The rest of the Semester

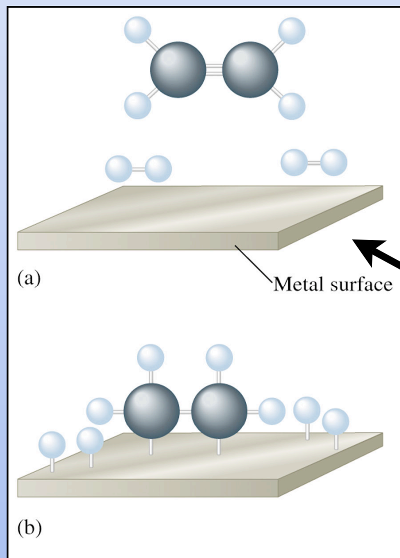
All of Chemistry

Today

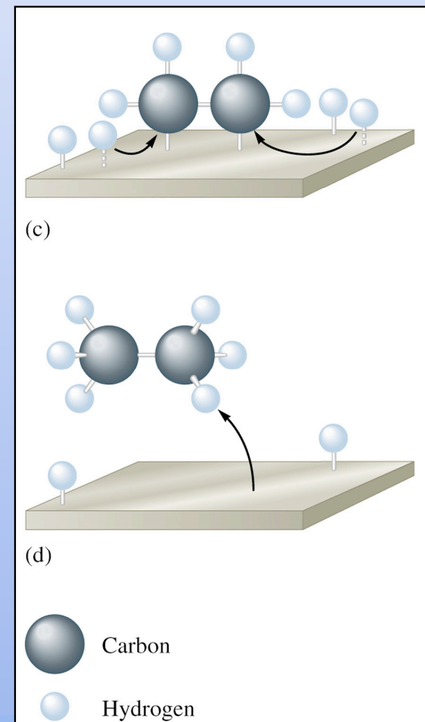
Groups 1-IV

One key key catalyst point
I want to re-emphasize

A catalyst is unchanged by a chemical reaction!
It is the same before and after



metal
unchanged



Things everyone should know

Get to know the chemistry of the elements

How is each element found in nature

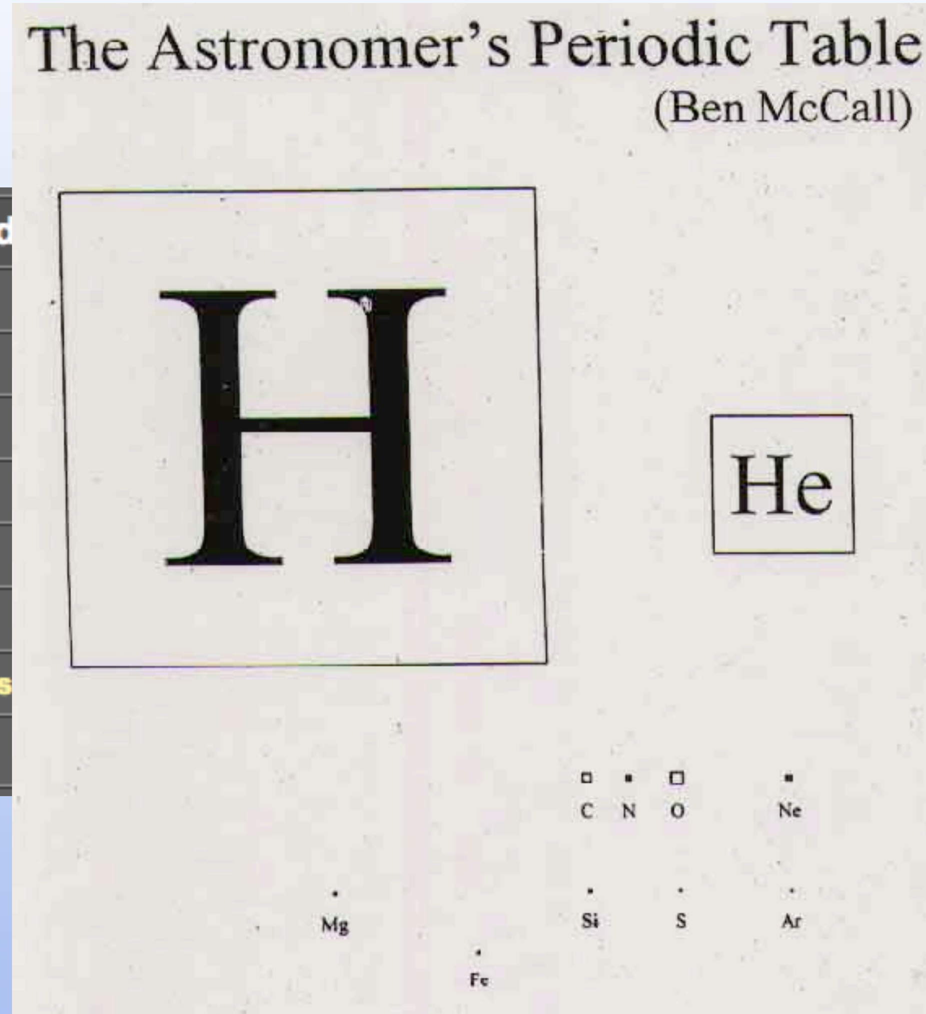
Reactions involving compounds with those elements

Practical uses of those compounds

First what is the most abundant element in the Universe?

