

Group 13 - Overview

- The most stable oxidation states are +3 (B, Al, Ga, In) and +1 (Tl).
- The acidic character of the hydroxides decreases with Z: B(OH)_3 is acidic, Al(OH)_3 and Ga(OH)_3 are amphoteric and In(OH)_3 and Tl(OH)_3 are basic. TlOH is a strong base.

The Boron Group

5	B
13	Al
31	Ga
49	In
81	Tl



Boron

- Important mineral: borax $\text{Na}_2\text{B}_4\text{O}_7 \times 10 \text{H}_2\text{O}$.
- The only non-metal in Group III ('**metalloid**').
- Boron compounds show preferentially covalent bonds. There are no salts with B^{3+} ions.
- All modifications of boron are very hard (after diamond the hardest element) and semi-conducting.



Boron

Metalloids Periodic Table																		
1 H HYDROGEN 1.008															2 He HELIUM 4.003			
3 Li LITHIUM 6.941	4 Be BERYLLIUM 9.012											5 B BORON 10.811	6 C CARBON 12.011	7 N NITROGEN 14.007	8 O OXYGEN 15.999	9 F FLUORINE 18.998	10 Ne NEON 20.180	
11 Na SODIUM 22.990	12 Mg MAGNESIUM 24.305											13 Al ALUMINUM 26.982	14 Si SILICON 28.086	15 P PHOSPHORUS 30.974	16 S SULFUR 32.06	17 Cl CHLORINE 35.45	18 Ar ARGON 39.948	
19 K POTASSIUM 39.098	20 Ca CALCIUM 40.078	21 Sc SCANDIUM 44.956	22 Ti TITANIUM 47.88	23 V VANADIUM 50.942	24 Cr CHROMIUM 52.00	25 Mn MANGANESE 54.938	26 Fe IRON 55.845	27 Co COBALT 58.933	28 Ni NICKEL 58.69	29 Cu COPPER 63.546	30 Zn ZINC 65.38	31 Ga GALLIUM 69.723	32 Ge GERMANIUM 72.63	33 As ARSENIC 74.922	34 Se SELENIUM 78.96	35 Br BROMINE 79.904	36 Kr KRYPTON 83.798	
37 Rb RUBIDIUM 85.468	38 Sr STRONTIUM 87.62	39 Y YTTRIUM 88.906	40 Zr ZIRCONIUM 91.224	41 Nb NIOBIUM 92.906	42 Mo MOLYBDENUM 95.94	43 Tc TECHNETIUM 98.906	44 Ru RUTHENIUM 101.07	45 Rh RHODIUM 102.91	46 Pd PALLADIUM 106.37	47 Ag SILVER 107.87	48 Cd CADMIUM 112.41	49 In INDIUM 114.82	50 Sn TIN 118.71	51 Sb ANTIMONY 121.76	52 Te TELLURIUM 127.6	53 I IODINE 126.91	54 Xe XENON 131.29	
55 Cs CESIUM 132.91	56 Ba BARIUM 137.33	57-71* LANTHANIDE SERIES		72 Hf HAFNIUM 178.49	73 Ta TANTALUM 180.95	74 W TUNGSTEN 183.84	75 Re RHENIUM 186.21	76 Os OSMIUM 190.23	77 Ir IRIDIUM 192.22	78 Pt PLATINUM 195.08	79 Au GOLD 196.97	80 Hg MERCURY 200.59	81 Tl THALLIUM 204.38	82 Pb LEAD 207.2	83 Bi BISMUTH 208.98	84 Po POLONIUM 209	85 At ASTATINE 210	86 Rn RADON 222
87 Fr FRANCIUM 223	88 Ra RADIUM 226	89-103** ACTINIDE SERIES		104 Rf RUTHERFORDIUM 261	105 Db DUBNIUM 262	106 Sg SEABORGIUM 266	107 Bh BOHRHIUM 264	108 Hs HASSIUM 277	109 Mt MEITNERIUM 268	110 Ds DARMSTADTIUM 271	111 Rg ROENTGENIUM 272	112 Cn COPERNICIUM 285	113 Nh NIHONIUM 284	114 Fl FLEROVIUM 289	115 Uut UNUNPENTIUM 288	116 Lv LIVERMORIUM 293	117 Ts TENNESSINE 289	118 Og OGANESSON 294
Lanthanide Series																		
89 La LANTHANUM 138.91	90 Ce CELIUM 140.12	91 Pr PRASEODYMIUM 140.91	92 Nd NEODYMIUM 144.24	93 Pm PROMETHIUM 145	94 Sm SAMARIUM 150.36	95 Eu EUROPIUM 151.96	96 Gd GADOLINIUM 157.25	97 Tb TERBIUM 158.93	98 Dy DYSPROSIUM 162.50	99 Ho HOLMIUM 164.93	100 Er ERBIUM 167.26	101 Tm THULIUM 168.93	102 Yb YTERBIUM 173.05	103 Lu LUTETIUM 174.97				
Actinide Series																		
105 Ac ACTINIUM 227	106 Th THORIUM 232.04	107 Pa PROTACTINIUM 231.04	108 U URANIUM 238.03	109 Np NEPTUNIUM 237.05	110 Pu PLUTONIUM 244.06	111 Am AMERICIUM 243.06	112 Cm CURIUM 247.07	113 Bk BERKELIUM 247.07	114 Cf CALIFORNIUM 251.08	115 Es EINSTEINIUM 252.08	116 Fm FERMIUM 257.10	117 Md MENDELEVIUM 258.11	118 No NOBELIUM 259.10	119 Lr LAWRENCIUM 262.11				

Synthesis of Boron

- Crystalline boron of high purity is obtained by reduction of boron halides by hydrogen at 1000 – 1400 °C.

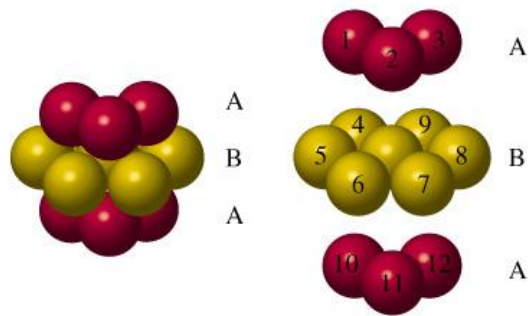


- Amorphous boron (brown powder) of low purity is obtained by reduction with magnesium.

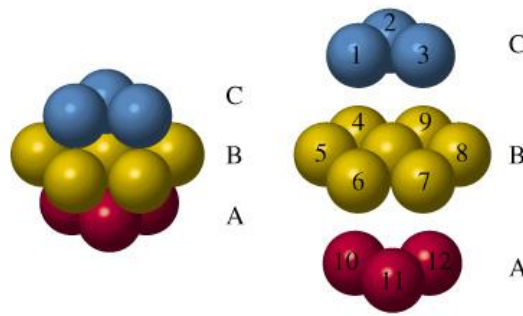


Modifications of Boron

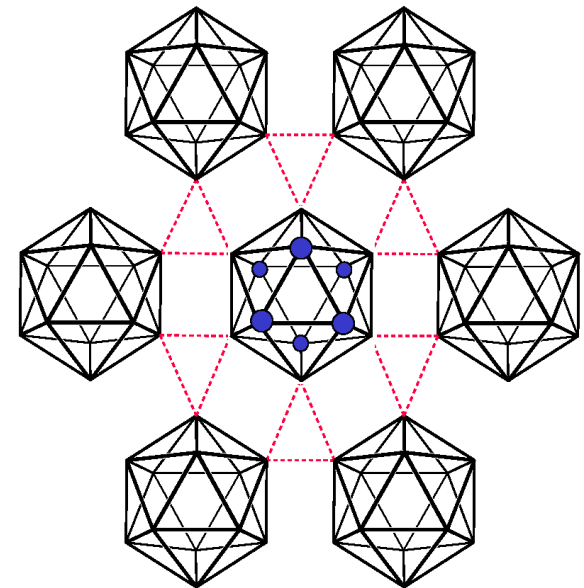
- Boron exists in several modifications (2 x rhomboedric; 2 x tetragonal). All contain covalently connected B_{12} icosahedra.
- The most stable modification is β -rhomboedric boron. α -rhomboedric boron consists of cubic closest packed icosahedra.



