

The rest of the Semester

All of Chemistry

Today

Groups IV-VIII

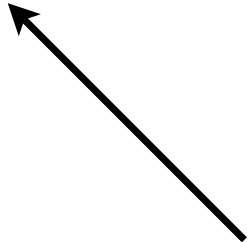
Aluminum is a very useful metal
Where does it come from?

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)

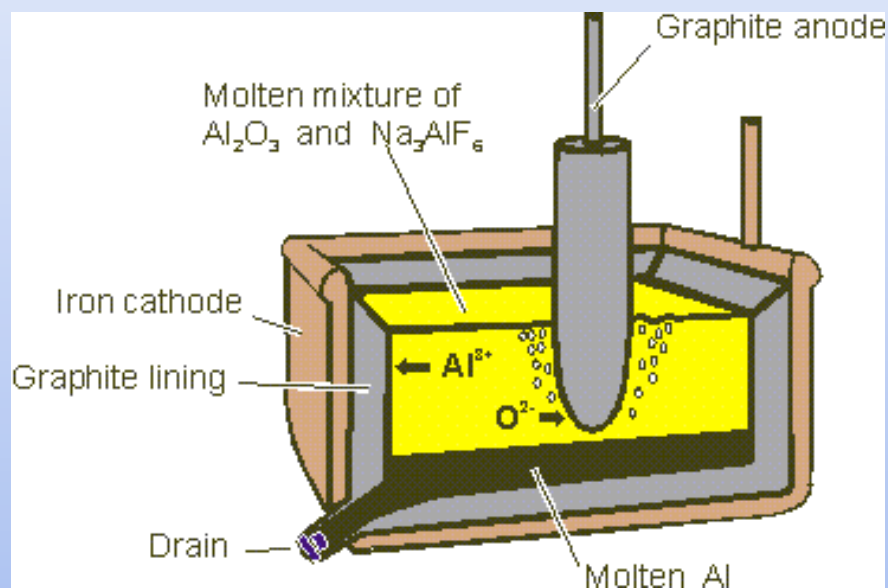
Then heat it up with Carbon to get $\text{Al} + \text{CO}_2$

The “Bayer Process” is

- A. The formation of ammonia from H_2 and N_2
 - B. The formation of nitric acid from NH_3
 - C. The purification of alumina from bauxite
 - D. Used in the production of sulfuric acid
- 

Or electrochemical reduction of alumina

Hall-Héroult process electrolytic reduction of molten Al_2O_3



Random fact of Energy

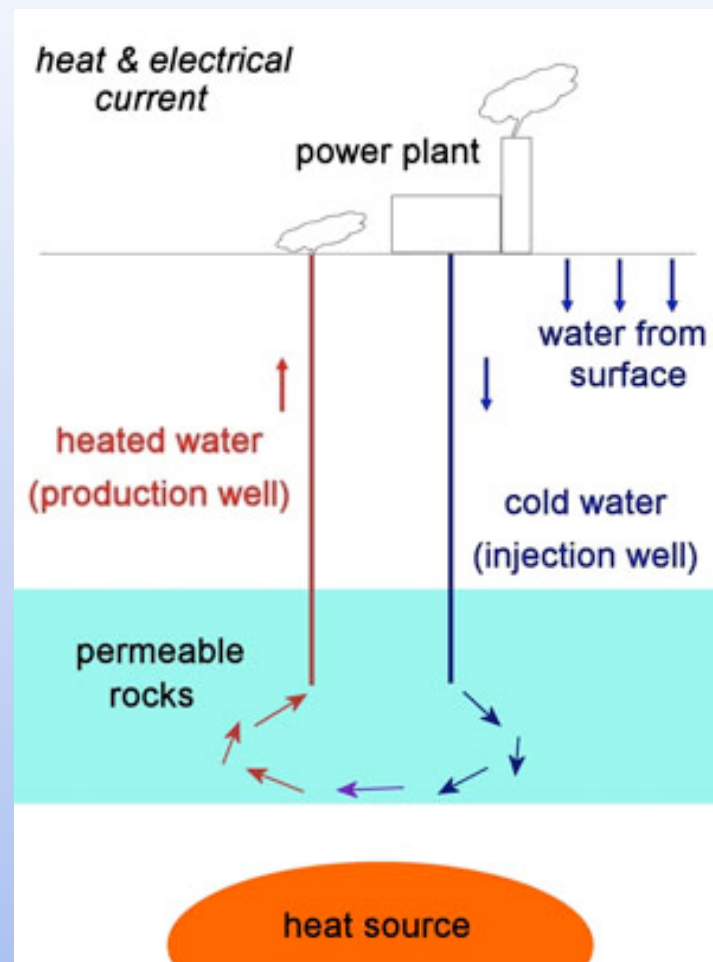
Geothermal energy in Iceland



What to do with all that energy?

