The Chemistry of the Main Group Elements

Chapter 18

Chemistry 223
Professor Michael Russell

Last update: 4/29/24

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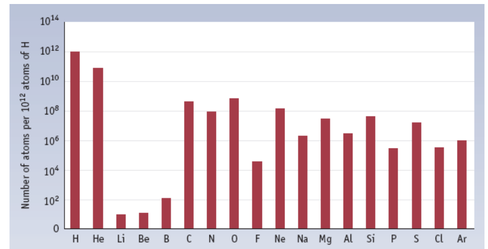
Abundance of Main Group Elements



- Note low abundance of Li, Be, and B
- See also alternation of abundance with atomic number.
- Even atomic number = more abundant

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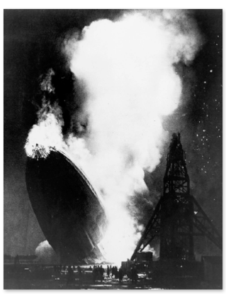
HYDROGEN CHEMISTRY



Hindenburg: A German dirigible filed with H_2 gas. Hindenburg crashed in New Jersey after a trans-Atlantic flight in May, 1937. Of 62 people, about half escaped uninjured.

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HYDROGEN CHEMISTRY

- **A modern use of H_2 in the Space Shuttle.**
- **The rocket engine in the Shuttle itself is fueled by H_2 + O_2.**

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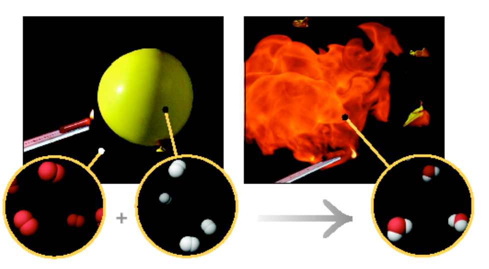
Hydrogen and Oxygen



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Hydrogen Isotopes

^1H	**1.007825 amu**	**protium**
^2H = D	**2.014102**	**deuterium**
^3H = T	**3.016049**	**tritium**

Half-life of tritium = 12.35 years

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Tritium

The tritium content of ground water is used to discover the source of the water, for example, in municipal water or the source of the steam from a volcano.

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Water Gas

- Also called "synthesis gas."
- Treat coal with steam
- $C + H_2O \text{ --> } H_2 + CO$
- Synthesis gas is the mixture of H_2 and CO.
- Much of the organic chemicals industry is changing to synthesis gas

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Catalytic Steam Hydrocarbon Reforming

Most H_2 is now produced by the steam reforming process using methane.

$$C_3H_8 + 3\ H_2O \rightleftharpoons 3\ CO + 7\ H_2$$

Done at 900 ˚C over a catalyst

Water gas shift reaction produces additional H_2 from CO

$$CO + H_2O \rightarrow CO_2 + H_2$$

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Electrolysis of Water

$H_2O \rightarrow H_2 + 1/2\ O_2$

Not widely used —

a) expensive

b) engineering problems

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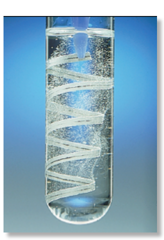
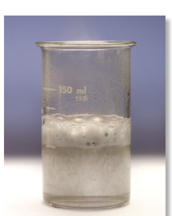
Lab Prep of H_2



Metal + Acid



Al + NaOH

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Reactions of H_2

- Virtually every element (except Group 8) will form compounds with H.
- See reaction with Br_2 to give HBr.

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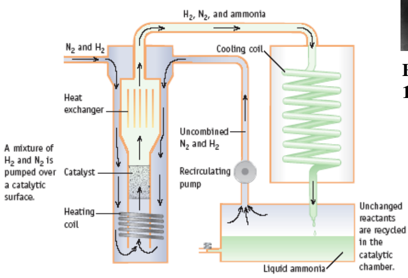
Haber Process

$N_2 + 3\ H_2 \rightarrow 2\ NH_3$



Fritz Haber
1868-1934

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Fuel Cells: H_2 as a Fuel

Fuel cell - reactants are supplied continuously from an external source. Cars can use electricity generated by H_2/O_2 fuel cells.

H_2 carried in tanks or generated from hydrocarbons.

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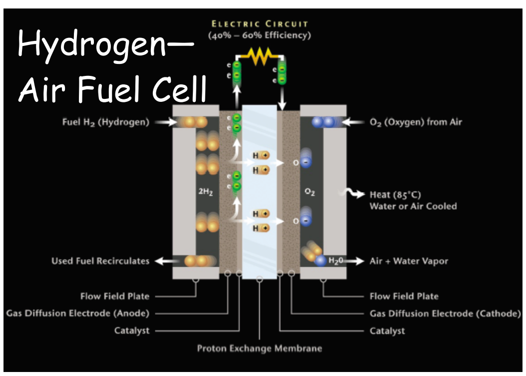

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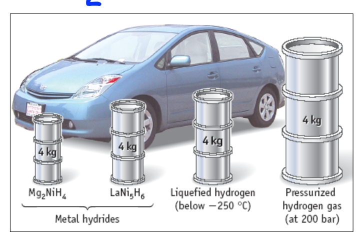
H_2 as a Fuel



Comparison of the volumes of substances required to store 4 kg of hydrogen relative to car size.

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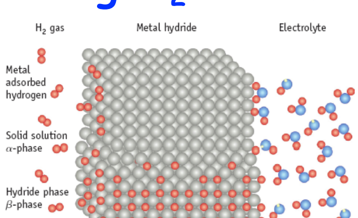
Storing H_2 as a Fuel



One way to store H_2 is to adsorb the gas onto a metal or metal alloy.

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Sodium and Potassium

The important characteristic of Group 1A elements is their vigorous reaction with water.

K and water

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Sodium and Potassium

All of the Group 1A metals are relatively soft and can be cut with a knife.

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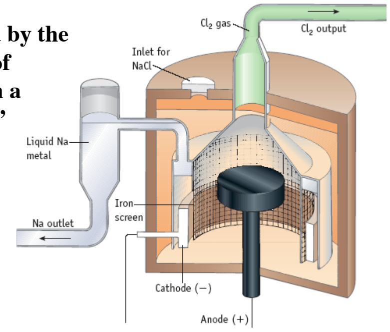
Sodium Preparation

Na is prepared by the electrolysis of molten Na in a "Downs cell"



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Reactions with O_2

- **2 Na(s) + O_2(g) → Na_2O_2 (s)**
  - **Sodium peroxide**
- **K(s) + O_2(g) → KO_2(s)**
  - **Potassium superoxide**
- **KO_2 used in breathing apparatus**
- **4 KO_2(g) + 2 CO_2 (g) → 2 K_2CO_3(s) + 3 O_2(g)**

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Na-Containing Compounds

Na_2CO_3: soda ash or washing soda

Used as an industrial base, in making soap, and in making glass.

Was made by "Solvay process" but now mined as trona: Na_2CO_3•$NaHCO_3$•$2H_2O$

Trona mine in CA

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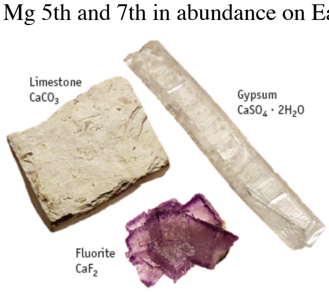
Alkaline Earth Elements

Ca and Mg 5th and 7th in abundance on Earth.