hexagonal closest packed
(hcp)



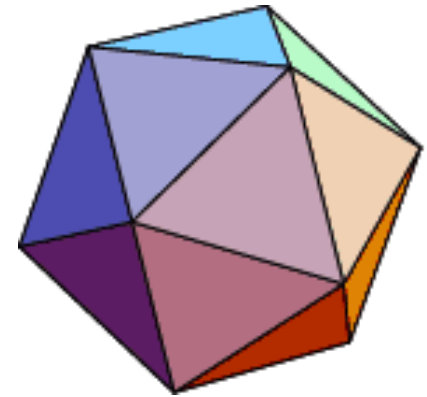
cubic closest packed
(ccp)



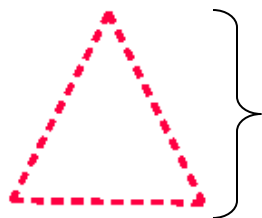
α -rhomboedric boron

The Icosahedron

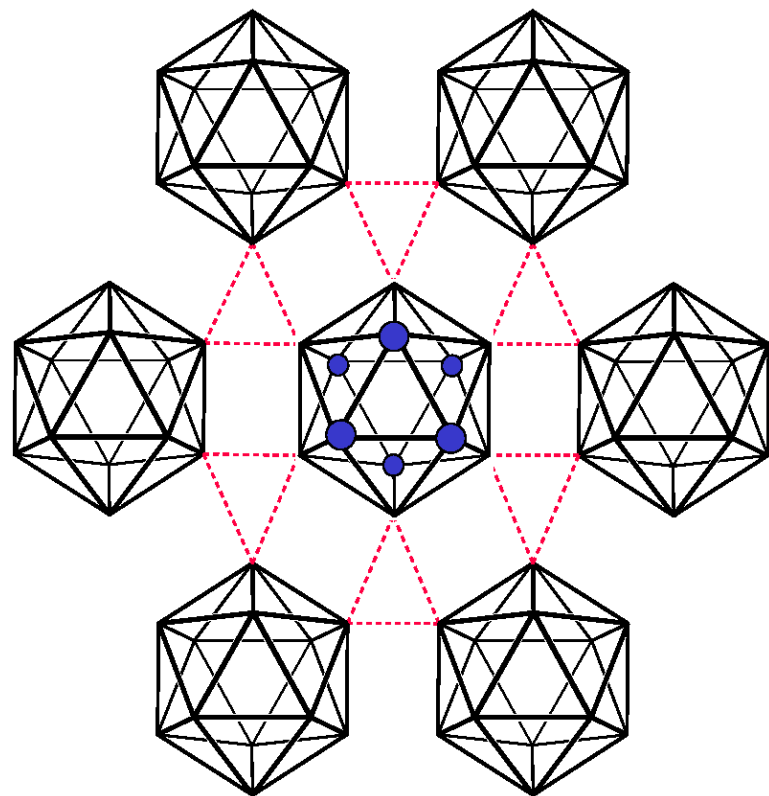
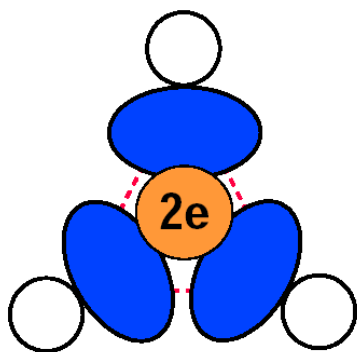
- The icosahedron has 12 polyhedron vertices, 30 polyhedron edges, and 20 equivalent equilateral triangle faces.
- It is one of the five Platonic solids (all sides, angles and faces are identical. In each corner of such a solid the same number of surfaces collide).



The Bonding in α -Rhomboedric Boron



Closed 3-center-2-electrons bond ($3c/2e^-$). In a three-center bond, a single pair of electrons joins three atoms rather than the usual two



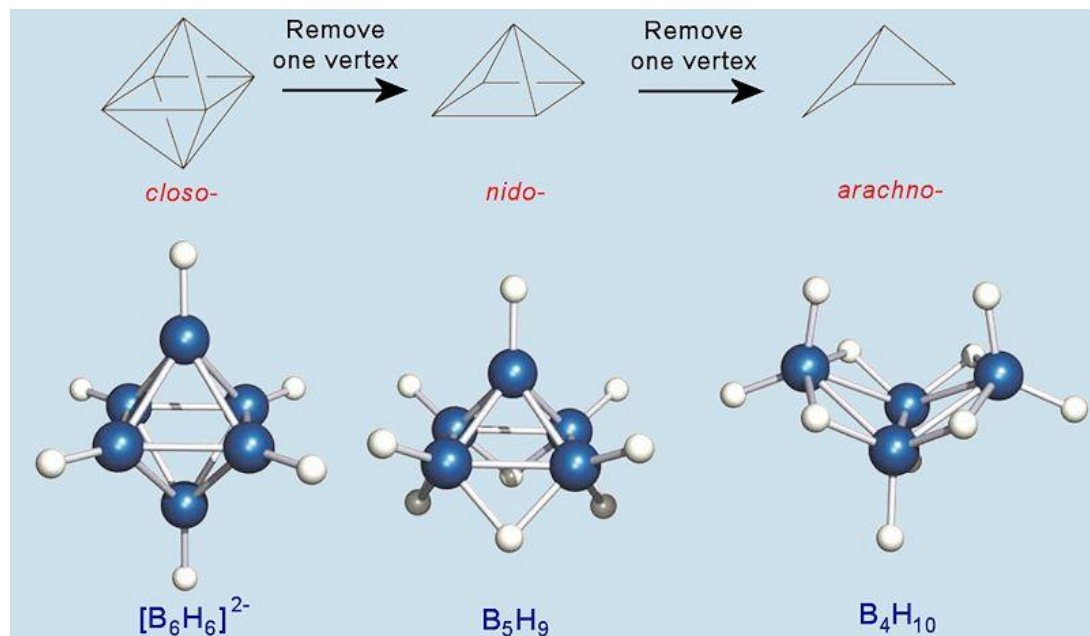
α -rhomboedric boron: 6 atoms with coordination number 6 and 6 atoms with coordination number 7.

Boron Hydrides (Boranes)

- Boron and hydrogen form binary compounds B_xH_y with unusual structures and compositions.
- First prepared by A. Stock. Since some of the boranes inflame spontaneously in air, he devised the now-standard technique of vacuum line chemistry.
- 1976: Nobel prize for W. N. Lipscomb for his investigations about boranes.