Make aluminum

Iceland refines huge amounts of aluminum (exports it geothermal energy)



Boric Acid



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

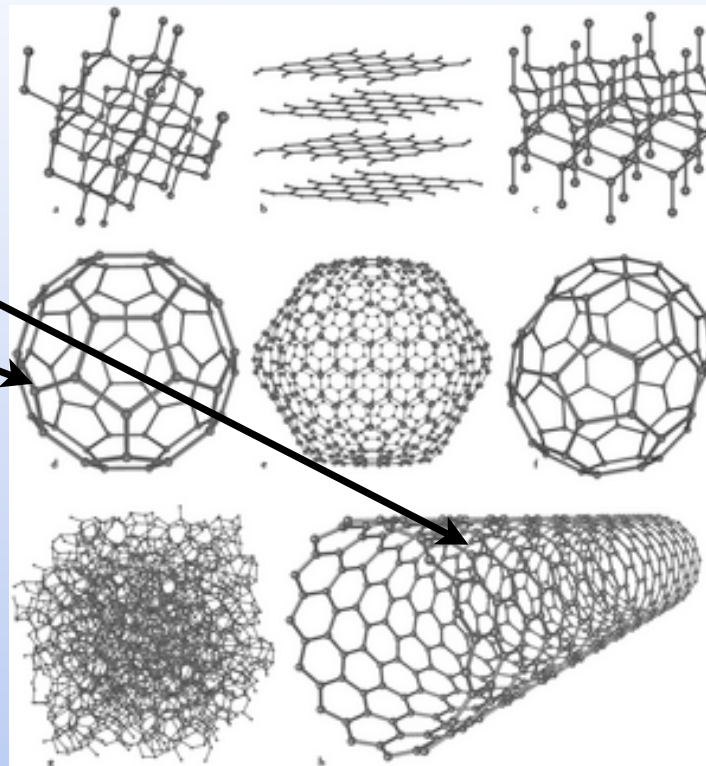


Strong Reducing Agent

BH₄⁻ ("excess electrons")

C_{60} + nanotubes

"wrapped up" graphite



Why are we excited about C₆₀ and nanotubes

Conducting

Soluble in different solvents

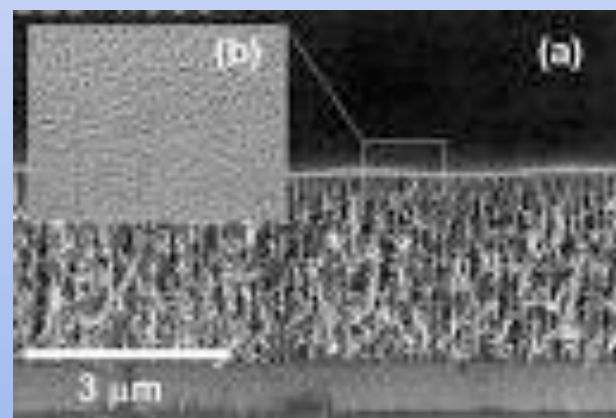
Strong materials (nanotubes)

Might be useful for electronics(nanotubes)

drug delivery (C₆₀)

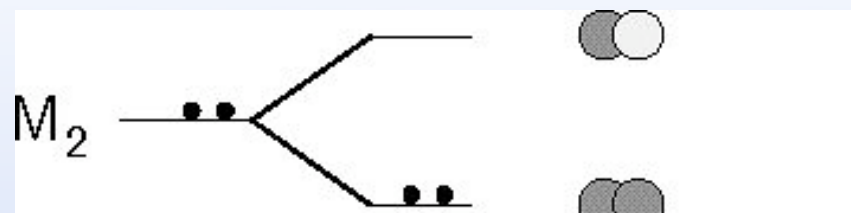
solar cells (C₆₀)

sensors (nanotubes)...



Remember Molecular Orbitals??

2
atoms



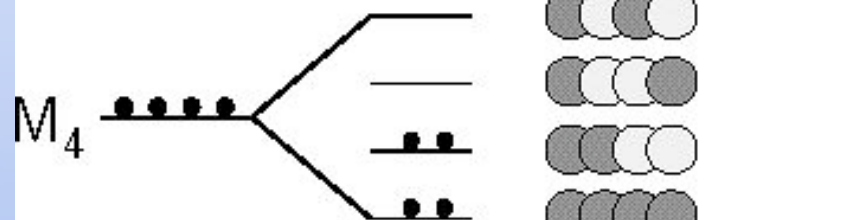
2 MO
(like H₂)