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Alkaline Earth Elements
Be, Ca, Mg, Sr, Ba

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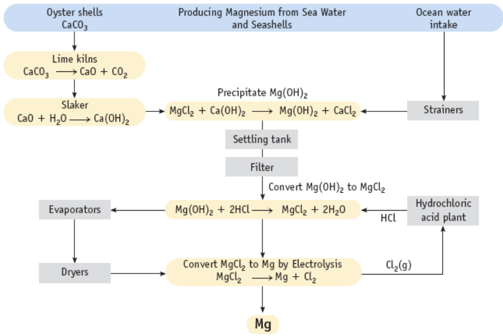
Magnesium from the Sea



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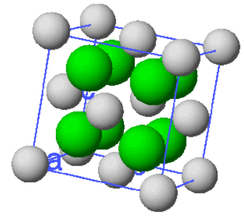
Calcium Minerals: CaF_2

CaF_2 (fluorite) used in making steel. Removes impurities from molten iron.

CaF_2 is a source of HF.

$$CaF_2 + H_2SO_4 \rightarrow 2\,HF + CaSO_4$$



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Calcium Minerals: $CaCO_3$

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

Limestone is mostly $CaCO_3$.

Heating $CaCO_3$ gives lime, CaO

$CaO + H_2O \rightarrow Ca(OH)_2$, slaked lime

$Ca(OH)_2$ is the most used industrial base.

$CaCO_3$ used in cement, fertilizer, and in making steel.

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Calcium Minerals: $CaCO_3$

- **Mortar -- a mixture of lime, sand, and water -- has been used for hundreds of years.**
- **Reactions involved:**
  - $CaO + H_2O \rightarrow Ca(OH)_2$, slaked lime
  - $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$
- **Sand grains bound together by $CaCO_3$**

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Calcium Minerals: $CaCO_3$

Hard water contains dissolved Ca^{2+} and Mg^{2+}

$$CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca^{2+} + 2\,HCO_3^-$$

If CO_2 is removed by boiling, $CaCO_3$ precipitates.

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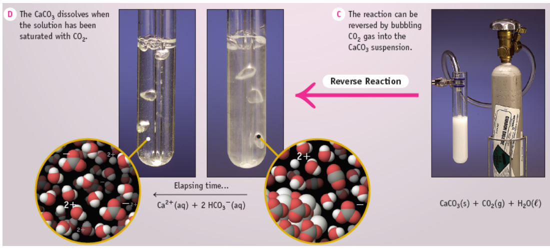
Calcium Minerals: $CaCO_3$

$CaCO_3$ dissolved in presence of CO_2



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Removing Ca^{2+} an Mg^{2+} by Ion Exchange

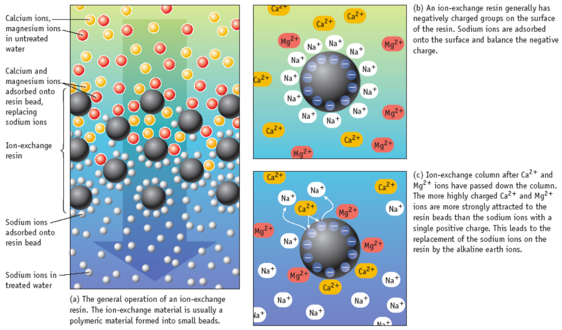

Figure 6 Water softening by ion exchange in the home.

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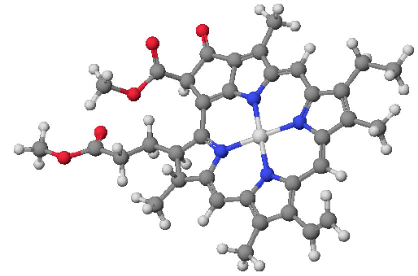
Chlorophyll, a molecule with Mg^{2+}



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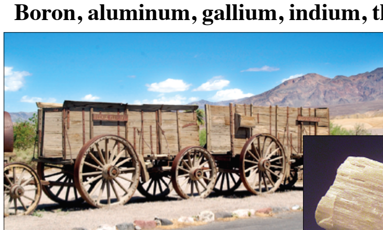
Group 3A Chemistry

Boron, aluminum, gallium, indium, thallium



"20 mule team borax" wagon in Death Valley and a borax sample

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Gems & Minerals

Sapphire: Al_2O_3 with Fe^{3+} or Ti^{3+} impurity gives blue whereas V^{3+} gives violet.

Ruby: Al_2O_3 with Cr^{3+} impurity

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Group 3A—General Aspects

All have ns^2np^1

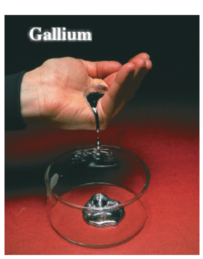
Maximum oxidation number is +3

- **But Tl^+ exists and is poisonous**

All are metals except B

Abundances vary greatly

B	10 ppm
Al	82,000 ppm
Ga	18 ppm
In/Tl	< 1



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Group 3A—General Aspects

Diagonal relation

Li Be B
  Mg Al Si

Al and Be are similar in that both form amphoteric hydroxides and inert oxides.

B and Si form acidic hydroxides [$B(OH)_3$ and $Si(OH)_4$] and both form volatile hydrides (B_2H_6 and SiH_4)

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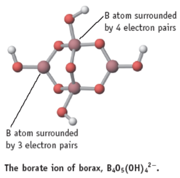
Sources of the Elements



Boron—borax, $Na_2B_4O_7$•$10H_2O$

Has been used for centuries to braze metals (and mummify the dead).

Production of ca. 2.6 x 10^6 tons annually

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Boron Recovery

- **$B_2O_3 + 3\,Mg \rightarrow 2\,B + 3\,MgO$**
  - **Impure B produced this way**
- **$2\,BBr_3 + 3\,H_2 \rightarrow 2\,B + 6\,HBr$**
  - **BBr_3 vapor + H_2 over hot Ta wire gives B whiskers.**

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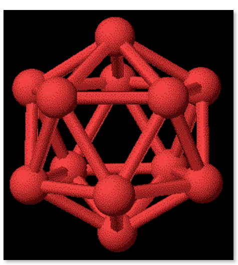
Elemental Boron

Pure boron consists of interconnected icosahedra



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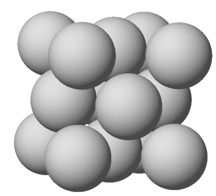
Aluminum

95% of the 90 million tons of bauxite mined is used in the Bayer process to give Al_2O_3 (corundum)

90% of the oxide is converted to Al metal



Unit cell of Al

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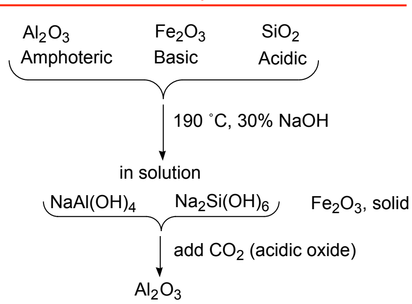
Aluminum—Bayer Process



$$H_2O + CO_2 + 2\,NaAl(OH)_4 \longrightarrow Na_2CO_3 + Al_2O_3 + 5\,H_2O$$

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Aluminum Metal

- **Al obtained by electrolysis of Al_2O_3/Na_2AlF_6 mixture**
  - **Na_2AlF_6 is CRYOLITE**
- **Called the Hall-Heroult process**
- **Charles M. Hall (1863-1914)**
- **http://www.oberlin.edu/chem/history/cmh/cmharticle.html**