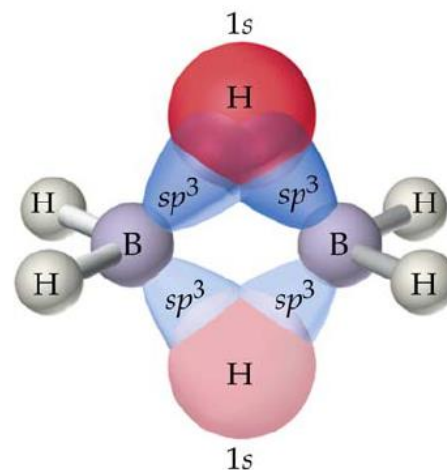
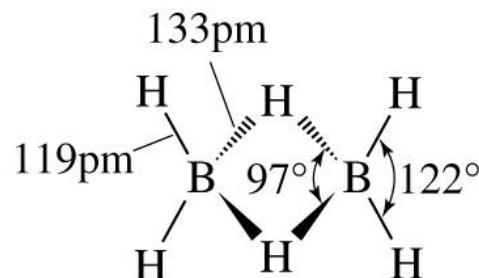
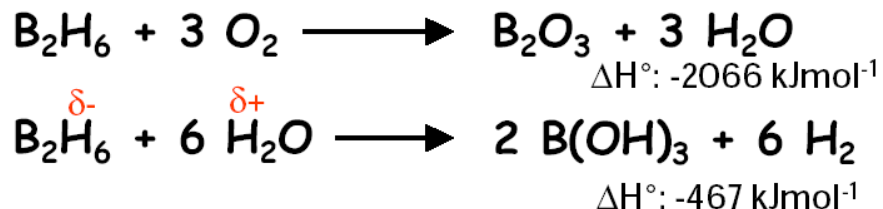
Alfred E. Stock
(1876 – 1946)



W. N. Lipscomb
(1919 – 2011)

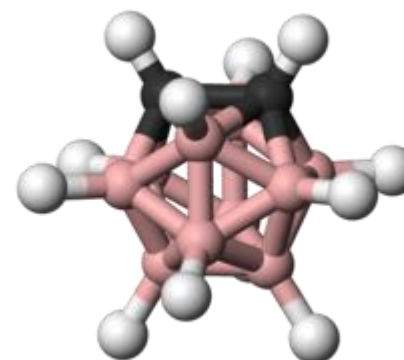
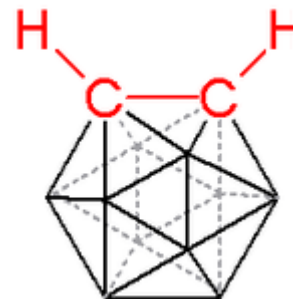
Diborane

- Colorless, toxic gas with an unpleasant smell.
- The dimer of the electronically unsaturated BH_3 . It has two $3c/2e^-$ bonds.
- With water there is a fast hydrolysis and with O_2 it oxidizes in a highly exothermic reaction.



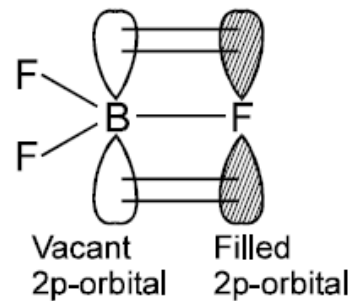
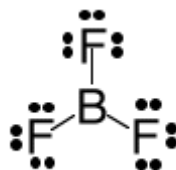
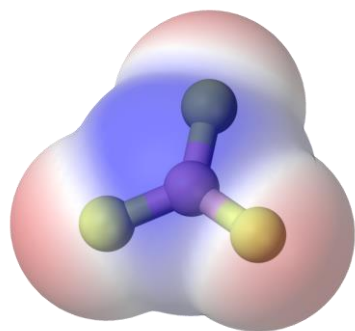
Carboranes

- Carboranes are compounds in which some of the BH groups in boranes have been replaced by CH groups.
- Best known: $B_{10}C_2H_{14}$. Structure: icosahedron; chemically very resistant: no reaction with water, acids, bases (similar to the hydridoborate $B_{12}H_{12}^{2-}$).

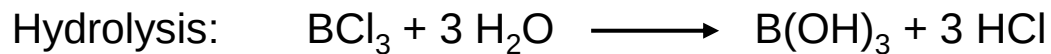


Boron Halides

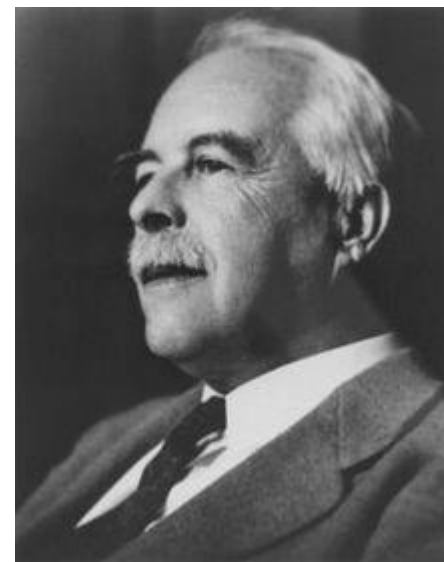
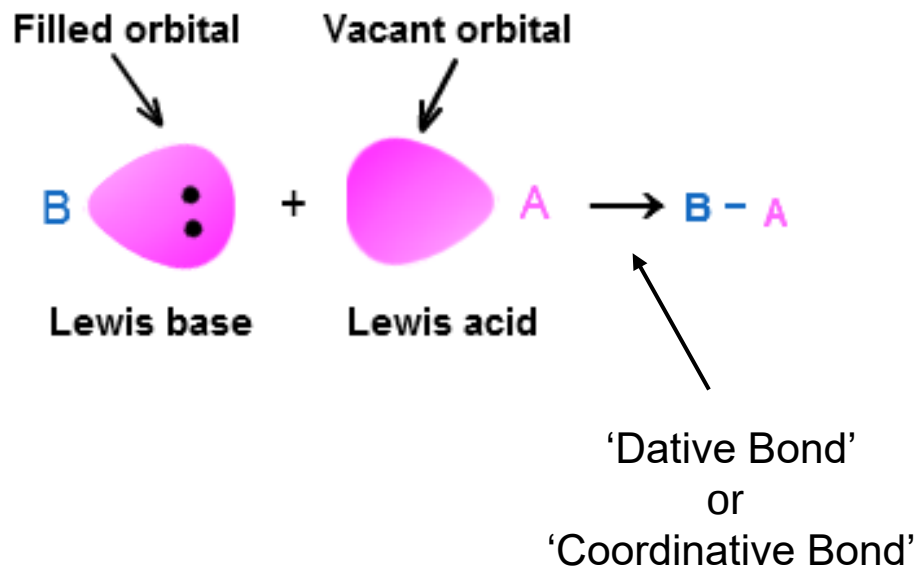
- BX_3 : Covalent, monomeric compounds with a trigonal planar structure. BF_3 and BCl_3 are colorless gases, BBr_3 is a liquid and BI_3 is a solid.



- BX_3 readily hydrolyzes; reactivity: $\text{I} > \text{Br} > \text{Cl} > \text{F}$.

