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 Al + CO_2

The "Bayer Process" is

A. The formation of ammonia from H_2 and N_2

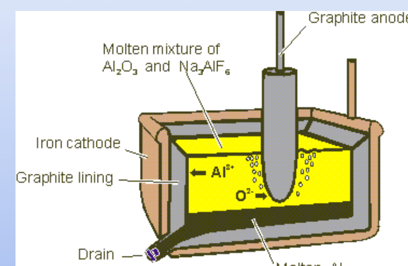
B. The formation of nitric acid from NH_3

C. The purification of alumina from bauxite

D. Used in the production of sulfuric acid

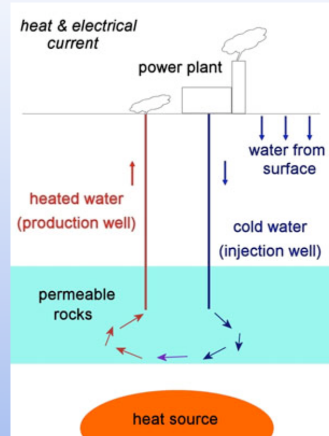
Or electrochemical reduction of alumina

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

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

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

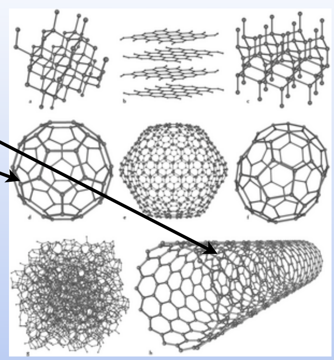
$NaBH_4$

Strong Reducing Agent

BH_4^- ("excess electrons")

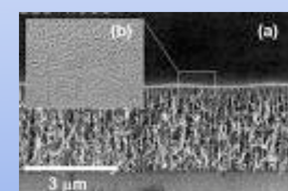
C_{60} + nanotubes

"wrapped up" graphite



Why are we excited about C_{60} and nanotubes

Conducting
Soluble in different solvents
Strong materials (nanotubes)
Might be useful for electronics(nanotubes)
drug delivery (C60)
solar cells (C60)
sensors (nanotubes)...



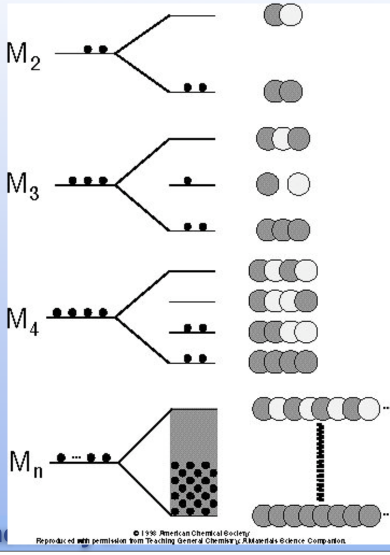
Remember Molecular Orbitals??

2 atoms — 2 MO (like H_2)

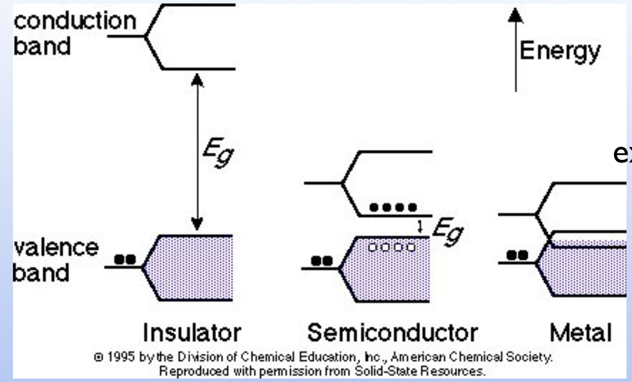
3 atoms — 3 MOs

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)

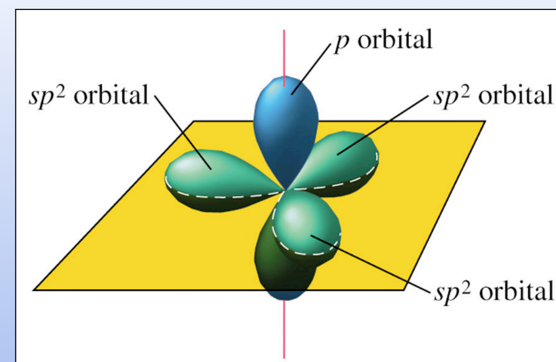
Why is Silicon semiconducting while Diamond is an insulator (same structure)

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

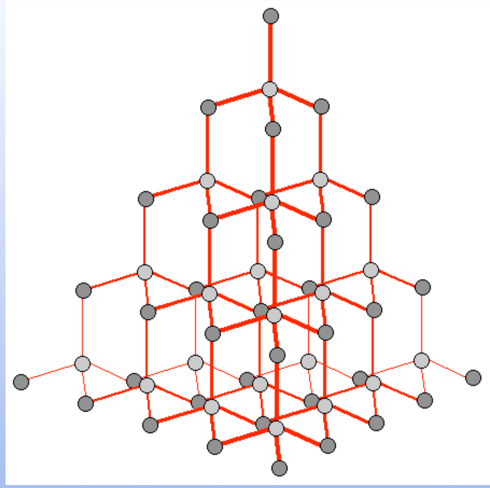
B. Silicon is smaller so their is less interaction between the atoms and a lower splitting between the levels