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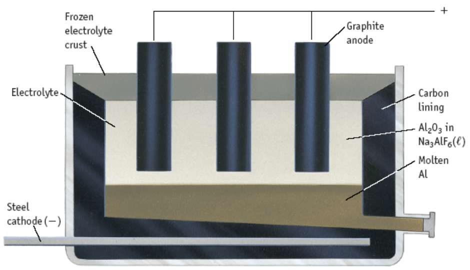
Al Production by Electrolysis



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Aluminum Metal

- Main use is as structural material
  - Strength, low density, corrosion resistance
- Strength improved by **ALLOYING**
  - Mn: cooking utensils, furniture, roofing
  - Cu: truck and plane parts

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Aluminum Metal

Corrosion resistance due to aluminum oxide coating.

$$4\,Al(s) + 3\,O_2(g) \rightarrow 2\,Al_2O_3(s)$$

$$\Delta H^\circ = -3351\ kJ$$

This illustrates the great reducing power of aluminum.

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Corrosion of Aluminum

Al is oxidized by Cu^{2+} in a NaCl solution.

Al metal can be oxidized if the protective Al_2O_3 coating is breached.

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Aluminum Metal

$4\,Al(s) + 3\,O_2(g) \rightarrow 2\,Al_2O_3(s)$

$\Delta H^\circ = -3351\ kJ$

Solid booster rocket fuel for Space Shuttle uses Al as reducing agent and NH_4ClO_4 as oxidizer.

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Group 3A Hydrides—Boranes

Boranes = B_xH_y

Began in 1912 with Alfred Stock

See Stock's book "Hydrides of Boron and Silicon"

Good account of Hg poisoning from Hg fumes in the lab

Alfred Stock, 1876-1946

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Mercury Poisoning

"Among the unpleasant accidents must be reckoned the fact that, through years of working with mercury apparatus, my collaborators contracted chronic mercurial poisoning. …[It] reveals itself as an affection of the nerves, causing headaches, numbness, mental lassitude, depression, and loss of memory; such are very disturbing to one engaged in an intellectual occupation."

Alfred Stock, "Hydrides of Boron and Silicon", 1933

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Diborane, B_2H_6

- $2\ NaBH_4 + 2\ H_3PO_4 \rightarrow$
  $B_2H_6 + 2\ NaH_2PO_4 + 2\ H_2$
- $2\ NaBH_4 + I_2$ (in ether) $\rightarrow$
  $B_2H_6 + 2\ NaI + H_2$
- Mp = -165.5 ˚C and Bp = -87.55 ˚C
- $\Delta H^\circ_f = +35.6$ kJ/mol
- $B_2H_6 + 3\ O_2$ --> $B_2O_3 + 3\ H_2O + 2165$ kJ
- Higher $\Delta H_{combustion}$ than any other fuel (per gram) than H_2

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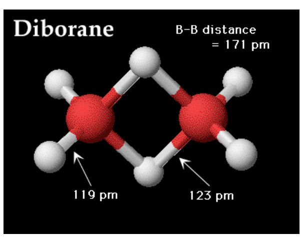
Diborane Structure



External H-B-H angle = 121.8˚
Internal H-B-H angle = 96.5˚

An "electron-deficient" or "twisted metal" compound

12 valence e- but 8 "apparent" bonds.

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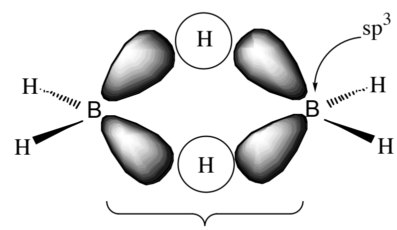
3-Center, 2-Electron Bond



2e- spread over 3 orbitals

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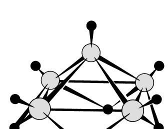
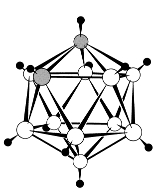
HIGHER BORANES

Boranes with more than 2 B atoms can be like spider webs or closed cages.



1 B_5H_9 ○ = B ● = H



$B_{10}C_2H_{12}$ ○ = B ● = C ● = H

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Commercial Uses of BH Compounds

- Important compound = $NaBH_4$
- Used to bleach wood pulp
- Electrode-less plating of metals onto plastics
  - $BH_4^- + 8\ OH^- \rightarrow H_2BO_3^- + 5\ H_2O + 8\ e^-$
  - $E^\circ = +1.24$ V
- Used as reducing agent in organic chemistry

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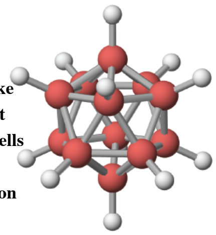
BNCT

Boron Neutron Capture Therapy

- ^{10}B isotope (not ^{11}B) has the ability to capture slow neutrons
- In BNCT, tumor cells preferentially take up a boron compound, and subsequent irradiation by slow neutrons kills the cells via the energetic ^{10}B --> ^{7}Li neutron capture reaction (that produces a photon and an alpha particle)
- $^{10}B + {}^{1}n \rightarrow {}^{7}Li + {}^{4}He$ + photon



One of the compounds used in BNCT is $Na_2[B_{12}H_{12}]$. The structure of the $B_{12}H_{12}^{2-}$ anion is a regular polyhedron with 20 sides, called an icosahedron.

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Group 3A Hydroxides

- $B(OH)_3$ is an acid
- $B(OH)_3 + H_2O \rightarrow B(OH)_4^- + H^+$
  - $K_a = 7.3 \times 10^{-10}$
- $Al(OH)_3$ and $Ga(OH)_3$ are **amphoteric**
- $Al^{3+}(aq)$ is a weak acid
  - $Al(H_2O)_6^{3+} \rightarrow [Al(H_2O)_5(OH)]^{2+} + H^+$
  - $K_a = 7.9 \times 10^{-6}$

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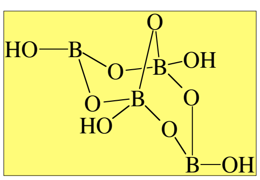
Boron-Oxygen Compounds

Boron is never found in nature bonded to any other element than O.

Borax, $Na_2B_4O_7 \cdot 10H_2O$



$Na_2[B_4O_5(OH)_4] \cdot H_2O$

- Note 6-membered rings
- All borates are fragments of of this structure.

