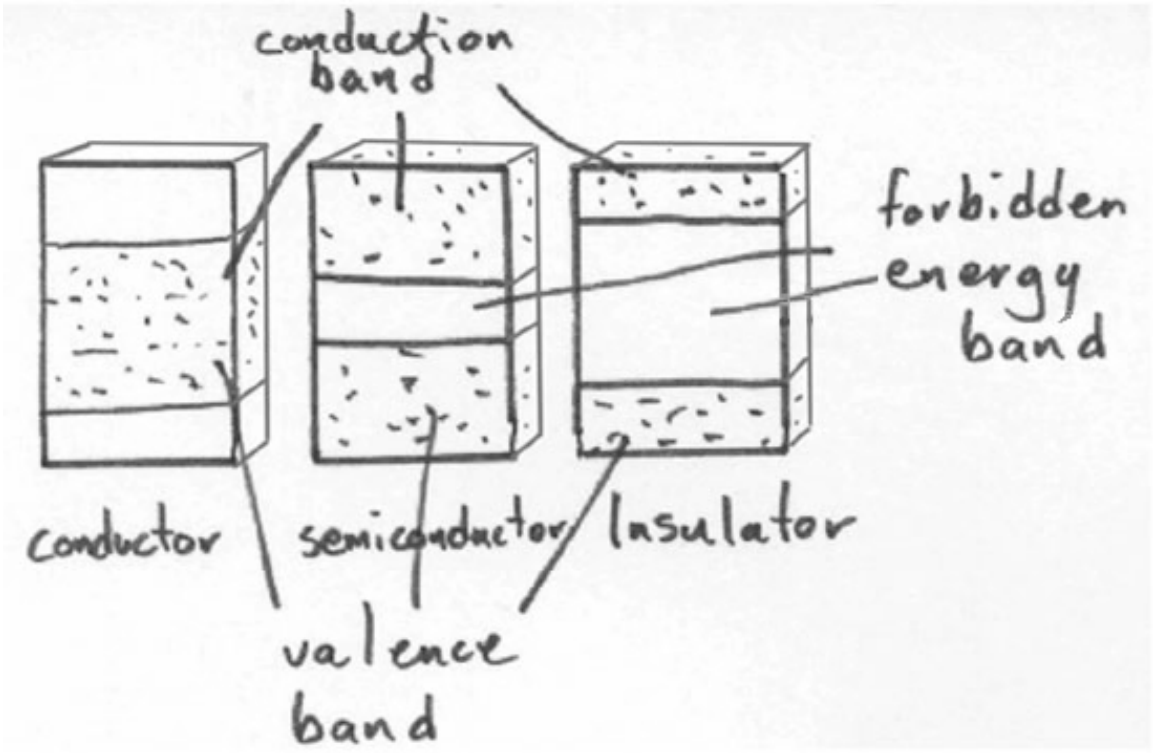
http://www.chem.queensu.ca/people/faculty/mombourquette/FirstYrChem/Molecular/bands/index.asp

N orbitals form band with N levels can contain 2N electrons since can have 2 e in orbital

Valence band- band formed from outer electrons
Conduction band- empty sites available for electrons to move in
Forbidden energy zone (band gap)- gap between energy bands



http://neon.chem.uidaho.edu/~honors/bands.html



http://hsc.csu.edu.au/physics/core/implementation/9_4_3/943net.html

Electronic Conductivity of semiconductor increases with increase in temperature so the electrons move up to the conduction band.
Electronic conductivity of metals decreases with increase in temperature so the vibration of atoms limits flow of electrons.

Extrinsic Semiconductor- semiconductor in which impurities have been added

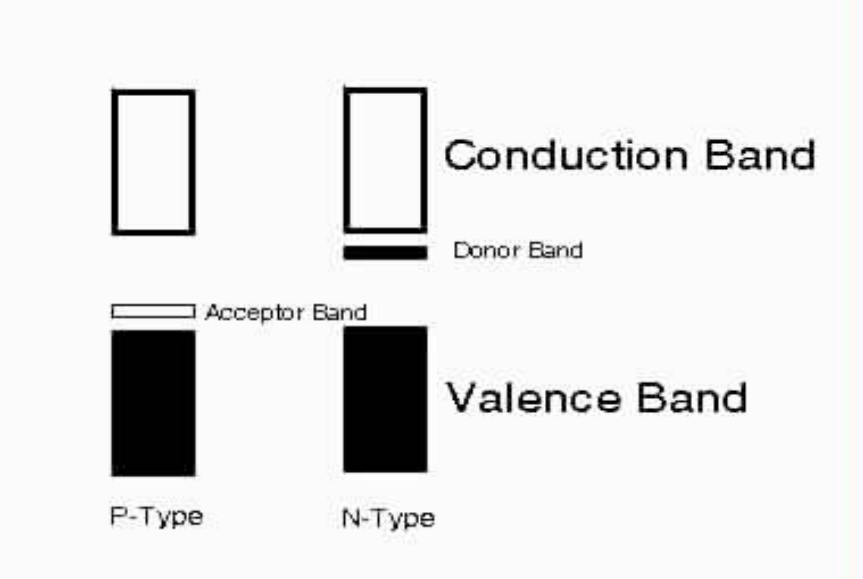
Si, Ge diamond lattice 4 valence e-

Low conductivity

Add B (low concentration) with 1B/ million Si atoms will change conductivity by factor of 100000