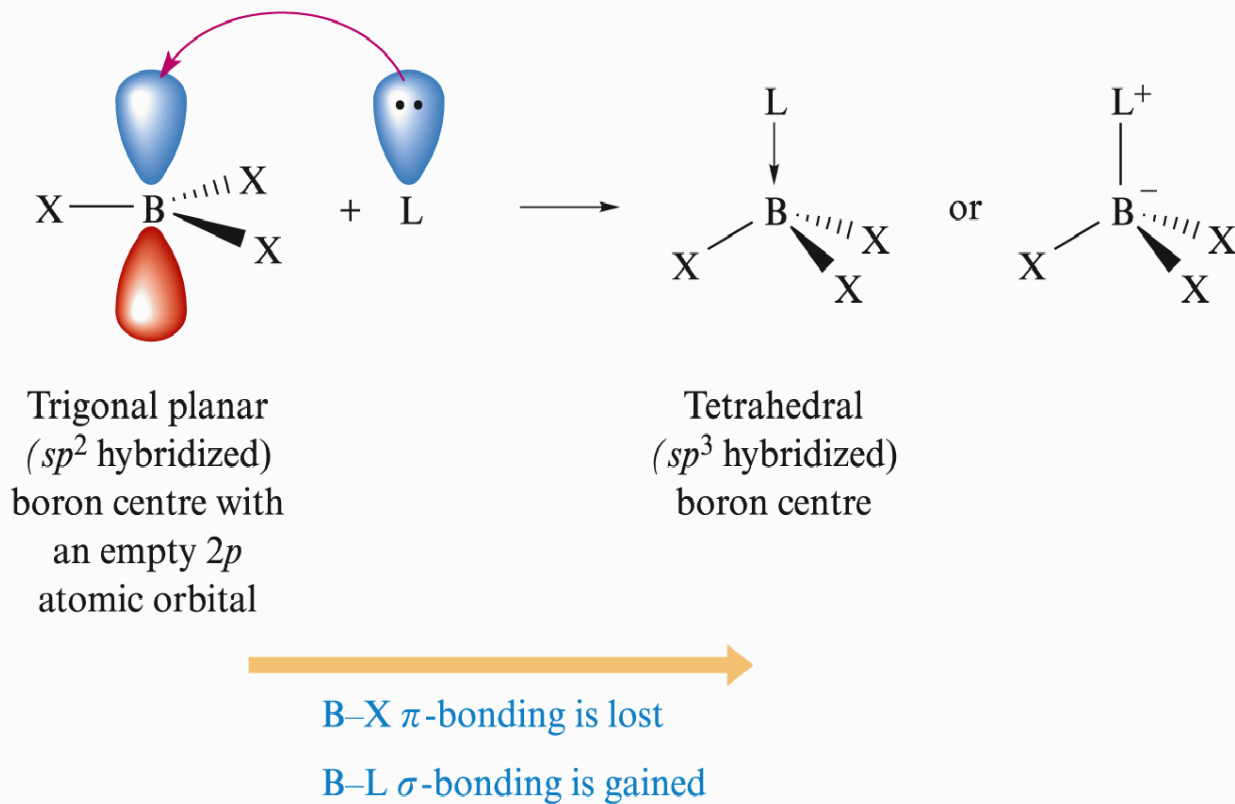


Lewis Acid Base Theory



Gilbert N. Lewis
(1875-1946)

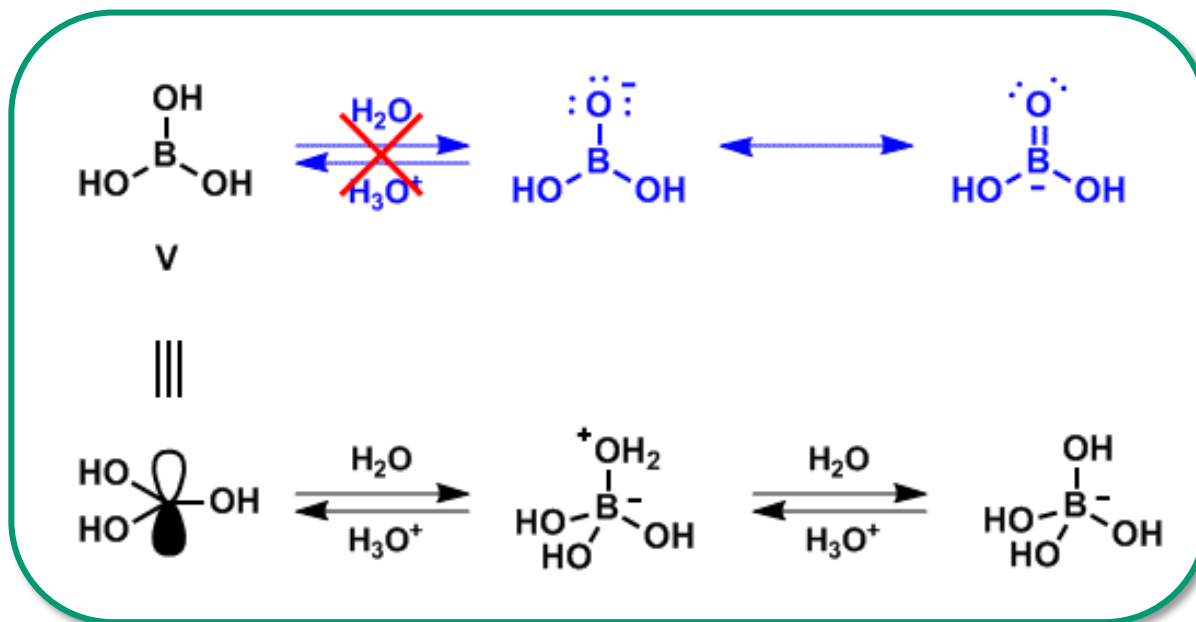
Boron Halides



Boron halides are powerful Lewis acids (L = ethers etc.).

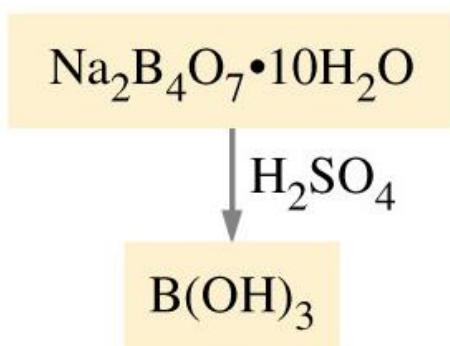
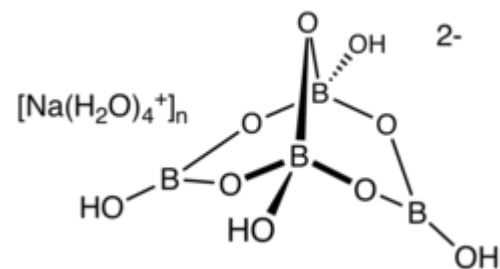
Orthoboric Acid B(OH)_3

- Weak acid ($\text{p}K_{\text{a}} = 9.2$). Found in some hot springs.
- Used as a mild antiseptic: eyewash, mouthwash.
- Behaves as a monobasic acid only: hydroxide acceptor into empty orbital on B.



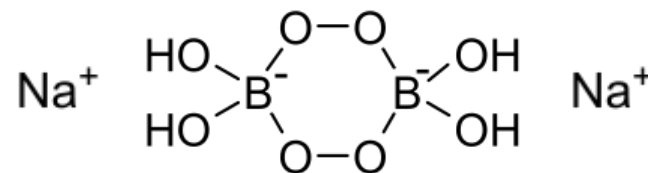
Borax

- A naturally occurring borate is "borax" $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, better described by the chemical formula $[\text{Na}(\text{H}_2\text{O})_4]_2[\text{B}_4\text{O}_5(\text{OH})_4]$.
- Use: pesticide, component of glass, aging of wood, component of cleaning products, etc.
- Reaction with sulfuric acid gives orthoboric acid.



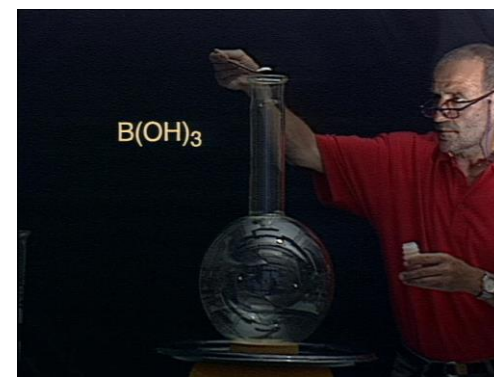
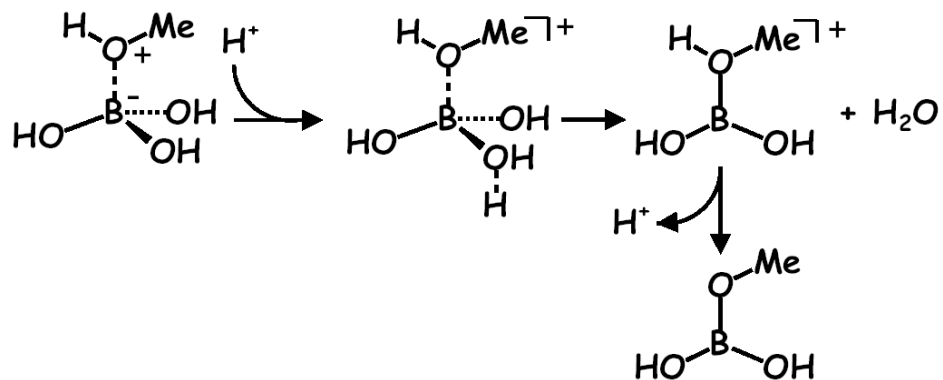
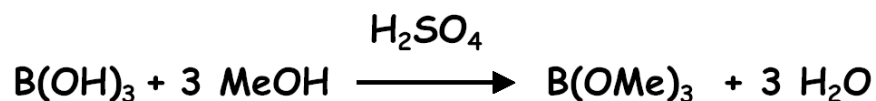
Sodium Perborate ('NaBO₃ x H₂O')

- Mild oxidant.
- Washing powder often contain sodium perborate.
- O-atoms are substituted with peroxo groups ('peroxoborates').
- Also used for teeth bleaching.