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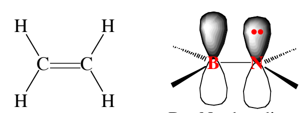
Boron-Nitrogen Compounds



B—N π bonding

Element	B	C	N
Valence e-	3	4	5
Electroneg.	2.0	2.5	3.0
Radius	88	77	70 pm

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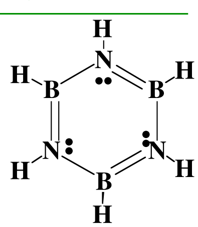
Borazine—Analog of Benzene

$B_2H_6 + NH_3$ ⟶

$BCl_3 + NH_4Cl$ ⟶ ($NaBH_4$)



Borazine: Mol. wt. = 80.5
Mp = -57 ˚C; Bp = 55 ˚C
B—N = 144 pm

Benzene: Mol. wt. = 78.1
Mp = 6 ˚C; Bp = 80 ˚C
C—C = 142 pm

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Boron Halides

	Mp, ˚C	Bp, ˚C
BF_3	-127.1	-99.9
BCl_3	-107	12.5
BBr_3	-46	91.3
BI_3	49.9	210

All are volatile
Monomeric - contrast with BX_3 and Al_2X_6

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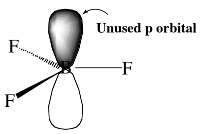
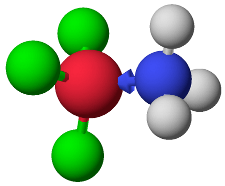
All Form Lewis Acid-Base Complexes





Order of Lewis acidity: $BF_3 < BCl_3 < BBr_3 < BI_3$

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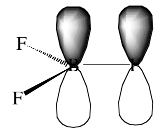
All Form Lewis Acid-Base Complexes

Order of Lewis acidity: $BF_3 < BCl_3 < BBr_3 < BI_3$

Order of acidity is inverse of expectation due to a small degree of B—X π bonding



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Aluminum Halides

Compound	AlF_3	$AlCl_3$	$AlBr_3$	AlI_3
Mp, ˚C	1290	192.4	97.8	189.4
Subl. Temp.	1272	180	256	382

Synthesis

$Al_2O_3 + 6\ HF \rightarrow 2\ AlF_3 + 3\ H_2O$

$2\ Al + 3\ X_2 \rightarrow 2\ AlX_3$ (for X = Cl, Br, I)

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Synthesis of Al_2Br_6

$2\ Al + 3\ Br_2 \rightarrow Al_2Br_6$

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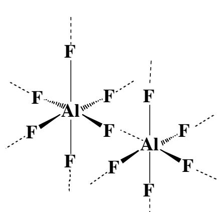
Aluminum Fluoride



- AlF_3 is a lattice of Al^{3+} and F^- ions
- Octahedral Al^{3+}
- F^- bridges
- Found in cryolite, Na_2AlF_6

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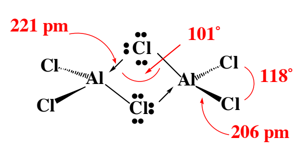
AlX_3 where X = Cl, Br, I

Solid $AlCl_3$ is a layer lattice of 6-coordinate Al^{3+} ions.

At mp the solid volume increases 85% and electrical conductivity decreases



In liquid and gas phase $AlCl_3$ is dimer. $AlBr_3$ and AlI_3 are dimers in all phases.

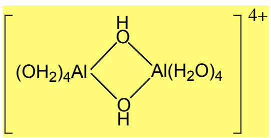
MAR

Aluminum in Water Purification

Aluminum sulfate is the most important Al compound after $Al(OH)_3$ and Al_2O_3.

Used in paper industry and as a flocculent in water purification.

As pH increases, associated species form. Their large charge nucleates fine, suspended dirt particles.



MAR

Aluminum Hydroxide & Oxide

Many different forms

α–Al_2O_3	Corundum
α -AlO(OH)	Diaspore
α -$Al(OH)_3$	Bayerite
γ -Al_2O_3	
γ -AlO(OH)	Boehmite
γ -$Al(OH)_3$	Gibbsite

MAR

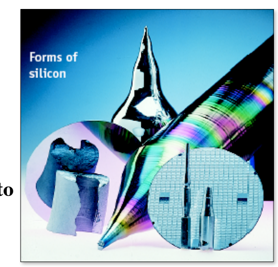
Corundum: α-Al_2O_3

- Very hard—so used as an abrasive in sandpaper and toothpaste
- Emery = Al_2O_3 + Fe_2O_3 / SiO_2
- Chemically inert and insulating
  - Used in refractories and ceramics

MAR

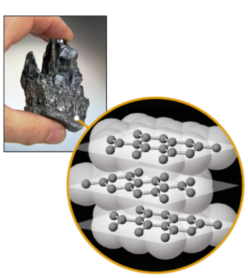
Group 4A

- C, Si, Ge, Sn, Pb
- General features
  - Moving away from metallic character
  - ns^2np^2 configurations
  - "inert pair" effect leads to Ge^{2+}, Sn^{2+}, Pb^{2+}



MAR

Carbon Allotropes: Graphite



Layers of 6-member carbon rings.

sp^2 C atoms

Extended π bonding throughout the layers.

MAR

Carbon Allotropes: Diamond

6-member carbon rings.

Tetrahedral sp^3 C atoms

Bonding extends throughout the crystal.

MAR

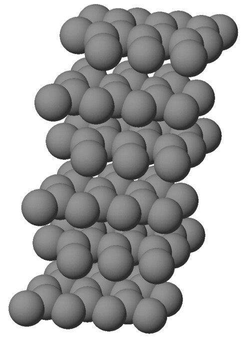
Properties of Graphite and Diamond

Allotrope	Graphite	Diamond
Density	2.266	3.514 g/cm³
Hardness	<1	10 Mohs
ΔH°_{f}	0	+1.90 kJ/mol

Graphite has high electrical conductivity

Diamond—has highest thermal conductivity of any known material

MAR



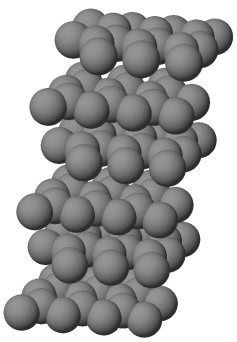
Graphite

Uses of natural graphite

- Steelmaking
- Refractories, crucibles
- Lubricants
- Brake linings
- Pencil lead

About 75000 tons/year

MAR



Graphite

Artificial graphite

$SiO_2 + C \rightarrow (SiC) + CO_2$

SiC (2500 ˚C) → Si + C

Used for electrodes, crucibles, motor brushes, fibers

About 350,000 tons/year

MAR

Coke & Carbon Black

- **Heat coal in absence of air → coke**
  - **About 370 x 10^6 tons/year**
  - **Steelmaking**
- **Carbon black—incomplete combustion of hydrocarbons**
  - **> 10 million tons/day!**
  - **93% in tires (3 kg in car tire and 9 kg in truck tire)**
  - **~3% in printing ink**

MAR

Activated Charcoal

Made by burning carbon in high oxygen atmosphere.

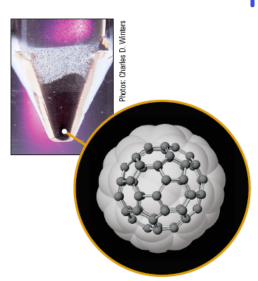
Leaves small holes with diameters of 1-8 nanometers

Surface area of 1 g of charcoal can be about 1000 m².

Used in water and air filters.

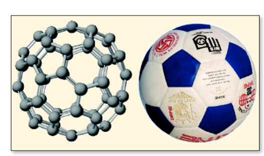
MAR

Carbon Allotropes: Fullerenes



5- and 6-member carbon rings.

C atoms are bound into a sphere with 60 C atoms.