A. Hydrogen
B. Helium
C. Oxygen
D. Silicon
E. Iron

Number of atoms per 10,000,000 of hyd		
hydrogen	10,000,000	sulfur
helium	1,400,000	iron
oxygen	6,800	argon
carbon	3,000	aluminum
neon	2,800	sodium
nitrogen	910	calcium
magnesium	290	all other elements
silicon	250	



What about in our part of the universe?

First what is the most abundant element on the Earth's crust?

A. Hydrogen

B. Helium

C. Oxygen

D. Silicon

E. Iron

TABLE 18.1 Distribution (Mass Percent) of the 18 Most Abundant Elements in the Earth's Crust, Oceans, and Atmosphere

Element	Mass Percent	Element	Mass Percent
Oxygen	49.2	Titanium	0.58
Silicon	25.7	Chlorine	0.19
Aluminum	7.50	Phosphorus	0.11
Iron	4.71	Manganese	0.09
Calcium	3.39	Carbon	0.08
Sodium	2.63	Sulfur	0.06
Potassium	2.40	Barium	0.04
Magnesium	1.93	Nitrogen	0.03
Hydrogen	0.87	Fluorine	0.03
		All others	0.49

Monahans Sand Dune's State Park

Sand is SiO_2

Elemental Makeup of you?

A. Hydrogen

B. Helium

C. Oxygen

D. Silicon

E. Iron

TABLE 18.2 Abundance of Elements in the Human Body

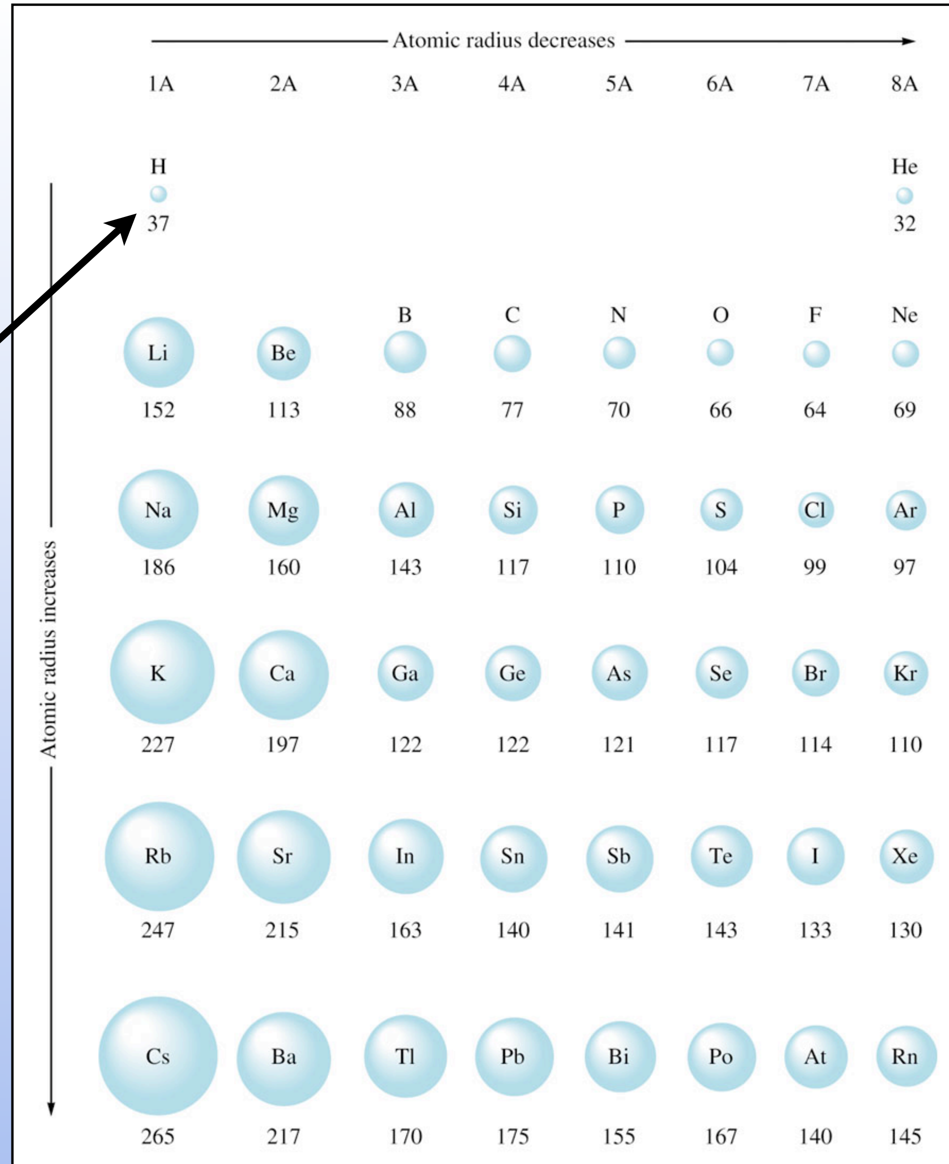
Major Elements	Mass Percent	Trace Elements (in alphabetical order)
Oxygen	65.0	Arsenic
Carbon	18.0	Chromium
Hydrogen	10.0	Cobalt
Nitrogen	3.0	Copper
Calcium	1.4	Fluorine
Phosphorus	1.0	Iodine
Magnesium	0.50	Manganese
Potassium	0.34	Molybdenum
Sulfur	0.26	Nickel
Sodium	0.14	Selenium
Chlorine	0.14	Silicon
Iron	0.004	Vanadium
Zinc	0.003	