3
atoms



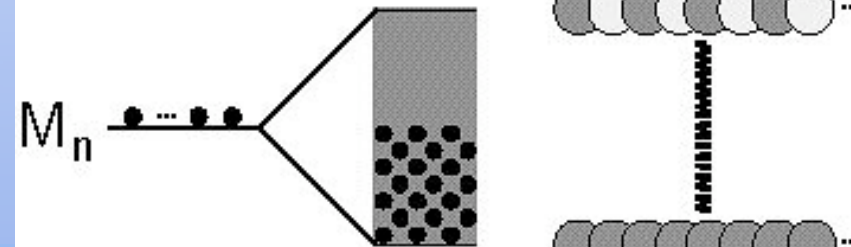
3 MOs

3
atoms



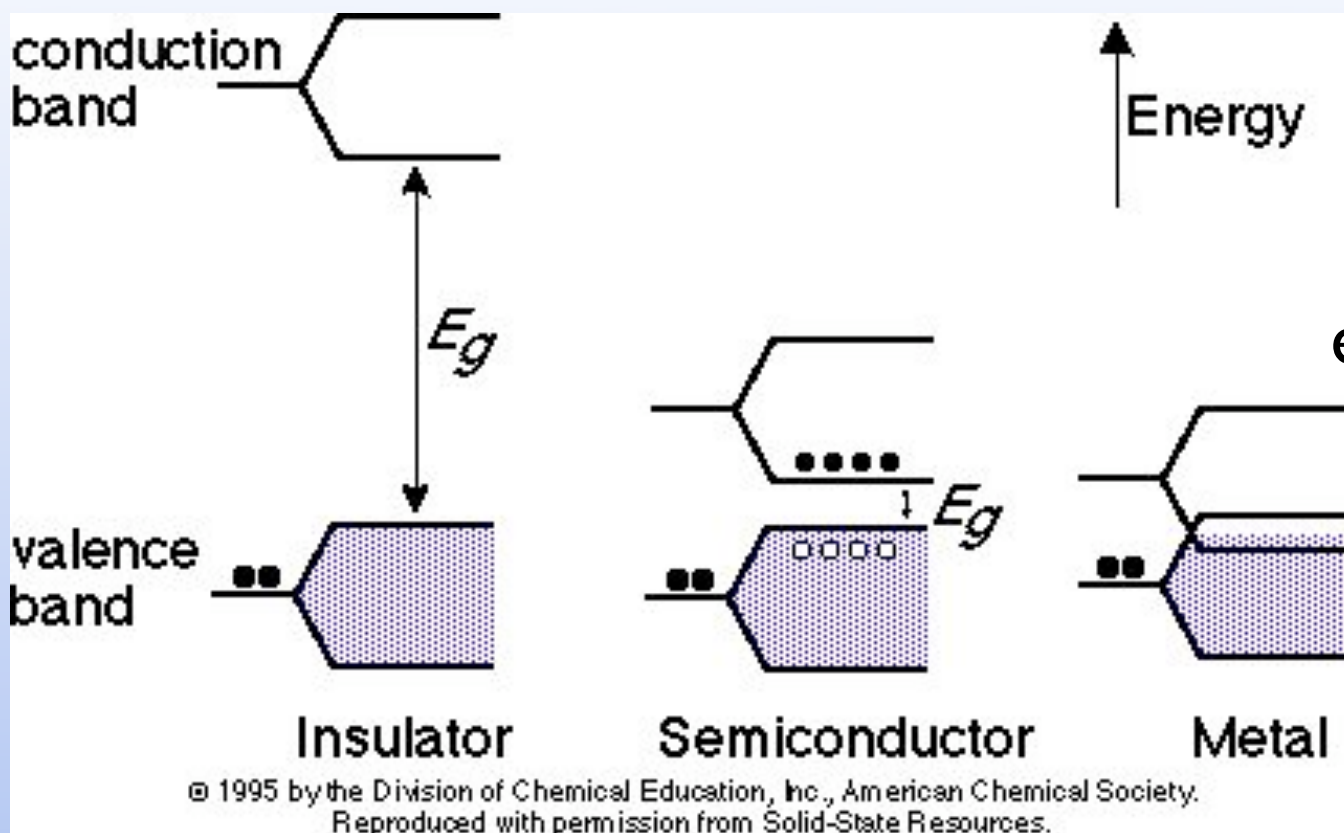
4 MOs

n
atoms



n MOs
1/2 filled

Metals, Insulators, Semiconductors



Mg
example

2P

2S

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

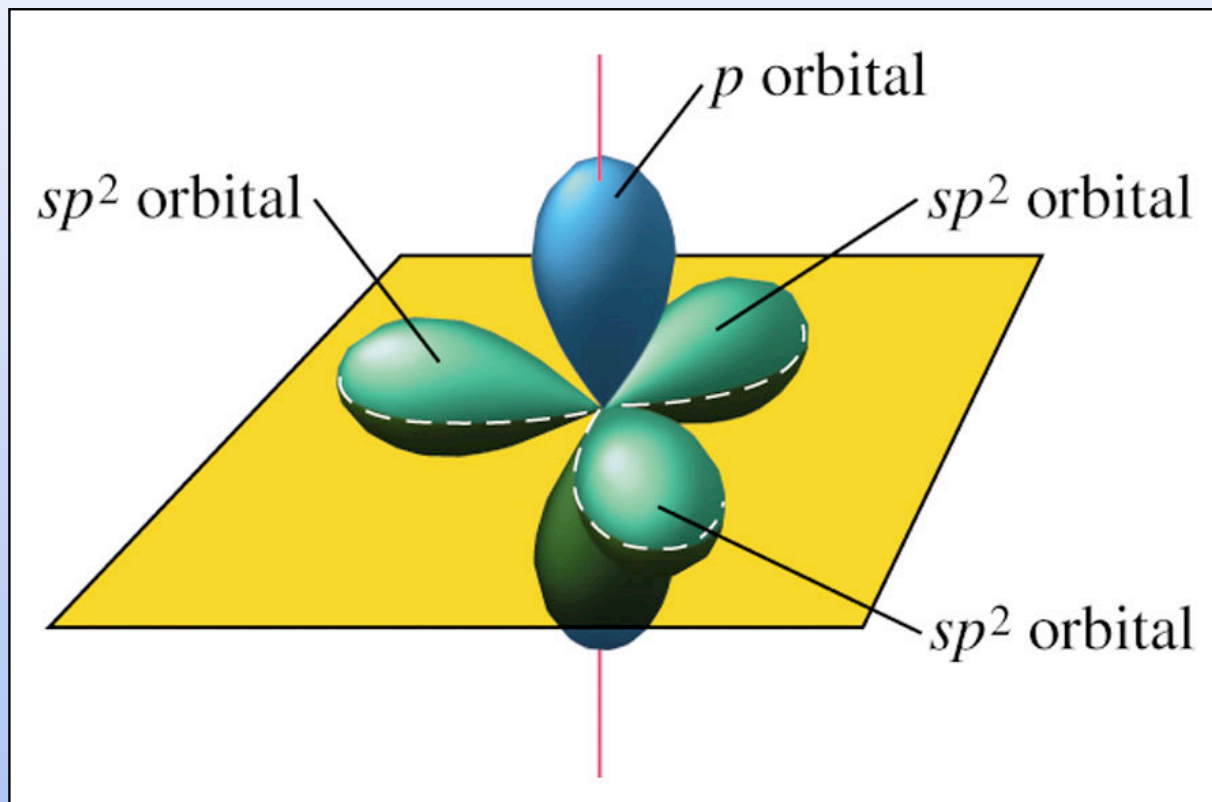