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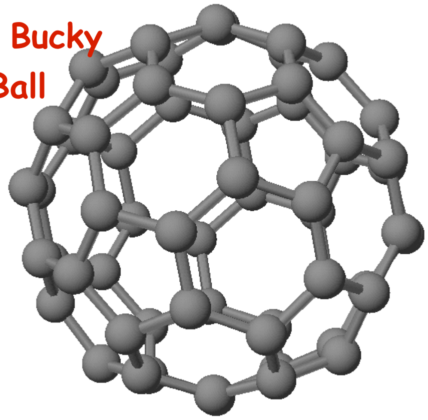
C_{60}, Bucky Ball



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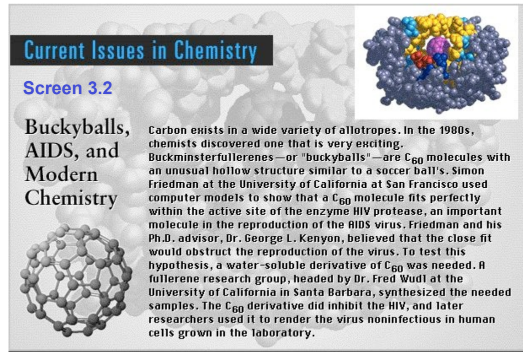


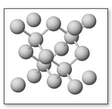
Current Issues in Chemistry

Screen 3.2

Buckyballs, AIDS, and Modern Chemistry

Carbon exists in a wide variety of allotropes. In the 1980s, chemists discovered one that is very exciting. Buckminsterfullerenes—or "buckyballs"—are C_{60} molecules with an unusual hollow structure similar to a soccer ball's. Simon Friedman at the University of California at San Francisco used computer models to show that a C_{60} molecule fits perfectly within the active site of the enzyme HIV protease, an important molecule in the reproduction of the AIDS virus. Friedman and his Ph.D. advisor, Dr. George L. Kenyon, believed that the close fit would obstruct the reproduction of the virus. To test this hypothesis, a water-soluble derivative of C_{60} was needed. A fullerene research group, headed by Dr. Fred Wudl at the University of California in Santa Barbara, synthesized the needed samples. The C_{60} derivative did inhibit the HIV, and later researchers used it to render the virus noninfectious in human cells grown in the laboratory.

MAR



Silicon

- Quartz or sand + high purity coke → Si
  - $SiO_2 + 2\,C \rightarrow Si + 2\,CO$
- Making very pure silicon:
  - $Si + Cl_2 \rightarrow SiCl_4$
  - $SiCl_4 + Mg \rightarrow MgCl_2 + Si$
- To purify the silicon, it is zone-refined

MAR

Tin, Sn

- Sn is relatively expensive, but used because it resists corrosion.
  - About 40% used in "tin plate"
- "Tin cans" have 0.0004 - 0.025 mm layer of Sn on iron
- About 30 x 10^9 cans plated annually in US

MAR

Tin Alloys

Solder: 1/3 Sn and 2/3 Pb

Bronze: 5-10% Sn + Cu

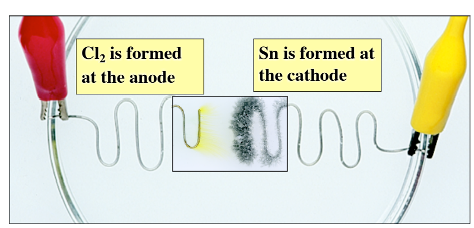
Pewter: 90-95% Sn, 1-8% Sb, and < 3% Cu

Bearing metal: 80-90% Sn, 5% Cu, and Pb

MAR

Tin

Tin metal can be recovered by electrolysis of an aqueous solution of tin(II) chloride.



MAR

Lead, Pb

- Most abundant of the "heavy metals"
- Romans used it in "plumbing"
  - the word comes from the Latin name for the element
- Main ore is galena, PbS

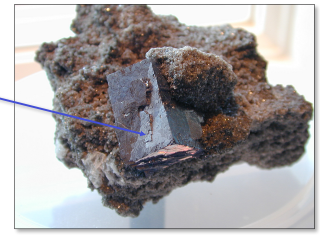
MAR

Producing Lead

$2\ PbS + 3\ O_2 \rightarrow 2\ PbO + 2\ SO_2(g)$

$PbO + C \rightarrow Pb + CO$

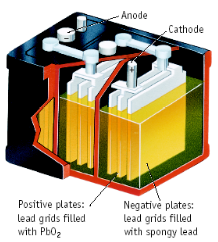
Galena
PbS



MAR

Lead Storage Batteries

About 60% of the batteries sold are Pb storage batteries



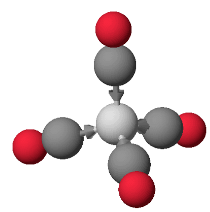
ANODE:
$Pb(s) + HSO_4^- \rightarrow PbSO_4(s) + H^+(aq) + 2e^-$

CATHODE:
$PbO_2(s) + 3\ H^+(aq) + HSO_4^-(aq) + 2e^- \rightarrow PbSO_4(s) + 2\ H_2O$

MAR

Carbon-Oxygen Compounds

- CO—used as reducing agent in metal purification—the Mond process
  - $NiO + 4\ CO$ (at 50 °C) $\rightarrow Ni(CO)_4$ (liq)
  - $Ni(CO)_4$ (at 230 °C) $\rightarrow$ pure Ni + 4 CO



MAR

Carbon-Oxygen Compounds

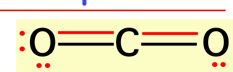
CO_2 — over 30 x 10^6 tons produced in US/year
- 1/2 used as refrigerant and propellant in aerosols
- 1/4 used to "carbonate" soft drinks

CO_2 is a "greenhouse" gas

MAR

Silicon-Oxygen Compounds

SiO_2 is not like CO_2



Reason is that 2 Si=O bonds are weaker (~640 kJ each) than 4 Si-O bonds (464 kJ each)

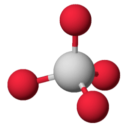
Also orbital overlap to form Si=O is not efficient.

Most common form is alpha-quartz

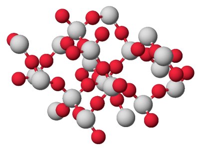
Less pure forms are rose quartz, smoky quartz, amethyst, citrine.

MAR

Silicon Dioxide



- All silicon-oxygen compounds have corner-shared SiO_4 tetrahedra
- α-Quartz has interlinked helical chains of SiO_4 tetrahedra.
- Helices can be right- or left-handed, so crystals are optically active.



Large SiO_2 crystal

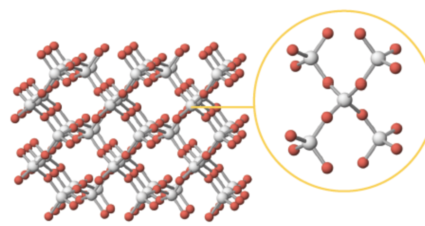
MAR

Quartz

- Quartz is a key electronic material, 2nd only to Si in volume.
- Citrine and amethyst have Fe^{2+}/Fe^{3+} impurities in quartz that give color.

MAR

Quartz



Quartz consists of interlinked chains of SiO_4 units

MAR

Piezoelectricity

- Quartz exhibits the property of **piezoelectricity**.
  - The production of an electric dipole when the crystal is deformed.
- Piezoelectric effect is used to control oscillators in electric circuits such as watches and radios.