Note by atoms, Hydrogen is the most abundant

Hydrogen
In a group of its own

very small
only a single
1s electron

greater
electronegativity
than other group 1



Hydrogen

electronegativity of 2.1
(nearly exactly the same as carbon)

might lose an electron (+1 oxidation state)
might gain an electron (-1 oxidation state)

$$2K(s) + H_2(g) \longrightarrow 2KH(s)$$

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$$

Reactant	Reaction with hydrogen
Group 1 metals (M)	$2\ M(s) + H_2(g) \longrightarrow 2\ MH(s)$
Group 2 metals (M, not Be or Mg)	$M(s) + H_2(g) \longrightarrow MH_2(s)$
some *d*-block metals (M)	$2\ M(s) + x\ H_2(g) \longrightarrow 2\ MH_x(s)$
oxygen	$O_2(g) + 2\ H_2(g) \longrightarrow 2\ H_2O(l)$
nitrogen	$N_2(g) + 3\ H_2(g) \longrightarrow 2\ NH_3(g)$
halogen (X_2)	$X_2(g,l,s) + H_2(g) \longrightarrow 2\ HX(g)$

Who cares about hydgrogen

$$2H_2 + O_2 \longrightarrow 2H_2O$$

reaction = 2x(enthalpy of formation of water)
$-475\ kJ\ mol^{-1}$

Most energy per mass of any reaction

In the photograph above the first bus is unloaded from the ship, with the pure steam rising from its exhaust pipe visible at the rear.

The problem is there is no H_2

Where to get it?

Steam reforming of methane (1000°C, Ni Catalyst)

$$CH_4(g) + H_2O(g) \longrightarrow CO(g) + 3H_2(g)$$

Water gas shift (130°C)

$$CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)$$

Other fun with H_2

H^+ can oxidize metals

$$Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$$

Other fun with H_2

H_2 can reduce oxides

$$CuO + H_2 \longrightarrow Cu + H_2O$$

TABLE 20.1 Standard Reduction Potentials in Water at 25°C

Standard Potential (V)	Reduction Half-Reaction
+2.87	$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$
+1.51	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$
+1.36	$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$
+1.33	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
+1.23	$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$
+1.06	$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$
+0.96	$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + H_2O(l)$
+0.80	$Ag^+(aq) + e^- \longrightarrow Ag(s)$
+0.77	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$
+0.68	$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$
+0.59	$MnO_4^-(aq) + 2H_2O(l) + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$
+0.54	$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$
+0.40	$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$
+0.34	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$
0	$2H^+(aq) + 2e^- \longrightarrow H_2(g)$
−0.28	$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$
−0.44	$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$
−0.76	$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$
−0.83	$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$
−1.66	$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$
−2.71	$Na^+(aq) + e^- \longrightarrow Na(s)$
−3.05	$Li^+(aq) + e^- \longrightarrow Li(s)$

Hydrogen

How is each element found in nature

(its almost all in water and hydrocarbons)
H_2 made from methane reforming with steam

Reactions involving compounds with those elements
H^+ oxidizing metals
H_2 reducing compounds (like oxides)

Practical uses of those compounds

$$2H_2 + O_2 \longrightarrow 2H_2O$$

Hydrogen

How is each element found in nature

(its almost all in water and hydrocarbons)
H_2 made from methane reforming with steam