Why is Silicon semiconducting while Diamond is an insulator (same structure)

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

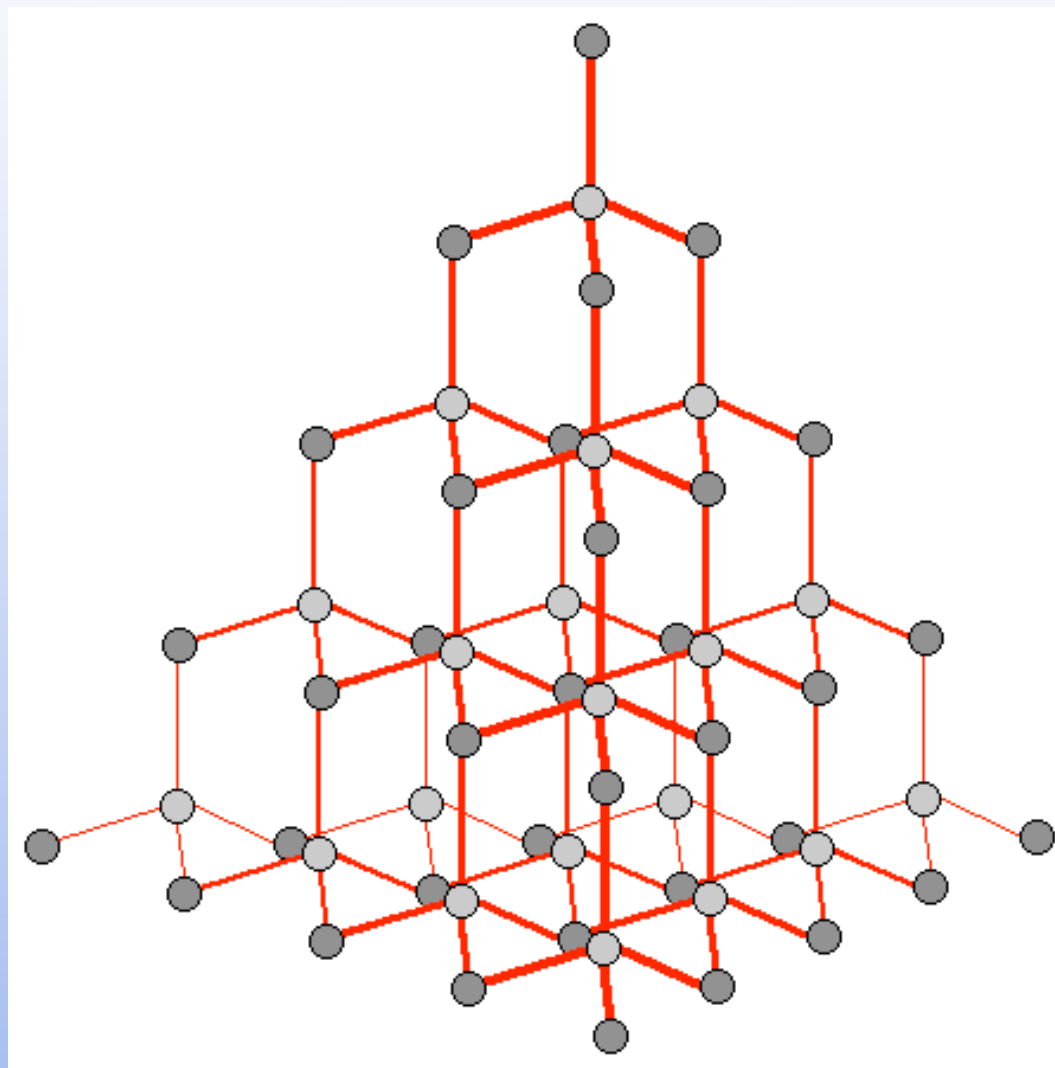
B. Silicon is smaller so there is less interaction between the atoms and a lower splitting between the levels