P- type semiconductor
Add IIIA (group 3) element
B three valence e- to bulk Si create a hole vacancy neutral charge but e- can move

N-type semiconductor
Add VA (group 5) element
P five valence e- to bulk Si creates an extra electron



e- removed e- added

http://www.chembio.uoguelph.ca/educmat/chm729/band/psemi.htm

Group 1 (IA) metals- alkali metals (more)

Reactions

2M	+ X_2 →	2 MX		Halogens → Halide
2M	+ H_2 →	2 MH		Hydrogen → Hydride
2M	+ S →	M_2S		Sulfur → Sulfide
2M	+ H^+ (aq) →	2 M^+ + H_2		Violent reaction
2M	+ 2 H_2O →	2 MOH (aq)	+ H_2(g)	Can be violent reaction

Production – Laboratory

Very Reactive metals – react with water
Group 1 Li, Na, K, Rb explosive reaction
Group 2 Ca, Sr, Ba vigorous

$2\ Na\ (s) + 2\ H_2O \rightarrow 2\ Na^+\ (aq) + 2\ OH^- + H_2$

Oxidation: $2\ Na \rightarrow 2\ Na + 2\ e^-$
Reduction: $2\ e^- + 2\ H_2O \rightarrow 2\ OH^- + H_2$

Metals have strong tendency to oxidize $+E^o_{ox}$
The larger the $+E^o_{ox}$ the more the energetic the reaction

Less reactive metals will react with acid in water

$Zn\ (s) + 2\ H^+\ (aq) \rightarrow Zn^{2+}\ (aq) + H_2\ (g)$

$Na \rightarrow Na^+ + e^-$ +2.71V more reactive than Zn
$Zn \rightarrow Zn^{2+} + 2\ e^-$ +.76 V

Reactions - metals

Because of the high bond energy, most reactions with H_2 require high temperature to form metal hydrides

Salt-like Hydrides (M+ H- like ionic solids)
Group 1 and heavy Group 2 (Ca , Sr, Ba)

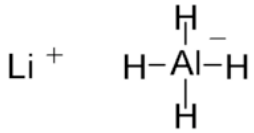
2 Na (s)	+ H_2 (g) →	2 NaH (s)	
Ca (s)	+ H_2 (g) →	CaH_2 (s)	

Interstitial Hydrides

Pt, Pd, Ni
Hydrogen absorbed H-H bond broken, atomic hydrogen is found between layers of metal

Complex Hydrides

Lithium Aluminum hydride



http://en.wikipedia.org/wiki/LiAlH4

with metal oxides to produce water and metal

WO_3 (s) + 3 H_2 (g) → W (s) + 3 H_2O (g)

Commercial production of tungsten is an expensive process

Reactions – Non metals

Oxygen

2 H_2 + O_2 → 2 H_2O
water

High T to start, oxyhydrogen torch 2800°C, space shuttle engines

Halogens

H_2 + F_2 → 2 HF
Hydrogen fluoride

F_2, Cl_2 room temp
Br_2, I_2 300°C

Nitrogen

3 H_2 (g) + N2 (g) → 2 NH_3 (g)
Fe catalyst
500 atm, 500°C

Haber process used to make ammonia

Sulfur

H_2 (g) + S (g) → H_2S (g)
Hydrogen sulfide
High Temp

Group 2 (IIA) Metals – alkaline earth metals (more)

Reactions

M	+	X_2 →	MX_2			X = halogen F, Cl, Br, I
2 M	+	O_2 →	2 MO			
M	+	S →	MS			
M	+	H_2 →	MH_2			
M	+	2 H_2O →	$M(OH)_2$	+	H_2	Ca, Sr, Ba (Be not react w/ H_2O)
M	+	2 H^+ →	M^{2+}	+	H_2	

Compare solubility of Group 1 and Group 2 salts
Most group 1 metal salts are very soluble
A number of group 2 metal salts are low solubility

OH-	Hydroxide
SO_4^{2-}	Sulfate
CO_3^{2-}	Carbonate
$C_2O_3^{2-}$	Oxalates
F^-	Fluorides
CrO_4^{2-}	Chromates

Metals Reducing Agents

Metals have low ionization energy, small electron affinity, and easily lose electrons to become positive

M → M^+ + e^-
M → M^{2+} + 2 e^-

Zn + 2 H^+ (aq) → Zn^{2+} (aq)+ H_2 (g)

Ca + 2 H^+ → no reaction
Ca + 2 NO_3^- + 4 H^+ → Ca^{2+} + 2 NO_2 + 2 H_2O
Oxidizing agent