Reactions involving compounds with those elements
H^+ oxidizing metals
H_2 reducing compounds (like oxides)

Practical uses of those compounds

$$2H_2 + O_2 \longrightarrow 2H_2O$$

Group 1 metals
Alkali Metals

All have a nS^1 electronic configuration
Very low ionization energy
Behave like a metal (easily oxidized)
From +1 ion always
low boiling and melting points
react violently with water (and most anything else)
from basic hydride and oxides

$$2Na + 2H_2O \longrightarrow 2Na^+ + 2OH^- + H_2(g)$$

TABLE 20.1 Standard Reduction Potentials in Water at 25°C

Standard Potential (V)	Reduction Half-Reaction
+2.87	$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$
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+1.06	$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$
+0.96	$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + H_2O(l)$
+0.80	$Ag^+(aq) + e^- \longrightarrow Ag(s)$
+0.77	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$
+0.68	$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$
+0.59	$MnO_4^-(aq) + 2H_2O(l) + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$
+0.54	$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$
+0.40	$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$
+0.34	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$
0	$2H^+(aq) + 2e^- \longrightarrow H_2(g)$
−0.28	$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$
−0.44	$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$
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−0.83	$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$
−1.66	$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$
−2.71	$Na^+(aq) + e^- \longrightarrow Na(s)$
−3.05	$Li^+(aq) + e^- \longrightarrow Li(s)$

← Best Reducing Agents

Group 1 elements will react with nearly anything

$$2Na(s) \;+\; Cl_2(g) \longrightarrow NaCl(s)$$

$$3Li(s) \;+\; N_2(g) \longrightarrow 2Li_3N(s)$$

$$4Na(s) \;+\; O_2(g) \longrightarrow 2Na_2O(s)$$

reactions with air

TABLE 18.6 Selected Reactions of the Alkali Metals

Reaction	Comment
$2M + X_2 \longrightarrow 2MX$	X_2 = any halogen molecule
$4Li + O_2 \longrightarrow 2Li_2O$	Excess oxygen
$2Na + O_2 \longrightarrow Na_2O_2$	
$M + O_2 \longrightarrow MO_2$	M = K, Rb, or Cs
$2M + S \longrightarrow M_2S$	
$6Li + N_2 \longrightarrow 2Li_3N$	Li only
$12M + P_4 \longrightarrow 4M_3P$	
$2M + H_2 \longrightarrow 2MH$	
$2M + 2H_2O \longrightarrow 2MOH + H_2$	
$2M + 2H^+ \longrightarrow 2M^+ + H_2$	Violent reaction!

Hydrides and oxides are basic

$Na_2O(s) \quad + H_2O(l) \longrightarrow 2NaOH(aq)$

Nucleophilic (wants nuclei) Electron rich

$NaH(s) \quad + H_2O(l) \qquad 2NaOH(aq) + H_2(g)$

H in -1 oxidation state (can deprotonate nearly anything)

Where are they?

Everywhere as ions

Na^+, K^+ are everywhere
(Li^+ because it has such a large charge density often makes insoluble compounds)
Rb, Cs, Fr very little in the universe

Na^+ and K^+ critical in biochemistry

TABLE 18.3 Sources and Methods of Preparation of the Pure Alkali Metals

Element	Source	Method of Preparation
Lithium	Silicate minerals such as spodumene, $LiAl(Si_2O_6)$	Electrolysis of molten LiCl
Sodium	NaCl	Electrolysis of molten NaCl
Potassium	KCl	Electrolysis of molten KCl
Rubidium	Impurity in lepidolite, $Li_2(F,OH)_2Al_2(SiO_3)_3$	Reduction of RbOH with Mg and H_2
Cesium	Pollucite ($Cs_4Al_4Si_9O_{26} \cdot H_2O$) and an impurity in lepidolite (Fig. 18.4)	Reduction of CsOH with Mg and H_2

Practical Uses

Na^+ and K^+ needed to keep your body functioning

Not to mention tasty

$$Li^+ + e^- \longrightarrow Li \qquad E = -3V \text{ (most negative)}$$

Make a great battery (high voltage)

Group II metals
Alkali Earth Metals

All have a nS^2 electronic configuration
Very low ionization energy
Behave like a metal (easily oxidized)
From +2 ion always
react with water (and most anything else)

Difference compared to group 1

+2 ions have a very high charge density
Often they make insoluble compounds

You'll find them as oxides, phosphates, sulfates, and carbonates

Sometimes mixed metal compounds
$Be_3Al_2Si_6O_{18}$ (Beryl)

Emeralds = Beryl + Cr^{3+} ions

Which is easier to oxidize?