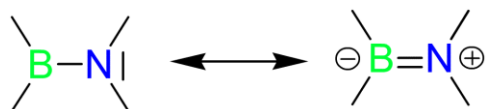
Boric Acid Trimethyl Ester B(OMe)₃

Shaking B(OH)₃, H₂SO₄ and MeOH produces the volatile boric acid trimethyl ester which, with the excess methanol and atmospheric oxygen, forms an inflammable gas mixture. Once lit, the boric acid ester burns with an intense green flame. Sulfuric acid, as a hygroscopic substance, serves to shift the equilibrium to the right.

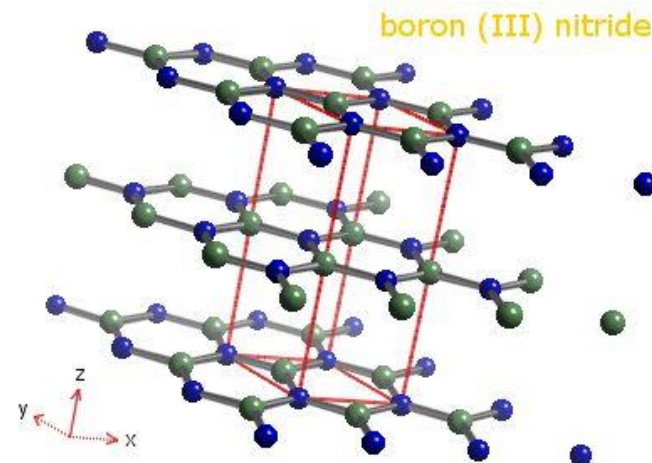


Boron Nitride

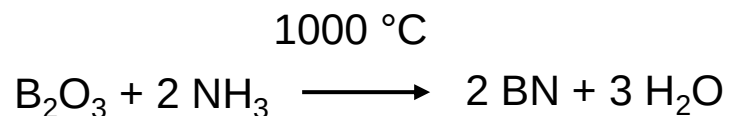
- The B-N group is isoelectronic to the C-C group. Because of the higher electronegativity of nitrogen, the electrons are dominantly located on N.



- Four modifications are known for BN. The thermodynamically most stable is hexagonal BN with a graphite-like structure. But the atoms lie on top of each other and there is no delocalization (white substance; no conductivity).
- Hexagonal BN is thermally very robust (Mp. 3270 °C) and chemically inert. Used as a lubricant and as a fire-resistant material.
- Cubic BN has a structure analogous to diamond. After diamond, the second hardest material (but more resistant to oxidation).

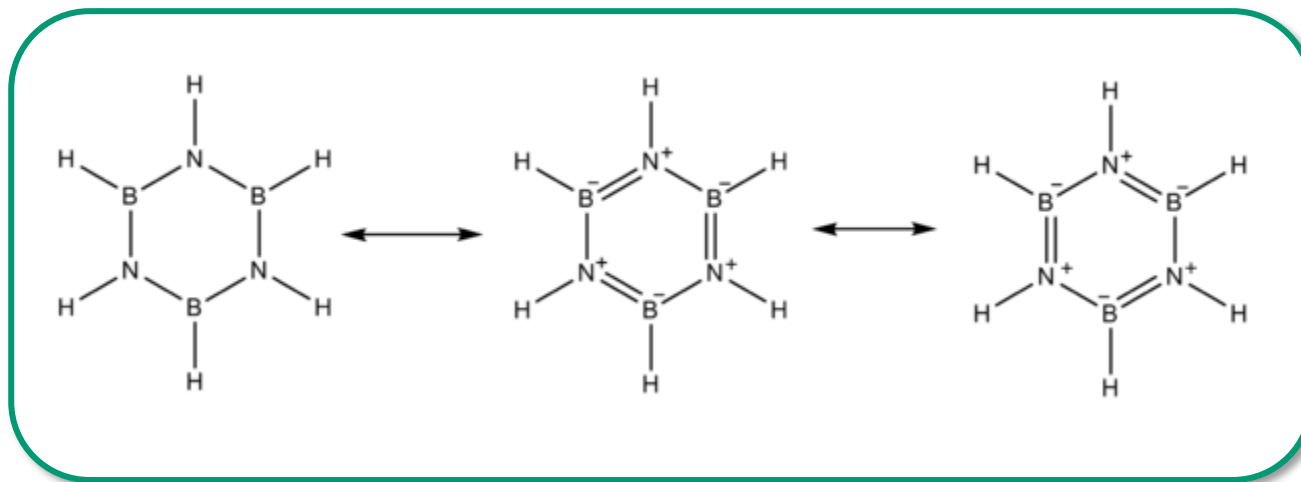


(hexagonal BN)



Borazine ('Inorganic Benzene')

- Borazine was first isolated by A. Stock.
- Borazine and benzene are chemically very different. The electron density along the boron-nitrogen π bond is not distributed evenly, due to the difference in electronegativities between the two types of atoms (δ^- on N !). This uneven distribution (little aromatic character) makes borazine prone to addition reactions (e.g. + H_2O , MeOH or HX).



Aluminium

- Most abundant metal on earth.
- Silvery, very light metal (2.7 g / cm^3), which conducts heat well.
- Commercially, the most important mineral is the oxide hydroxide bauxite $\text{AlO}_x(\text{OH})_{3-2x}$ ($0 < x < 1$).
- Many kitchen items (pots and pans, foil, dishes) are made of aluminum. Most materials used for transportation use large amounts of aluminum: cars, trucks, boats, aircraft, and aircraft engines. Road signs and high-voltage power lines are also made mostly of aluminum.
- About 64 million tonnes of aluminum was produced in 2019. China produces most of the world's aluminum (> 50%).



Aluminum – History

- A metal ornament, removed from a tomb of a military leader in 3rd century China, showed that it contained 85 % Al. How it was produced remains a mystery.
- 1825: Hans Christian Oersted, a Danish chemist, was the first to produce tiny amounts of aluminum by heating aluminum chloride with potassium.
- 1886: 8 months after graduating from college, 21 year old Charles M. Hall invented an inexpensive method for the production of aluminum. In the woodshed behind his family's home, Hall produced globules of Al metal by the electrolysis of aluminum oxide dissolved in a cryolite-aluminum fluoride mixture. Hall was granted a patent for his process in 1889. In the same year, Hall founded the Pittsburgh Reduction Company (later ALCOA). When it opened his company, he could produce about 25 kilograms of aluminum a day. By 1909, his company was producing about 41,000 kilograms of aluminum a day. The process was discovered nearly simultaneously by a 23 year old Frenchman called Héroult.