Ease of oxidation is same as reactivity with H^+

Group 1 is most reactive (lowest ionization energy) and Group 2 is less reactive

Compare ability of one metal to react by oxidizing another

$Zn\ (s) + Cu^{2+}\ (aq) \rightarrow Zn^{2+}\ (aq) + Cu\ (s)$

So Zn is more reactive than Cu because it is more easily oxidized or causes Cu to be reduced
Can quantify relative reactivity in electrochemistry chapter

<u>Nonmetals as Oxidizing Agents</u>

Strongest oxidizing agents are found going up and across to the right of the periodic table

$F \rightarrow F^-$
$Cl \rightarrow Cl^-$

F will go to an ion more than Cl

$Cl_2 + 2\ Br^- \rightarrow 2\ Cl^- + Br_2$

Cl is reduced (gain e)
Br is oxidized (lose e)

Reactions with Oxygen:

Metals-

$2\ Fe + 3/2\ O_2 + x\ H_2O\ (l) \rightarrow Fe_2O_3 \cdot xH_2O$
rust

Iron oxide crystal includes water molecules

Cu	+	$O_2\ (g) \rightarrow$	$CuO\ (s)$	Slow at room T
$2\ Mg\ (s)$	+	$O_2\ (g) \rightarrow$	$2\ MgO\ (s)$	Fast at high T

Can predict product if unique ox nu of metal

Nonmetals-

$2\ H_2\ (g)$	+	$O_2\ (g) \rightarrow$	$2\ H_2O$
$C\ (s)$	+	$O_2\ (g) \rightarrow$	$CO_2\ (g)$
$S\ (s)$	+	$O_2\ (g) \rightarrow$	$SO_2\ (g)$

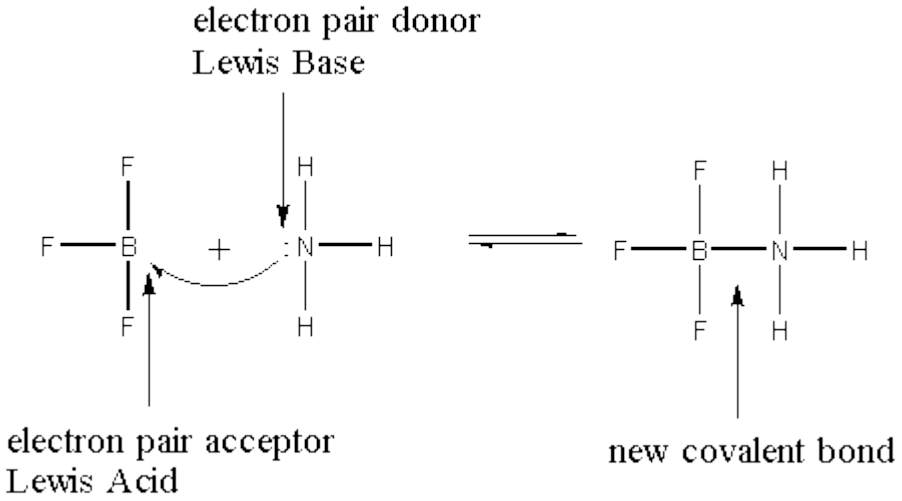
N_2 + $O_2 \rightarrow 2\ NO$ Only at very high T, otherwise not in atmosphere

$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$

These more complicated molecules react to form as direct elements

Lewis Acids and Bases

Lewis acid- electron pair acceptor
Lewis base – electron pair donor



http://bilbo.chm.uri.edu/CHM112/lectures/Image1110.gif

Bronsted Lowry acid and base also fits Lewis definition but there is also a more general definition

Acid	Base	
H_3O^+	$+ OH^-$ →	$2\ H_2O$
Ag^+	$+ Cl^-$ →	AgCl

Ore

Naturally occurring material from which pure metal may be extracted

Ores when mined include other unwanted materials such as silica, clay, granite, and gangue (worthless rocks in which minerals are found)

Metallurgy

extraction of metals from ores and converting into usable form

Three stages

1. preliminary treatment – desired part of ore concentrated impurities removed or mineral converted to another form
2. reduction – metal compound reduced to free metal
3. refining – metal purified and if needed other substances added to give desired product

Preliminary Treatment

Concentration of ore removal of gangue
Physical separation
Mineral particles may be separated by floatation

Oil – mineral particles go into oil
Water – used to remove gangue

Chemical separation

Example make steel from Fe_3O_4

Iron containing ore crushed
Magnetic Fe_3O_4 separated from gangue by attracting it with electromagnets

Reduction

Reduction in blast furnace

$$Fe_3O_4\ (s) + CO\ (g) \xrightarrow{\text{Heat}} 2\ FeO\ (s) + CO_2\ (g)$$

$$FeO\ (s) + CO\ (g) \xrightarrow{\text{Heat}} Fe\ (l) + CO_2\ (g)$$

Hot air reacts with carbon to form CO
Gives off heat
CO reacts with iron oxide

Refining
Pig iron contains up to 40% C, 2% Si, P, S
These impurities are remeoved by direct stream of high pressure oxygen into pig iron
Oxides formed as gases and removed by stream of oxygen

Steel- other metals added as needed to improve properties