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

Graphite is sp^2 carbons



Diamond and
Silicon all sp^3



Carbon (diamond)

close atomic spacing leads to strong orbital overlap and large splitting between the bonding and antibonding bands

INSULATOR

Silicon

larger atomic spacing leads to weak orbital overlap and a small splitting between the bonding and antibonding bands

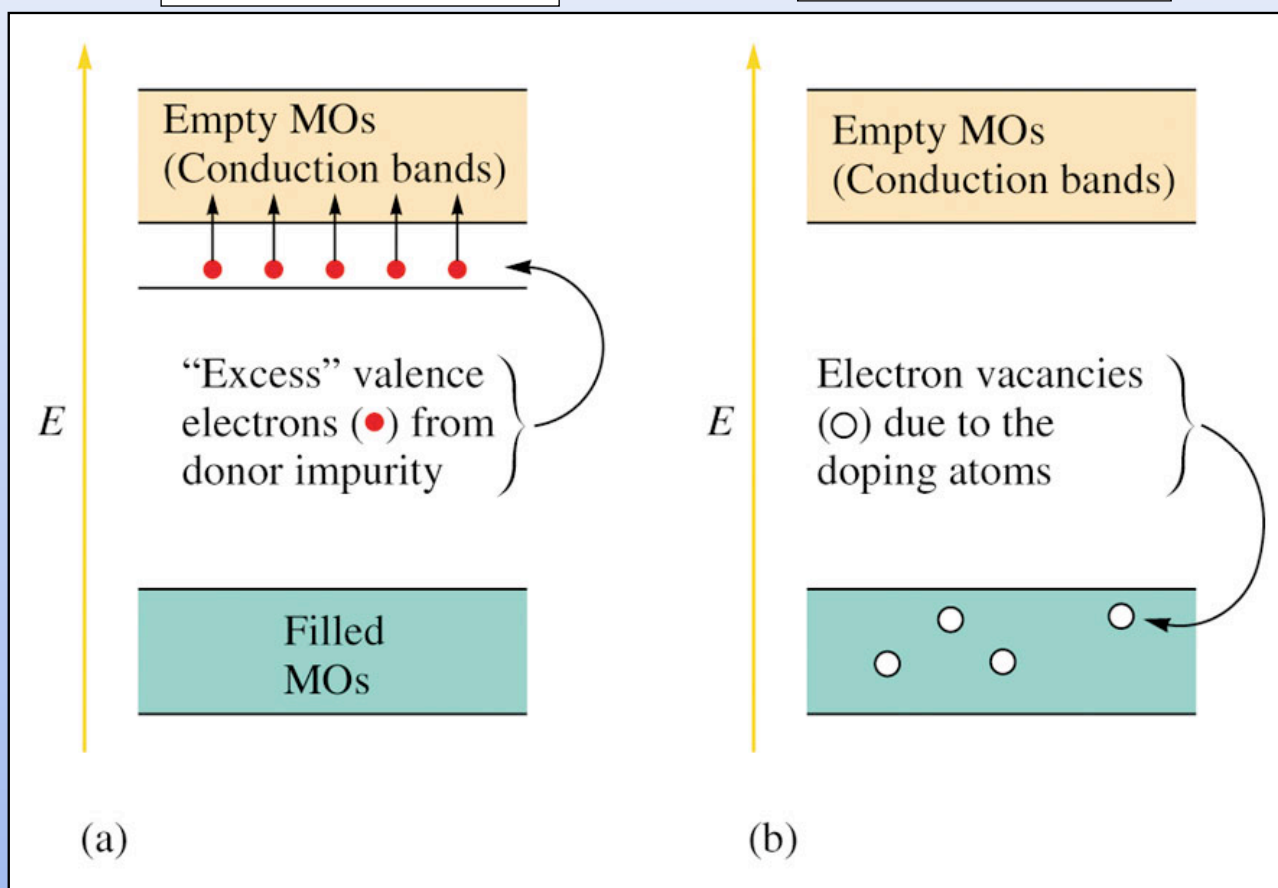
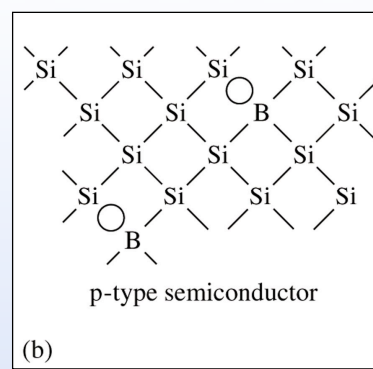
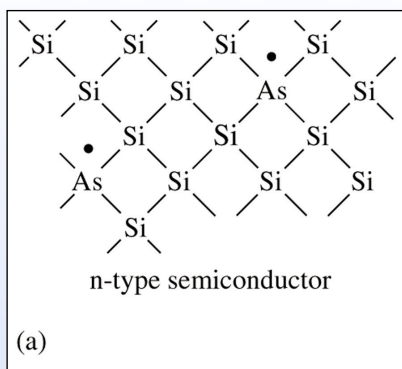
SEMI-CONDUCTOR