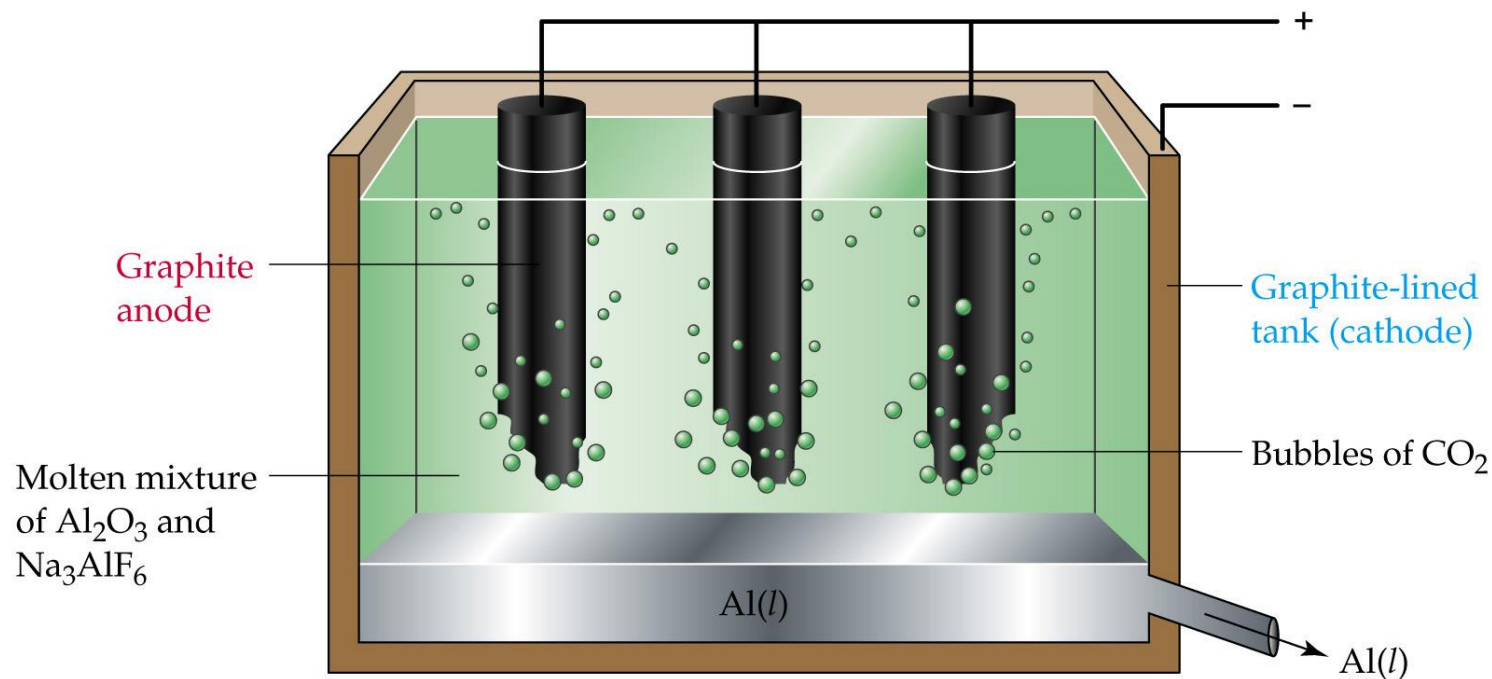


Aluminium production
1700 years ago ?



Hall cells for the production of Al

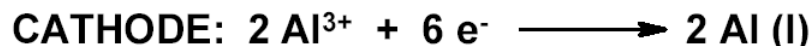
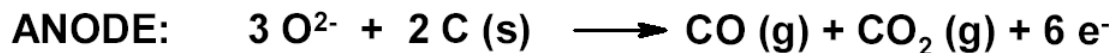
The Hall-Héroult Process



An electrolytic cell for production of aluminum by the Hall-Héroult process. Molten aluminum metal forms at the graphite cathode that lines the cell. Because molten aluminum is more dense than the Al_2O_3 - Na_3AlF_6 mixture, it collects at the bottom of the cell and is drawn off periodically.

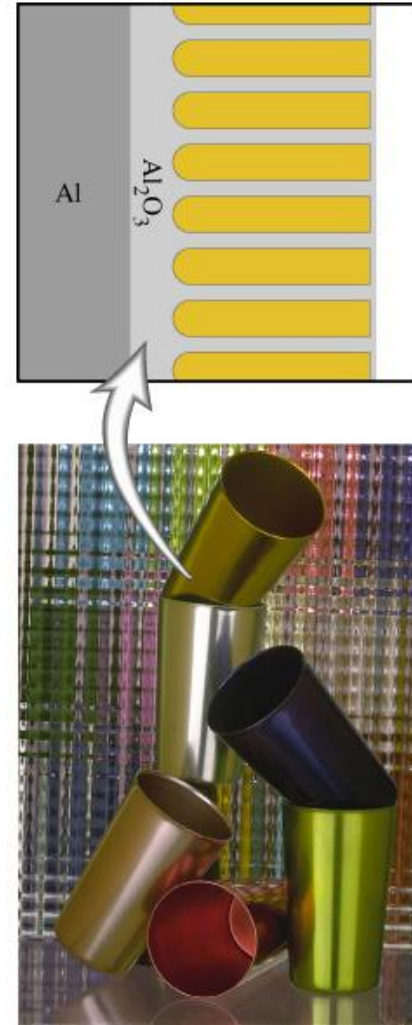
Technical Production of Aluminum

- Al_2O_3 has to be dissolved in cryolite, Na_3AlF_6 (Mp. 1000°C), because the melting point of Al_2O_3 is too high (Mp. 2050°C). Together they form an eutectic mixture with a Mp. of 960°C .
- Anodes last approx. 3 weeks before they have to be replaced.
- The production is a very energy intensive process: approx. 25 % of the costs are electricity (Canada has no bauxite but is a main producer because of cheap hydro power). One third is used to do the chemistry and two thirds are used to heat the cell.
- The aluminum production consumes 5 % of the electricity generated in the USA.



Anodized Aluminum

- Aluminum is stable in air because it is protected by a thin layer of Al_2O_3 ('passivation').
- The passivation also prevents the reaction of Al with oxidizing acids (e.g. HNO_3).
- Anodized aluminum: the protection can be increased by electrochemical deposition of Al_2O_3 (0.02 mm).

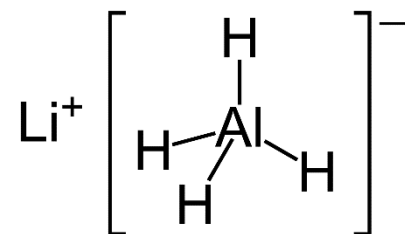
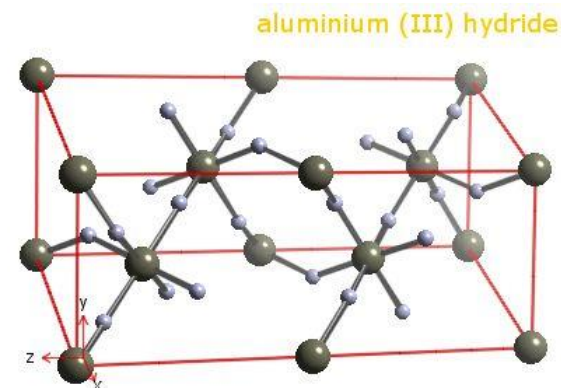
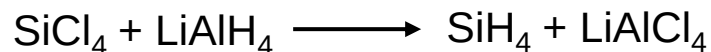