A. Magnesium

B. Carbon

C. They are the same

Common Reactions

$$Ca + 2H_2O \longrightarrow Ca^{2+} + 2OH^- + H_2$$

TABLE 18.8 Selected Reactions of the Group 2A Elements

Reaction	Comment
$M + X_2 \longrightarrow MX_2$	X_2 = any halogen molecule
$2M + O_2 \longrightarrow 2MO$	Ba gives BaO_2 as well
$M + S \longrightarrow MS$	
$3M + N_2 \longrightarrow M_3N_2$	High temperatures
$6M + P_4 \longrightarrow 2M_3P_2$	High temperatures
$M + H_2 \longrightarrow MH_2$	M = Ca, Sr, or Ba; high temperatures; Mg at high pressure
$M + 2H_2O \longrightarrow M(OH)_2 + H_2$	M = Ca, Sr, or Ba
$M + 2H^+ \longrightarrow M^{2+} + H_2$	
$Be + 2OH^- + 2H_2O \longrightarrow Be(OH)_4^{2-} + H_2$	

Oxides are highly reactive

Very Basic

$$CaO + H_2O \longrightarrow Ca^{2+} + 2OH^-$$

Key component in cement

$$CaCO_3 + \text{heat} \longrightarrow CaO + CO_2$$

Ca^{2+} has a very high charge density
Make strong compounds
Not a surprise to find it in bones, teeth, concrete...

Oddball Be makes some covalent compounds

All other are metallic

Group III

TABLE 18.9 Selected Physical Properties, Sources, and Methods of Preparation for the Group 3A Elements

Element	Radius of M^{3+} (pm)	Ionization Energy (kJ/mol)	$\mathscr{E}°$ (V) for $M^{3+} + 3e^- \longrightarrow M$	Sources	Method of Preparation
Boron	20	798	—	Kernite, a form of borax ($Na_2B_4O_7 \cdot 4H_2O$)	Reduction by Mg or H_2
Aluminum	50	581	−1.66	Bauxite (Al_2O_3)	Electrolysis of Al_2O_3 in molten Na_3AlF_6
Gallium	62	577	−0.53	Traces in various minerals	Reduction with H_2 or electrolysis
Indium	81	556	−0.34	Traces in various minerals	Reduction with H_2 or electrolysis
Thallium	95	589	0.72	Traces in various minerals	Electrolysis

Found as oxides

Al_2O_3 + Cr^{3+} = ruby

Al_2O_3 + Ti = sapphire

Aluminum is a very useful metal
Where does it come from?

All "Bauxite" to begin with
A mix of aluminum, iron, and silicon oxides

"Bayer process" to purify to only Al_2O_3 (Alumina)
(first dissolve in base only Al and Si compounds dissolve
the lower the temp and Al_2O_3 is less soluble so it fall out first)

Then heat it up with Carbon to get $Al + CO_2$

Boric Acid

$$B(OH)_3 + H_2O \longrightarrow B(OH)_4^- + H^+$$

(toxic to many insects. Disrupts metabolism and its abrasive)

$NaBH_4$

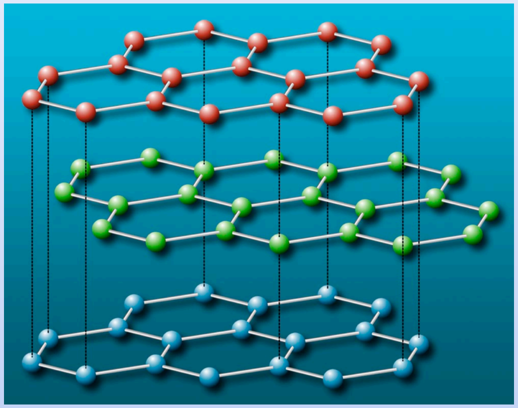
Strong Reducing Agent

BH_4^- ("excess electrons")