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. Substitute 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



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

Phosphoric Acid (H_3PO_4)

Ammonia (NH_3)

Sulfuric Acid (H_2SO_4)

Chlorine Gas (Cl_2)

4 Largest Production Chemical in the US

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	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	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	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	2,868
Chlorine ^g	11,572	11,757	12,079	12,187	12,395	12,460	12,922	12,841	13,353	13,131	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	4,718
Hydrogen, bcf, 100% ^{i,j}	153	162	213	331	352	386	526	552	454	481	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	8,479
Nitrogen gas, bcf, 100% ^{i,l}	770	818	796	870	844	816	809	871	858	933	933
Oxygen, bcf, 100% ⁱ	470	515	547	605	630	682	743	676	685	661	661
Phosphoric acid, P ₂ O ₅	12,109	12,826	11,515	12,792	13,134	13,210	13,159	13,891	13,708	13,143	13,143
Sodium chlorate	449	555	539	559	617	662	626	779	818	939	939
Sodium hydroxide	11,713	12,244	12,466	12,539	11,408	11,563	10,973	13,113	13,199	11,518	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

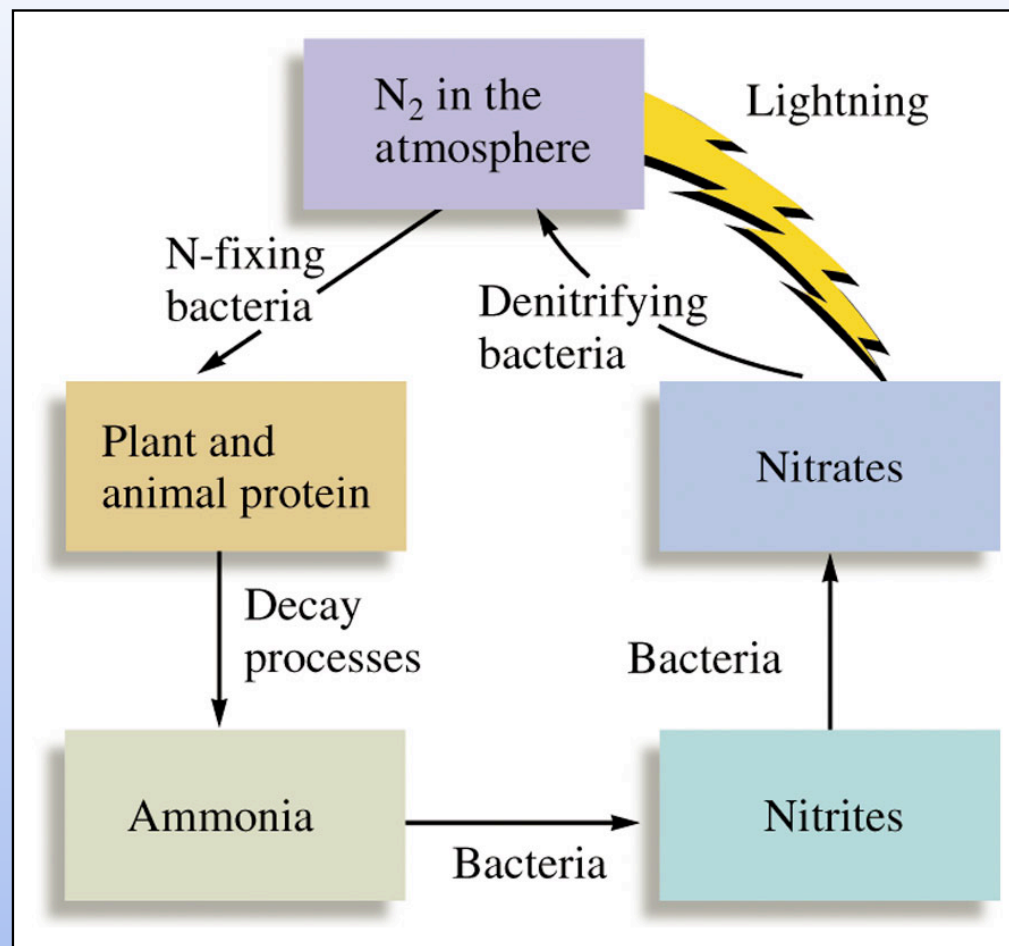
Recovery of Ammonia in Steel Production

Industrialized Nation = Nation with lots of Sulfuric Acid

Oxidizing Agent

Strong Acid

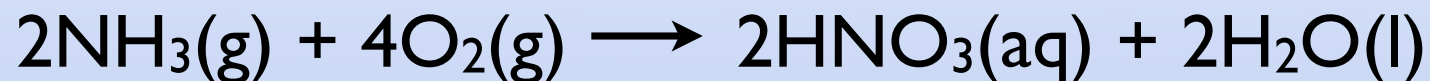