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

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

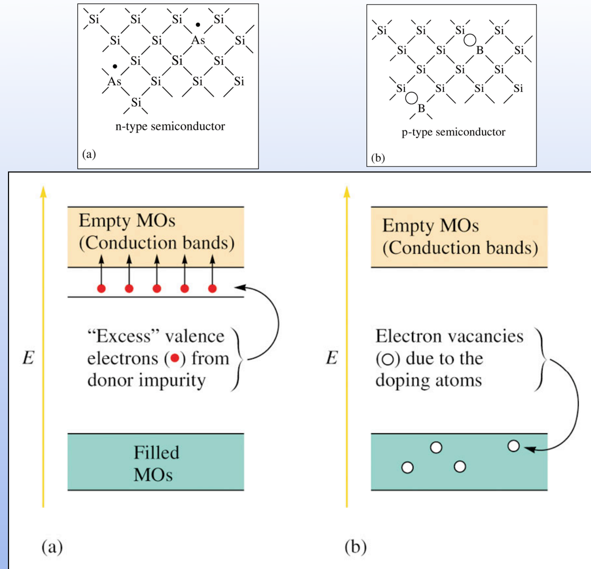
C. Substitue a C for a silicon atom in the solid

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)

4 Largest Production Chemical in the US

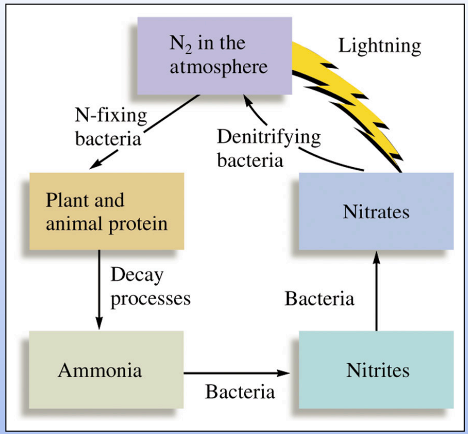
PRODUCTION

THOUSANDS OF TONS UNLESS OTHERWISE NOTED	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

Oxidizing Agent
Strong Acid
Dehydrating Agent



Fertilizer

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

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

$$2NH_3(g) + 4O_2(g) \longrightarrow 2HNO_3(aq) + 2H_2O(l)$$
$$HNO_3(aq) + NH_3(g) \longrightarrow NH_4NO_3(s)$$

Sulfuric Acid used to make soluble phosphates

$$Ca_3(PO_4)_2 + 2H_2SO_4 \longrightarrow 2CaSO_4 + Ca(H_2PO_4)_2$$

Ammonia

Production **Haber Process**

$$3H_2(g) + N_2(g) \xrightarrow{\text{catalyst}} 2NH_3(g)$$

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 NO_2 + OH = HNO_3 = 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 [$Ca_3(PO_4)_2$], fluorapatite [$Ca_5(PO_4)_3F$]	$2Ca_3(PO_4)_2 + 6SiO_2 \longrightarrow 6CaSiO_3 + P_4O_{10}$ $P_4O_{10} + 10C \longrightarrow 4P + 10CO$
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

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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	

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Important Chemistry

Nearly everything oxidizes
Lots of oxides very stable

Sulfur Chemistry

H_2SO_4 very important
see previous comments

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Halogens

Need one electron to make a nobel 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	Fluorospar (CaF_2), cryolite (Na_3AlF_6), fluorapatite [$Ca_5(PO_4)_3F$]	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)	$\mathscr{E}°$ (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)	CX_4 (X = F, Cl, Br, I)	NX_3 (X = F, Cl, Br, I)	OF_2	ICl
BF_4^-		N_2F_4	O_2F_2	IBr
	SiF_4		OCl_2	BrF
	SiF_6^{2-}	PX_3 (X = F, Cl, Br, I)	OBr_2	BrCl
	$SiCl_4$	PF_5		ClF
		PCl_5	SF_2	
	GeF_4	PBr_5	SCl_2	ClF_3
	GeF_6^{2-}		S_2F_2	BrF_3
	$GeCl_4$	AsF_3	S_2Cl_2	ICl_3
		AsF_5	SF_4	IF_3
			SCl_4	
		SbF_3	SF_6	ClF_5
		SbF_5		BrF_5
			SeF_4	IF_5
			SeF_6	
			$SeCl_2$	IF_7
			$SeCl_4$	
			$SeBr_4$	
			TeF_4	
			TeF_6	
			$TeCl_4$	
			$TeBr_4$	
			TeI_4	

Cl_2 Used for halogenating compounds

also used as a disinfectant
Very poisonous (highly reactive)

"pool chlorine" HOCl

$$Cl_2 + H_2O \longrightarrow HOCl + HCl$$

"chlorine bleach"

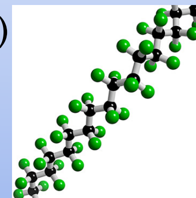
NaOCl
OCl^- is a strong oxidizing agent

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)