Group IV

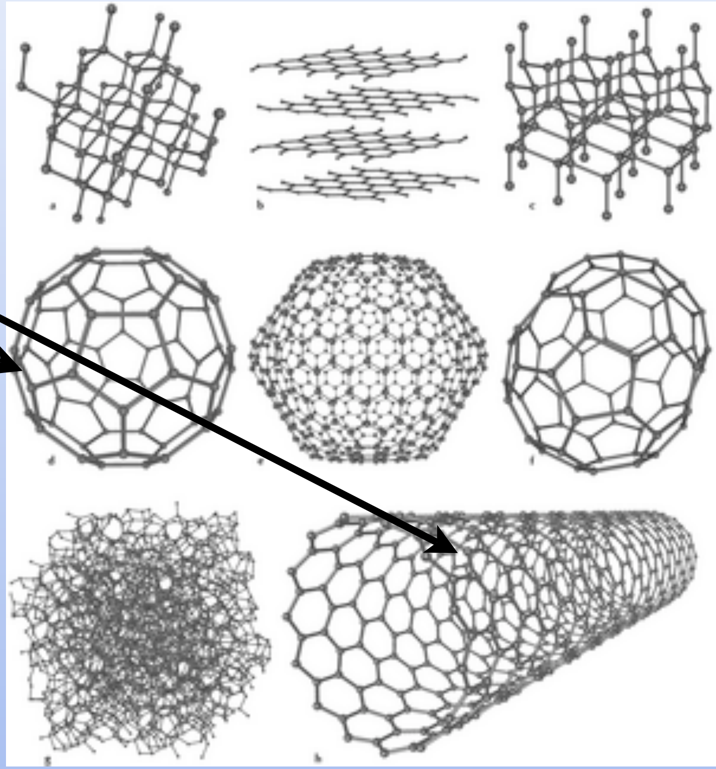
Carbon Allotropes

Diamond   All sp^3 carbon
Very strong tetrahedral network
insulating



Graphite   All sp^2 carbon in a plane
other p orbital give in-plane pi bond
delocalized pi electrons make graphite conductive
plane can "slip" over each other = pencil

C_{60} + nanotubes



"wrapped up" graphite

Carbon chemistry = Organic Chemistry

We'll have two whole lectures just on this

The other major player in Group IV

Silicon

the basis of all computer chips

Metallic Bonding
"thinking of all the atoms as one big molecule"

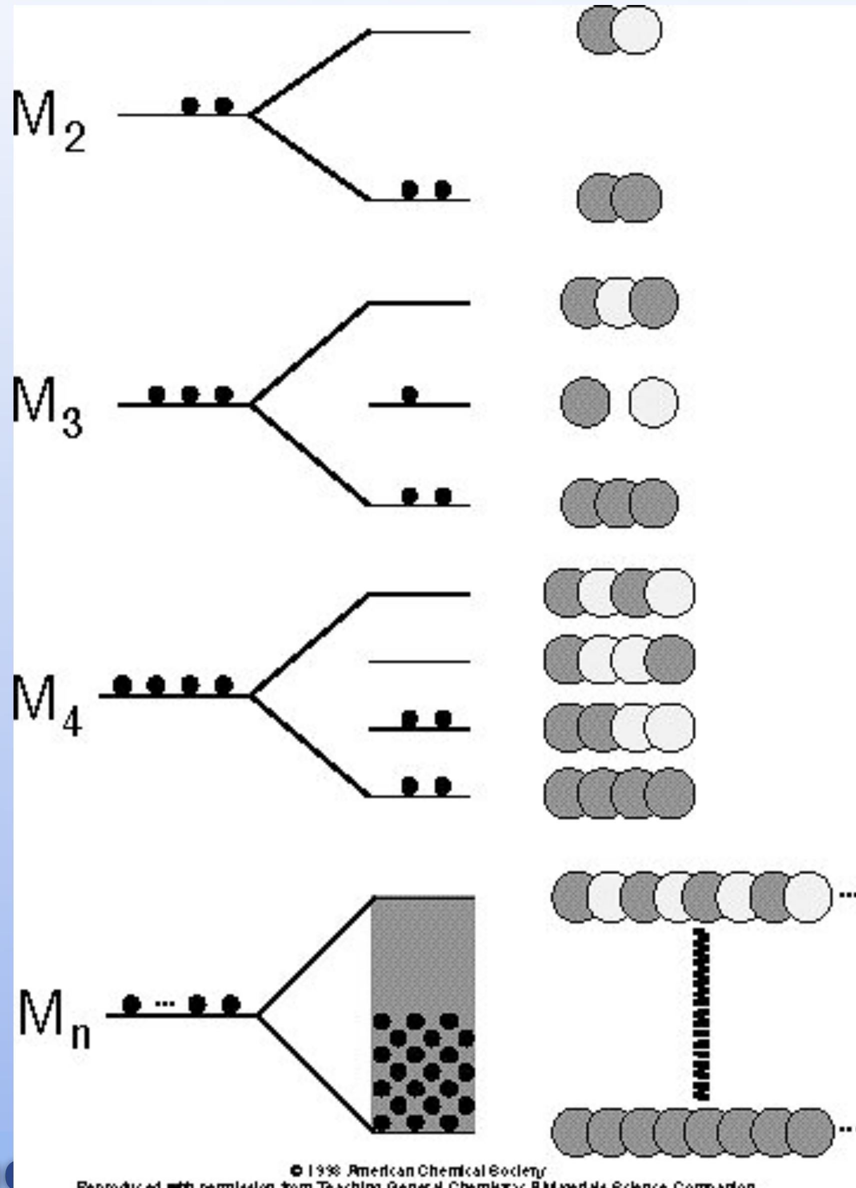
Remember Molecular Orbitals??