MAR

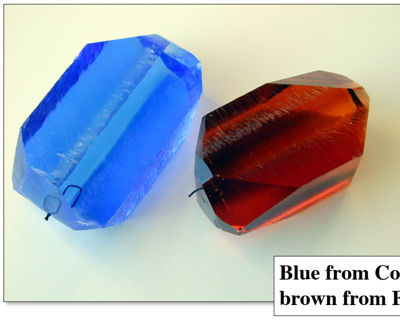
Hydrothermal Growth of Quartz

- Most quartz used commercially is synthetic
- At 350-400 ˚C and 1-4 kilobars, SiO_2 dissolves slightly in 1 M NaOH
- $3\ SiO_2 + 2\ OH^- \rightarrow Si_3O_7^{2-} + H_2O$
- SiO_2 crystallizes on quartz seed crystals.

"Hydrothermal Synthesis of Crystals," Robert A. Laudise, *Chemical & Engineering News*, Vol.65 (39), 30, 1987

MAR

Synthetic Quartz

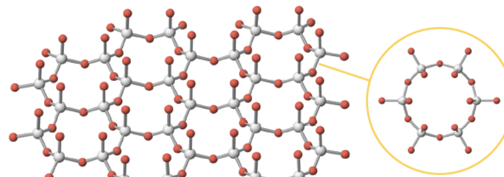


Blue from Co^{2+} ions and brown from Fe^{2+} ions.

MAR

Silicates

Silicates have chains of SiO_4 tetrahedra, often linked into a sheet structure.



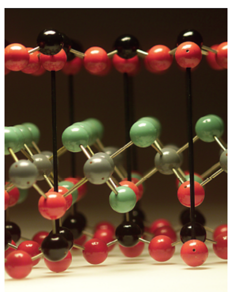
Sheet structure in mica

MAR

Clays

Clays have sheets of SiO_4 tetrahedra bound to sheets of AlO_6 octahedra.

A large variety of clays



MAR

Clays

Remedies for stomach upset can contain clays.

Clays absorb toxins.

The large disk is baked clay from Africa; used medicinally.

MAR

Glass

When quartz is melted, it forms silica glass.

Add CaO and Na_2CO_3 → ordinary glass

See Corning Glass Museum: www.cmog.org

MAR

Soda-Lime Glass

Most common type and least expensive

60-75% silica, 12-18% soda, 5-12% lime

Poor resistance to sudden temperature changes and to corrosive chemicals

MAR

Lead Glass

About 20% PbO

Relatively soft

High refractive index gives it brilliance

Used for art glass and electrical applications

MAR

Borosilicate Glass

Any silicate glass with at least 5% B_2O_3

High resistance to temperature change and chemical corrosion

Pipelines, light bulbs, photochromic glasses, sealed-beam headlights, lab ware, baking ware

MAR

Photochromic Glass

Glass contains AgCl and CuCl

$Cl^- + \text{light} \rightarrow Cl + e\text{-}$

Darkening reaction

$e\text{-} + Ag^+ \rightarrow Ag\ (s)$

Reversing reactions

$Cl + Cu^+ \rightarrow Cu^{2+} + Cl^-$

$Cu^{2+} + Ag \rightarrow Cu^+ + Ag^+$

MAR

Colored Glass

- Old glass often colored due to impurities
  - Fe^{2+} gives blue-green
  - Fe^{3+} gives yellow-green
- Colored glass
  - Blue glass: Co^{2+}
  - Purple: Mn^{2+}
  - Fe^{2+} + Cr salts --> green wine bottles
  - Fe^{2+} + S --> brown
  - U^{2+}: yellow
  - Se^{2-}: red (as in traffic lights)

MAR

Silicones: organosilicon polymers

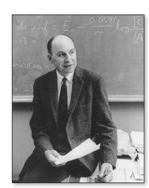
MAR

Silicones

$2\ CH_3Cl + Si \rightarrow SiCl_2(CH_3)_2$

Also produces $SiCl_3(CH_3)$, $SiCl\,(CH_3)_3$, and $SiCl_4$

Patented by E. G. Rochow of GE in 1945



Eugene Rochow

MAR

Silicones

$(CH_3)_3SiCl + 2\ H_2O\ \rightarrow$

$(CH_3)_3Si{-}O{-}Si(CH_3)_3\ +\ 2\ HCl$

$R_2SiCl_2 + 2\ H_2O\ \rightarrow$

$HO{-}SiR_2{-}OH + 2\ HCl$

$2\ HO{-}SiR_2{-}OH\ \rightarrow$

$HO{-}SiR_2{-}O{-}SiR_2{-}OH + H_2O$

Units link to give polymers!

MAR

Silicones

- **Properties of silicones**
  - Good thermal and oxidative stability
  - Resistant to high and low temperatures
  - Water repellent
  - Antistick and antifoam properties
  - Resistant to UV radiation and weathering
  - Physiologically inert (*see breast implant studies)
- **Can be made into oils, greases, emulsions, elastomers, and resins**

MAR

Silicones

Production of >350,000 tons annually

1000 different products

65-70% fluid silicones

25-30% elastomers

5-10% resins

MAR

Silicones: Fluids

Cosmetics — suntan lotion, lipstick

Antifoams — sewage treatment

Antifroth — cooking oil

Car polish

Lubricants

Release agents

MAR

Silicones: Elastomers

SiO_2 added to linear dimethylpolysiloxane

Retains inertness, flexibility, elasticity, and strength up to 250 ˚C and down to –100 ˚C.

Industrial sealants, belts and gaskets, medical tubing, space suits, etc.

MAR

Silicones: Resins

Pure silicone resins are poly(organosiloxanes) with a large proportion of branched siloxyl groups

Used as raw materials for paints, binders and in building preservation.

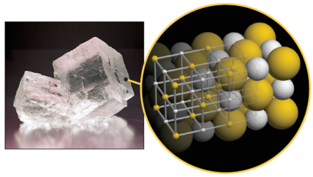
Electrical industry: insulating lacquers

High temperature enamels

MAR

Chemistry of Main Group Elements Groups 5A-8

Red and white P



Sodium chloride

MAR

Group 5A

Nitrogen, phosphorus, arsenic, antimony, and bismuth

N exists as N_2 molecules. Others have more complex forms.

MAR

Nitrogen

N_2 is quite unreactive owing to the NN triple bond.

Atmosphere is about 80% N_2

N_2 easily liquefied. Boils at -196 ^{0}C.

Used as a refrigerant

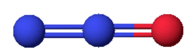
MAR

Nitrogen Oxides, N_2O

$NH_4NO_3 \rightarrow N_2O + 2\ H_2O$

N_2O, nitrous oxide (dinitrogen oxide), used as an anesthetic.

Soluble in fats. Used as propellant in whipped cream cans.



MAR

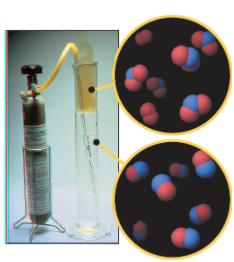
Nitrogen Oxides, NO

NO, nitrogen oxide, is present in polluted air.

NO = 11 valence e$^-$

Implicated in biological processes

Reacts readily with O_2 to give NO_2.



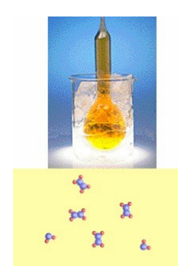
MAR

Nitrogen Oxides, NO_2

$HNO_3 \rightarrow 2\ N_2O + H_2O + 1/2\ O_2$

NO_2, nitrogen dioxide, is a brown gas in equilibrium with N_2O_4, a colorless gas.