Dehydrating Agent



Fertilizer

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

Ammonia used to make Nitric Acid (**Ostwald Process**)

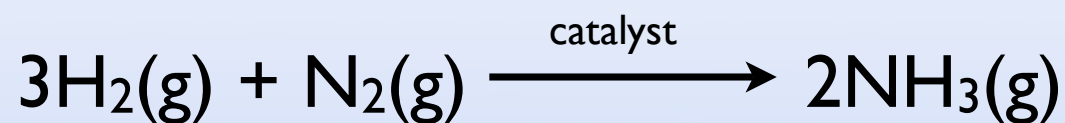


Sulfuric Acid used to make soluble phosphates



Ammonia

Production **Haber Process**



Uses

Weak base (cleaning agent)
Refrigerant (no longer used)
fertilizer
nitric acid production

the Many NO compounds

N_2O nitrous oxide (anaesthesia)

NO neurotransmitter

NO_2 brown gas (NO_x smog)

also $\text{NO}_2 + \text{OH} = \text{HNO}_3 = \text{acid rain}$

TABLE 19.1 Selected Physical Properties, Sources, and Methods of Preparation for the Group 5A Elements

Element	Electronegativity	Sources	Method of Preparation
Nitrogen	3.0	Air	Liquefaction of air
Phosphorus	2.2	Phosphate rock $[\text{Ca}_3(\text{PO}_4)_2]$, fluorapatite $[\text{Ca}_5(\text{PO}_4)_3\text{F}]$	$2\text{Ca}_3(\text{PO}_4)_2 + 6\text{SiO}_2 \longrightarrow 6\text{CaSiO}_3 + \text{P}_4\text{O}_{10}$ $\text{P}_4\text{O}_{10} + 10\text{C} \longrightarrow 4\text{P} + 10\text{CO}$
Arsenic	2.2	Arsenopyrite (Fe_3As_2 , FeS)	Heating arsenopyrite in the absence of air
Antimony	2.1	Stibnite (Sb_2S_3)	Roasting Sb_2S_3 in air to form Sb_2O_3 and then reduction with carbon
Bismuth	2.0	Bismite (Bi_2O_3), bismuth glance (Bi_2S_3)	Roasting Bi_2S_3 in air to form Bi_2O_3 and then reduction with carbon

Group VI

TABLE 19.4 Selected Physical Properties, Sources, and Methods of Preparation for the Group 6A Elements