2 atoms — 2 MO (like H_2)

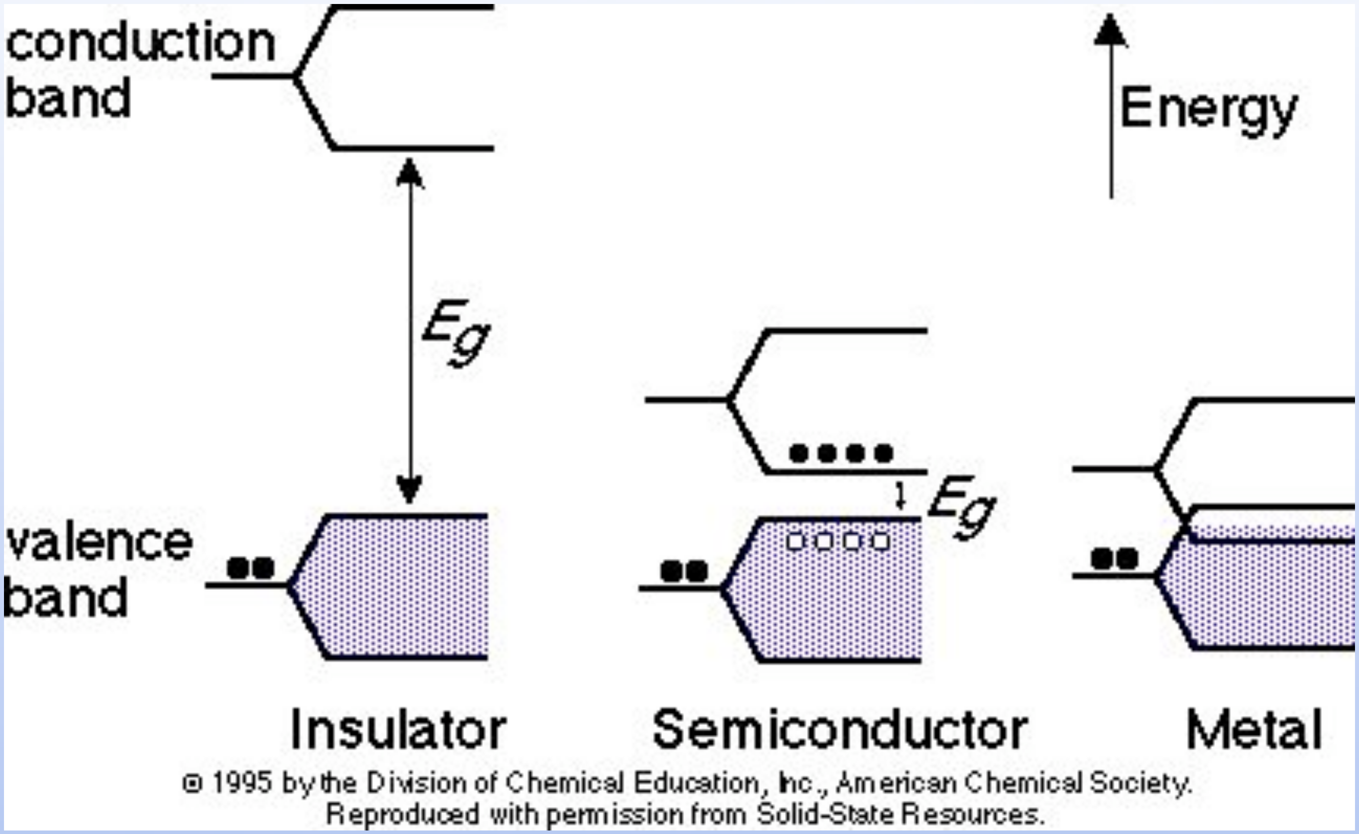
3 atoms — 3 MOs

3 atoms — 4 MOs

n atoms — n MOs, 1/2 filled

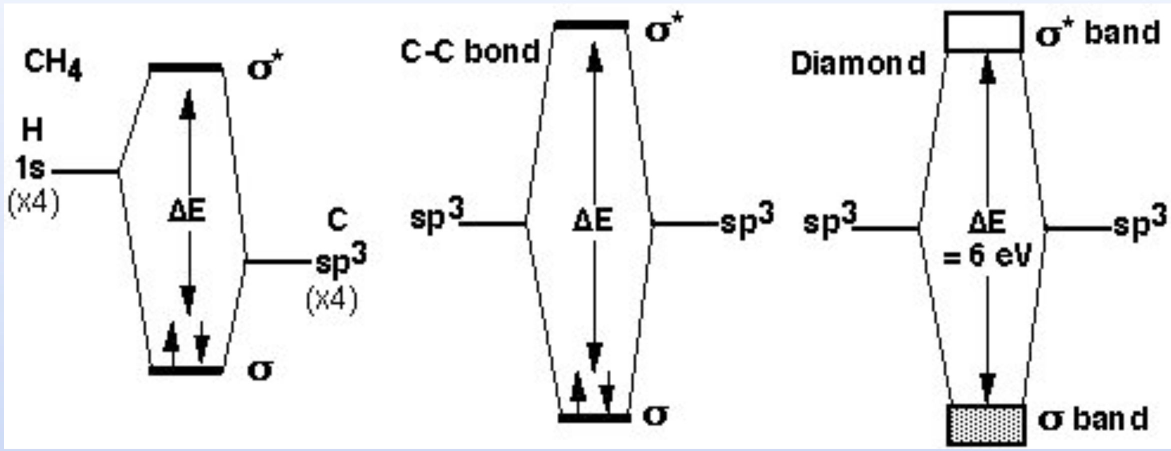


Metals, Insulators, Semiconductors



Semiconductors, bands are close but there is a gap.
Need thermal energy to move into unoccupied states
Or dopant (add or remove an electron)

Metals, Insulators, Semiconductors



Insulator unoccupied energy levels are much higher in energy

Note in graphite the sp2 electrons make a widely spaced band, but the remaining 2p orbitals make overlapping bands (metallic)

Why is Silicon semiconducting while Diamond is an insulator (same structure)

A. Silicon is larger so their is less interaction between the atoms and a lower splitting between the levels

B. Silicon is smaller so their is less interaction between the atoms and a lower splitting between the levels

C. Silicon is larger so their is more interaction between the atoms and a greater splitting between the levels

How might you "add an electron" to silicon?

A. Substitute a P for a silicon atom in the solid

B. Substitute a B for a silicon atom in the solid

C. Substitue a C for a silicon atom in the solid

Group III will take an electron and "leave" a positive charge in the Si lattice
P-doping (P = positive)

Group V will "give an electron" and resulting in a negative charge in the Si lattice
N-doping (N = negative)

Last but not least

Silicone (rubber)

Back bone

...-Si-O-Si-O-Si-O-Si-O-.....

Silicon can form two more bonds
Add various organic molecules for different properties

household "caulk", silly putty, ...

Group V, VI, VII

Four very important chemicals

Phophoric Acid (H_3PO_4)
Ammonia (NH_3)