A common air pollutant



MAR

Oxidation of NH_3

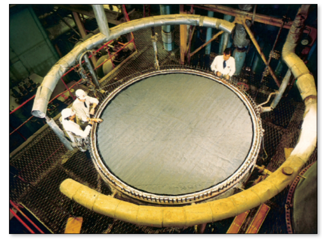
NH_3 gas is oxidized on Pt surface in air to NO

$4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H_2O$

Pt wire catalyzes reaction. Heat of reaction causes wire to glow.

MAR

Commercial Prep of HNO_3



NH_3 is oxidized on Pt surface in air to NO and NO_2. NO_2 in water gives HNO_3.

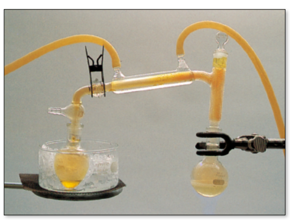
MAR

Nitric Acid, HNO_3

NO_2 in water gives HNO_3 (and HNO_2)

Better prepared from:

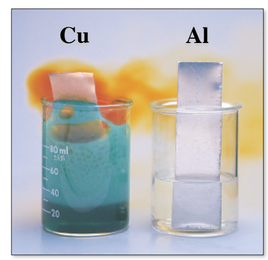
$2\ NaNO_3 + H_2SO_4 \rightarrow 2\ HNO_3 + Na_2SO_4$



MAR

Nitric Acid, HNO_3

HNO_3 readily reacts with almost all metals -- except Al -- to give metal nitrate and NO_2

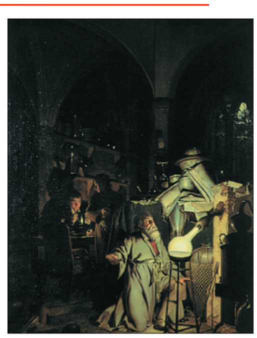


MAR

Phosphorus

Originally prepared from human waste

Now obtained from the reduction of P-containing minerals such as $Ca_3(PO_4)_2$.

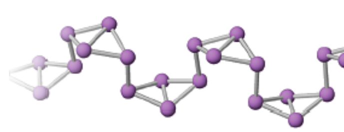


MAR

Phosphorus Allotropes

White = P_4 tetrahedron

Red = polymer of P_4 tetrahedra



MAR

Phosphorus Reactions

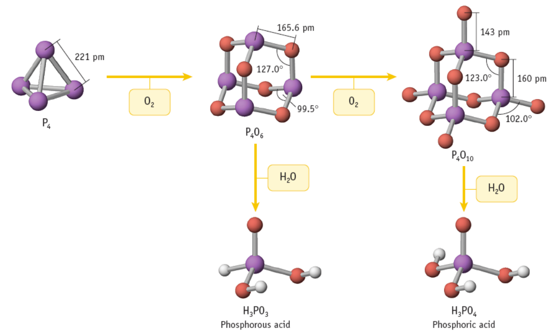
Yellow phosphorus spontaneously burns in air.

$P_4(s) + 5\ O_2(g) \rightarrow P_4O_{10}(s)$

Product: tetraphosphorus decaoxide.

MAR

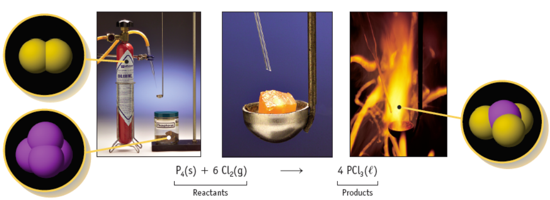
Phosphorus Oxides



MAR

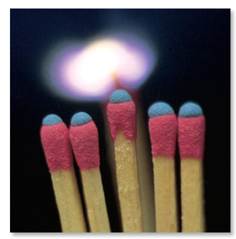
Phosphorus Reactions

Phosphorus reacts readily (is oxidized) with chlorine to give PCl_3 and PCl_5.



MAR

Phosphorus Reactions



A match head contains an oxidizing agent ($KClO_3$) and P_4S_3.

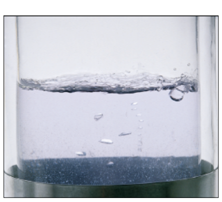
The striking strip on a match box contains red P.

Redox reaction lights the match.

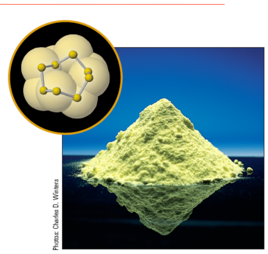
MAR

Group 6A

Oxygen, Sulfur, Selenium, Tellurium, Polonium



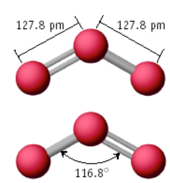
O_2 condenses to a pale blue liquid at -183 °C



MAR

Oxygen Allotropes

Liquid O_2 is paramagnetic and clings to a magnet.

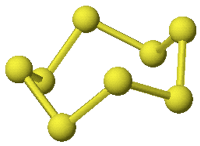


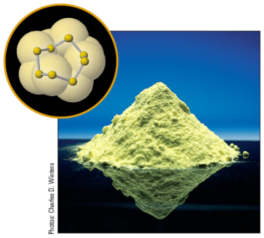
Ozone, O_3, is made by passing O_2 through electric discharge.

MAR

Sulfur

The most stable allotrope of S is a crown-shaped ring of 8 S atoms.





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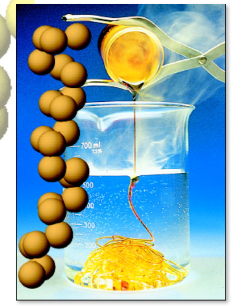
Polymeric Sulfur

Heating S to the melting point causes the rings to open and a polymeric allotrope forms.



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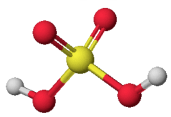
Sulfuric Acid



Sulfur is found in pure form in underground deposits along the coast of the U.S. It is recovered by pumping superheated steam into the beds to melt the S.

MAR

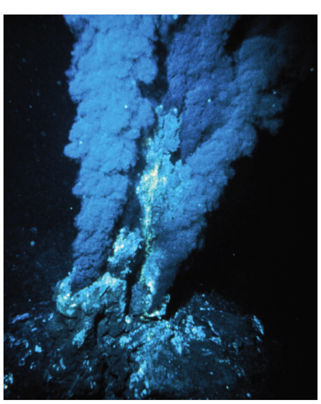
Sulfuric Acid, H_2SO_4

Sulfur is burned in air to give SO_2 and then SO_3.

SO_3 reacts with water → H_2SO_4

H_2SO_4 is the chemical produced in the largest amount in the U.S.

MAR



Black Smokers

Vents -- BLACK SMOKERS -- in the bottom of the world's oceans are a source of metal sulfides.