AlH_3 and LiAlH_4

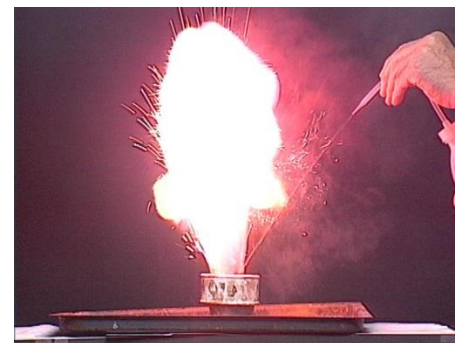
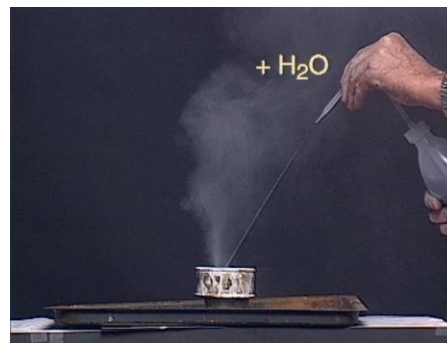
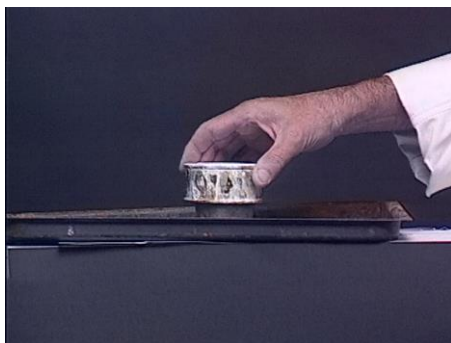
- Under normal conditions, neither AlH_3 nor Al_2H_6 are stable. Both compounds polymerize to give $(\text{AlH}_3)_n$ in which Al has the coordination number 6.
- $(\text{AlH}_3)_n$ can be synthesized from the elements:



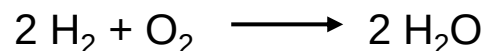
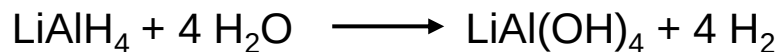
- LiAlH_4 is a strong reducing agent, which can be used to make many other hydrides.



Reactivity of LiAlH_4

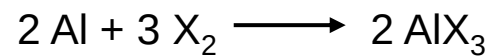


Chemistry: Lithium alanate is a metal hydride that produces elemental hydrogen on contact with water. This reaction is strongly exothermic. Once the reaction mixture has been heated sufficiently, the hydrogen self-ignites and burns with atmospheric oxygen to produce water



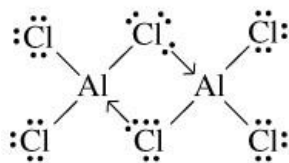
Aluminum – Reactions with Halogens

ALUMINIUM WITH THE
HALOGENS

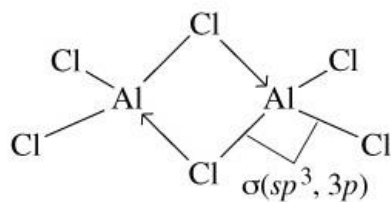


Aluminum Halides

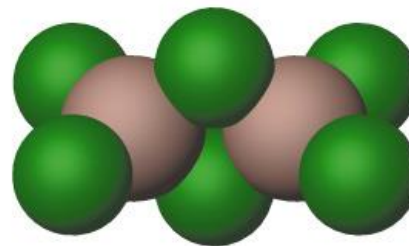
- Aluminum does not form (p-p) π bonds. Therefore, stabilization of the electronically unsaturated AlX_3 has to occur via aggregation and not via (p-p) π bonds as in BX_3 .
- For $\text{X} = \text{Cl}$, Br , and I , dimers of the formula Al_2X_6 are formed (for $\text{X} = \text{Cl}$ only in the liquid and gas phase).



Lewis structure



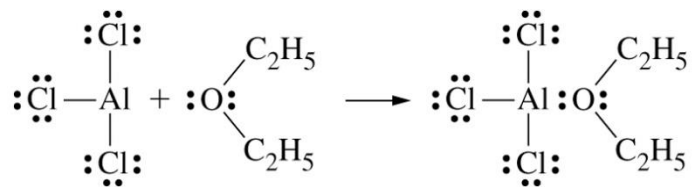
Bonding scheme



Space-filling model

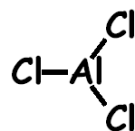
AlCl₃

- AlCl₃ is a white, hygroscopic substance which sublimes at 183 °C. In the solid state, it has a layered structure with AlCl₆ octahedra.
- AlCl₃ acts as a Lewis acid and a main application is the use as a catalyst in organic reactions (e.g. Friedel-Crafts).

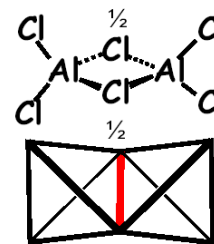


Adduct with ether

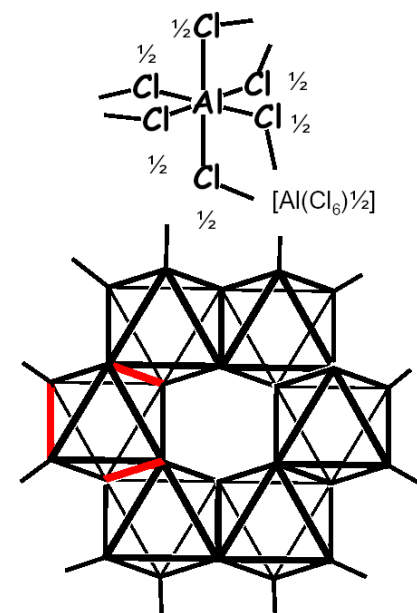
Gasphase
at high temp.



Liquid or gasphase
at low temp.

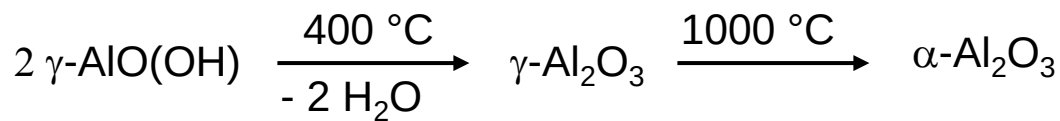


Solid state





- Corundum, $\alpha\text{-Al}_2\text{O}_3$: the second hardest natural mineral known to science. The hardest mineral, diamond is still four times harder than corundum. The red variety of corundum is known as ruby (+ Cr^{3+}) and all the other colors of corundum are known as sapphire (+ Fe^{2+} , Fe^{3+} , Ti^{4+}).
- Corundum structure : O^{2-} form a hcp structure with Al^{3+} in 2/3 of all octahedral interstitial sites.
- $\gamma\text{-Al}_2\text{O}_3$: white, hygroscopic powder with a high surface area and a good adsorption capability. Used as a support for catalysts or for chromatography. $\gamma\text{-Al}_2\text{O}_3$ is not found in nature.