Sulfuric Acid (H_2SO_4)
Chlorine Gas (Cl_2)

THOUSANDS OF TONS UNLESS OTHERWISE NOTED	PRODUCTION										
	1991	1992	1993	1994	1995	1996 1997	1998	1999	2000	2001[a]	
Aluminum sulfate[b]	1,185	1,047	1,050	1,140	1,144	1,197	1,161	1,166	1,196	1,091	
Ammonia[c,d]	17,169	17,924	17,195	17,869	17,403	17,923	17,891	18,475	17,337	16,806	
Ammonium nitrate[e]	7,819	7,981	8,280	8,568	8,489	8,498	8,604	9,079	7,630	7,498	
Ammonium sulfate[f]	2,243	2,391	2,432	2,584	2,647	2,662	2,702	2,787	2,599	2,868	
Chlorine[g]	11,572	11,757	12,079	12,187	12,395	12,460	12,922	12,841	13,353	13,131	
Hydrochloric acid[h]	3,301	3,610	3,492	3,754	3,904	4,116	4,570	4,659	4,499	4,718	
Hydrogen, bcf, 100%[i,j]	153	162	213	331	352	386	526	552	454	481	
Nitric acid, 100%[k]	7,927	8,136	8,254	8,714	8,840	9,205	9,433	9,285	8,945	8,479	
Nitrogen gas, bcf, 100%[i,l]	770	818	796	870	844	816	809	871	858	933	
Oxygen, bcf, 100%[l]	470	515	547	605	630	682	743	676	685	661	
Phosphoric acid, P_2O_5	12,109	12,826	11,515	12,792	13,134	13,210	13,159	13,891	13,708	13,143	
Sodium chlorate	449	555	539	559	617	662	626	779	818	939	
Sodium hydroxide	11,713	12,244	12,466	12,539	11,408	11,563	10,973	13,113	13,199	11,518	
Sodium sulfate[m]	794	609	592	652	711	664	706	629	660	509	569
Sulfuric acid[n]	43,466	44,524	39,839	44,813	47,519	47,770	47,929	48,512	44,756	44,032	40,054
Titanium dioxide[o]	1,095	1,253	1,279	1,380	1,382	1,352	1,466	1,459	1,493	1,547	1,463

Sulfuric Acid

used for lots of things
Steel production
Phosphoric Acid Production
Recovery of Ammonia in Steel Production
Industrialized Nation = Nation with lots of Sulfuric Acid

Fertilizer

Ammonia (N source) +
Phosphoric Acid (P source)

Ammonia used to make Nitric Acid