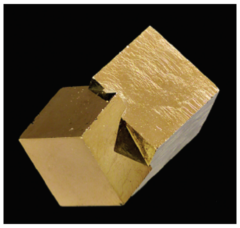
MAR

Sulfide-Containing Minerals

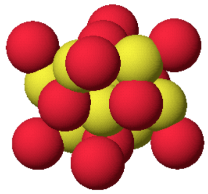
Orpiment
As_2S_3

MAR

Sulfide-Containing Minerals



FeS, iron pyrite
Fool's gold



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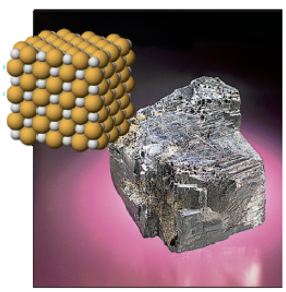
Sulfide-Containing Minerals



Lead sulfide, PbS, galena

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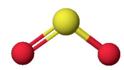

Sulfur Oxides

SO_2 is produced by burning sulfur in oxygen.

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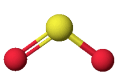


Sulfur Oxides

SO_2 is produced by treatment of metal sulfides with O_2.

$2\ ZnS + 3\ O_2 \rightarrow 2\ ZnO + 2\ SO_2$

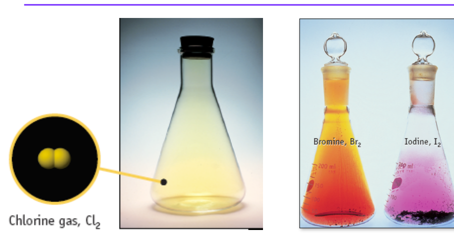
Also produced by burning fossil fuels

About 2 x 10^8 tons of sulfur oxides are released into the atmosphere by human activities annually.

MAR

Group 7A -- Halogens

Fluorine, Chlorine, Bromine, Iodine, Astatine

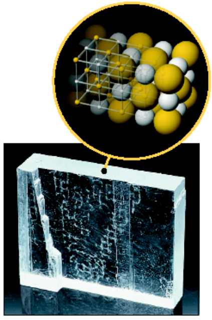


Diatomic elements: Cl_2 gas, liquid Br_2, and solid I_2

MAR

Group 7A, Halogens

Fluorine, Chlorine, Bromine, Iodine, Astatine



Cl is the most abundant in Group 7A.

Occurs in the sea and in salt (NaCl) deposits.

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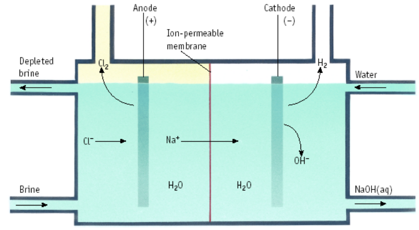
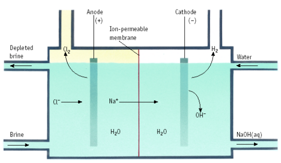
Commercial Preparation of Chlorine



Electrolysis of NaCl(aq) in a membrane cell.

MAR

Commercial Preparation of Chlorine

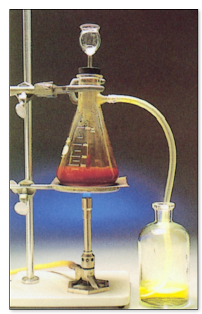


Anode: $2\ Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

Cathode: $2\ H_2O(liq) + 2e^- \rightarrow H_2(g) + 2\ OH^-(aq)$

MAR

Lab Preparation of Chlorine



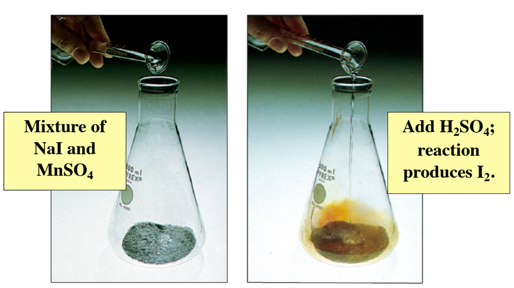
Oxidation of NaCl with strong oxidant ($K_2Cr_2O_7$)

Cl_2 gas bubbles into water.

MAR

Lab Preparation of Iodine

$$2\ I^- + 4\ H^+ + MnO_2 \rightarrow Mn^{2+} + I_2 + 2\ H_2O$$



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Reaction of Cl_2 and Na

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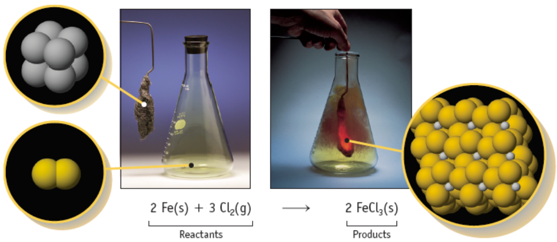
Reaction of Cl_2 and Fe



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Reaction of Br_2 and Al

Bromine reacts with metals to give metal bromides

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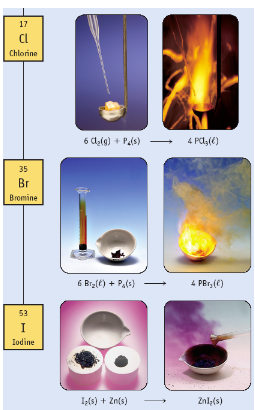

Reactions of Halogens

Halogens react with nonmetals and metals to give covalent or ionic halides.

MAR

End of Chapter 18

See:

- *Chapter Eighteen Study Guide*

MAR

Important Equations, Constants, and Handouts from this Chapter:

- **This chapter is intended as a review of the concepts found in CH 221, CH 222 and CH 223.**
- **If you see something you do not recognize, talk to the instructor!**

MAR

End of Chapter Problems: ***Test Yourself***

You will need a table of thermodynamic data found in CH 223 Problem Set #5

1. Write a balanced chemical equation for the preparation of H_2 (and CO) by the reaction of CH_4 and water. Using a table of thermodynamic data, calculate $\Delta H°$, $\Delta G°$, and $\Delta S°$ for this reaction.
2. Calcium oxide, CaO, is used to remove SO_2 from power plant exhaust. These two compounds react to give solid $CaSO_3$. What mass of SO_2 can be removed using 1.2×10^3 kg of CaO?
3. Aluminum dissolves readily in hot aqueous NaOH to give the aluminate ion, $Al(OH)_4^{1-}$, and H_2. Write a balanced equation for this reaction. If you begin with 13.2 g of Al, what volume (in milliliters) of H_2 gas is produced when the gas is measured at 735 mm Hg and 22.5 °C? *The reaction:* **$2\ Al(s) + 2\ NaOH(aq) + 6\ H_2O(l) \rightarrow 2\ Na^+(aq) + 2\ Al(OH)_4^{1-}(aq) + 3\ H_2(g)$**
4. If an electrolytic cell for producing F_2 operates at 5.00×10^3 amps (at 10.0 V), what mass of F_2 can be produced per 24-hour day? Assume the conversion of F^{-1} to F_2 is 100%.
5. How would you extinguish a sodium fire in the laboratory? What is the worst thing you could do?

MAR

End of Chapter Problems: *Answers*

1. $\Delta H° = 205.9$ kJ ,$\Delta G° = 141.9$ kJ, $\Delta S° = 214.7$ J/K
2. 1.4×10^6 g SO_2
3. 1.84×10^4 mL
4. 8.51×10^4 g F_2
5. Use an inert dry chemical fire extinguisher - do ***NOT*** pour water on the sodium fire, this would create flammable hydrogen gas!

You will need a table of thermodynamic data found in CH 223 Problem Set #5

MAR