Element	Electronegativity	Radius of X^{2-} (pm)	Source	Method of Preparation
Oxygen	3.4	140	Air	Distillation from liquid air
Sulfur	2.6	184	Sulfur deposits	Melted with hot water and pumped to the surface
Selenium	2.6	198	Impurity in sulfide ores	Reduction of H_2SeO_4 with SO_2
Tellurium	2.1	221	Nagyagite (mixed sulfide and telluride)	Reduction of ore with SO_2
Polonium	2.0	230	Pitchblende	

Important Chemistry

Nearly everything oxidizes
Lots of oxides very stable

Sulfur Chemistry

H_2SO_4 very important
see previous comments

Halogens

Need one electron to make a noble gas structure

Excellent oxidizing agents

High ionization energies

Small atoms and ions

Large electronegativities

TABLE 19.7 Some Physical Properties, Sources, and Methods of Preparation for the Group 7A Elements

Element	Color and State	Percentage of Earth's Crust	Melting Point (°C)	Boiling Point (°C)	Sources	Method of Preparation
Fluorine	Pale yellow gas	0.07	-220	-188	Fluorspar (CaF_2), cryolite (Na_3AlF_6), fluorapatite [$\text{Ca}_5(\text{PO}_4)_3\text{F}$]	Electrolysis of molten KHF_2
Chlorine	Yellow-green gas	0.14	-101	-34	Rock salt (NaCl), halite (NaCl), sylvite (KCl)	Electrolysis of aqueous NaCl
Bromine	Red-brown liquid	2.5×10^{-4}	-7.3	59	Seawater, brine wells	Oxidation of Br^- by Cl_2
Iodine	Violet-black solid	3×10^{-5}	113	184	Seaweed, brine wells	Oxidation of I^- by electrolysis or MnO_2

TABLE 19.6 Trends in Selected Physical Properties of the Group 7A Elements

Element	Electronegativity	Radius of X^- (pm)	\mathcal{E}° (V) for $X_2 + 2e \rightarrow 2X^-$	Bond Energy of X_2 (kJ/mol)
Fluorine	4.0	136	2.87	154
Chlorine	3.2	181	1.36	239
Bromine	3.0	195	1.09	193
Iodine	2.7	216	0.54	149
Astatine	2.2	—	—	—

Lot's of Chemistry

TABLE 19.11 Some Compounds of the Halogens with Nonmetals

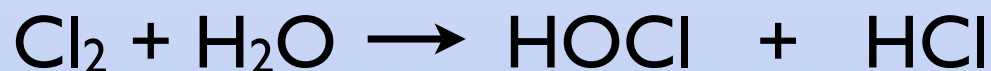
Compounds with Group 3A Nonmetals	Compounds with Group 4A Nonmetals	Compounds with Group 5A Nonmetals	Compounds with Group 6A Nonmetals	Compounds with Group 7A Nonmetals
BX_3 (X = F, Cl, Br, I) BF_4^-	CX_4 (X = F, Cl, Br, I) SiF_4 SiF_6^{2-} SiCl_4 GeF_4 GeF_6^{2-} GeCl_4	NX_3 (X = F, Cl, Br, I) N_2F_4 PX_3 (X = F, Cl, Br, I) PF_5 PCl_5 PBr_5 AsF_3 AsF_5 SbF_3 SbF_5	OF_2 O_2F_2 OCl_2 OBr_2 SF_2 SCl_2 S_2F_2 S_2Cl_2 SF_4 SCl_4 SF_6 SeF_4 SeF_6 SeCl_2 SeCl_4 SeBr_4 TeF_4 TeF_6 TeCl_4 TeBr_4 TeI_4	ICl IBr BrF BrCl ClF ClF_3 BrF_3 ICl_3 IF_3 ClF_5 BrF_5 IF_5 IF_7

Cl_2 Used for halogenating compounds

also used as a disinfectant

Very poisonous (highly reactive)

"pool chlorine" HOCl



"chlorine bleach"

NaOCl

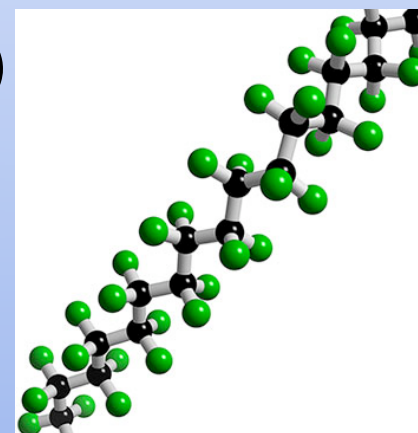
OCl^- is a strong oxidizing agent

Fluorine unusual

High charge density makes more insoluble salts

Also fluorinated compounds tend to be very stable and can have unique properties

polytetrafluoroethylene (Teflon)



True or False

Nobel Gases cannot form a compound with any other element?

A. True

B. False

Nobel Gases

Few reactions. Nearly all with Xe (highly polarizable)