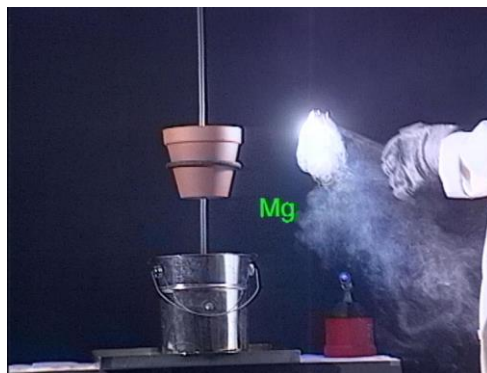


Ruby



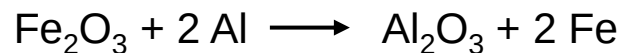
A sapphire larger than a chicken's egg that was once owned by Queen Marie of Romania was sold in 2003 for 1,916,000 Swiss francs

Aluminium – Reactions with Metal Oxides



(Video: <http://www.cci.ethz.ch>)

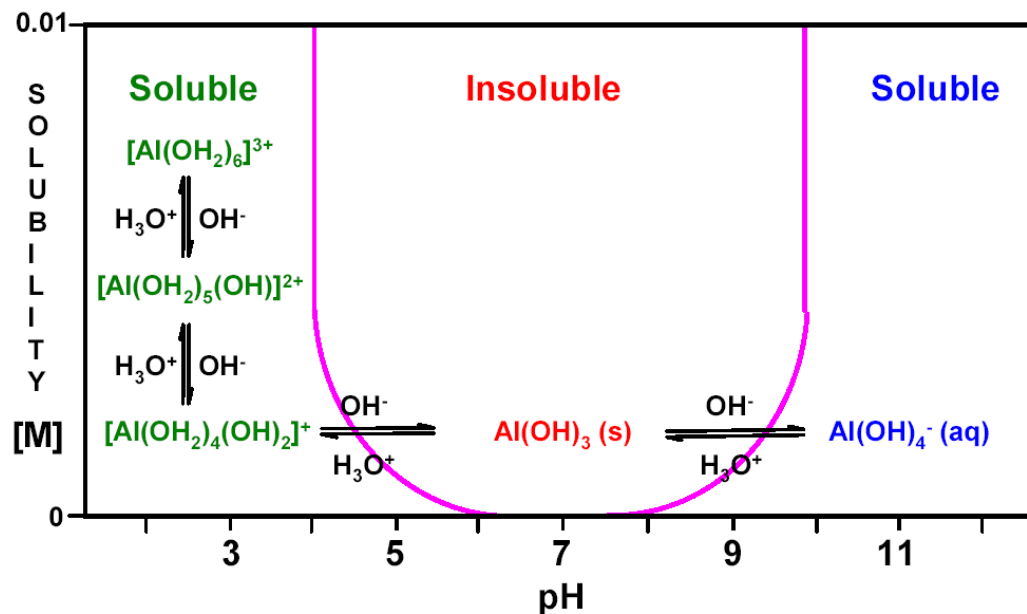
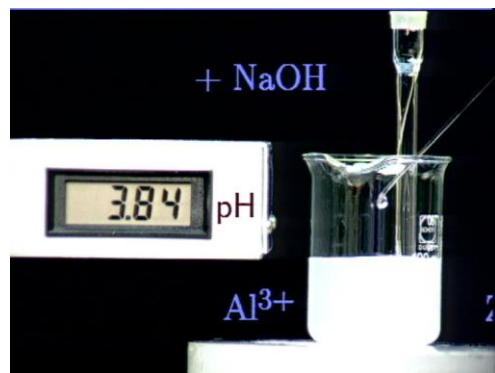
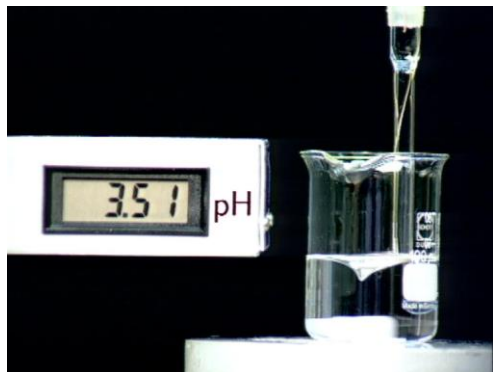
The reduction of iron(III) oxide to elementary iron by aluminum follows the following equation:



The energy released by this reaction amounts to $\Delta H = -730 \text{ kJ/mol}$. The principle of the reaction („Aluminothermisches Verfahren“ = Alumino-thermal processes) is also used for the reduction of other heavy metals oxides.

$\text{Al}(\text{OH})_3$

At neutral pH, $\text{Al}(\text{OH})_3$ precipitates as a hydrated, gel-like solid (extensive H-bonding) but it re-dissolves in excess base as $\text{Al}(\text{OH})_4^-$ forms (amphoteric behavior).



Bauxite

- Bauxite is a naturally occurring, heterogeneous material composed primarily of one or more aluminum oxide hydroxide minerals.
- Bauxite was named after the village Les Baux de Provence in southern France.
- There are numerous bauxite deposits, mainly in the tropical and subtropical regions, but also in Europe. Bauxite is generally extracted by open mining.
- Contains: $\text{AlO}_x(\text{OH})_{3-2x}$ ($0 < x < 1$).



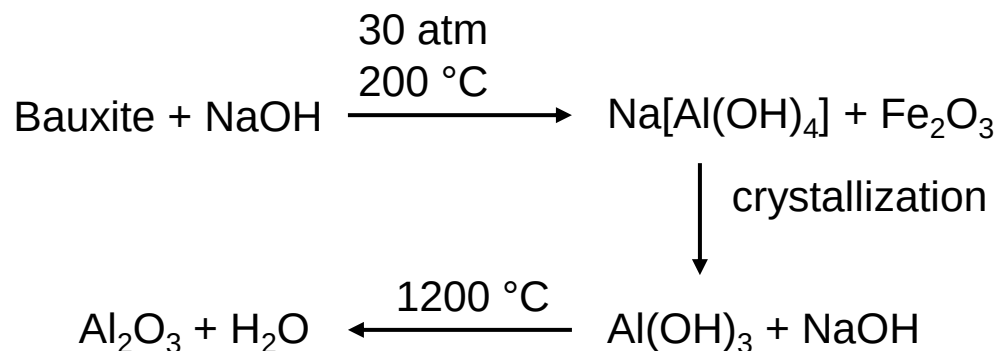
Sample of bauxite from Western Australia.



Bauxite mine.

The Bayer Process

- The process of producing pure alumina from bauxite has changed very little since the first plant was opened in 1893.
- Bauxite is purified by dissolving it in a NaOH solution.
- Removal of Fe_2O_3 and other oxides ('red mud') gives pure $\text{Al}(\text{OH})_3$ on cooling, which is dehydrated in a kiln at high temperature.



Gallium

- Predicted and described by Mendeleev as ekaaluminum.
- Sources: Gallium is often found as a trace element in diaspore, sphalerite, germanite, bauxite, and coal.
- It is one of four metals -- mercury ($-37\text{ }^{\circ}\text{C}$), cesium ($28\text{ }^{\circ}\text{C}$), and rubidium ($39\text{ }^{\circ}\text{C}$) -- which can be liquid near room temperature and, thus, can be used in high-temperature thermometers. It has one of the longest liquid ranges of any metal and has a low vapor pressure even at high temperatures.
- Gallium is widely used in doping semiconductors and producing solid-state devices such as transistors.



Partially melted gallium
(Mp. = $30\text{ }^{\circ}\text{C}$)

The Disappearing Spoon



Indium

- 1863: Indium was discovered.
- Until 1924, a gram or so constituted the world's supply of this element in isolated form but it is probably about as abundant as silver. Today, the world production is approx. 900 tonnes per year. Indium is most frequently associated with zinc materials (In^{3+} and Zn^{2+} have the same size).
- Indium is a very soft, silvery-white metal with a brilliant luster.
- Indium finds little use except in low melting alloys (an alloy of 24% indium - 76% gallium is liquid at room temperature).



If you read books about elements you will quite often come across the statement that "this element is soft enough to be cut with a knife". Vanadium and cadmium have all been thus described... although many a knife has been blunted in the attempt! At least with indium the statement is true.

Thallium

- Thallium was discovered spectroscopically in 1861. The element was named after the beautiful green spectral line, which identified the element (Gr. *thallos*: a green twig).
- A very soft, silvery white metal that tarnishes quickly in moist air but which is stable if kept away from oxygen under water.
- Thallium is one of the most toxic elements in the periodic table. It disrupts the normal metabolism of many cells by substituting potassium. Estimates of the lethal dose range from a gram down to just 50 mg. It was once an effective murder weapon before its effects became well understood and an antidote - prussian blue – was discovered.
- The halides TlX resemble AgX in color and solubility.



Thallium under water