3. Boron Group

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Gruppe
13 or IIIA

5 **B**	*1808*
13 **Al**	*1825*
31 **Ga**	*1875*
49 **In**	*1863*
81 **Tl**	*1861*
113 ***Nh***	*1998*

„Triels“

3.1 Occurrence

The Elements of the Third Main Group Do Not Exist As Elements, Because of Their High Reactivity (Aluminium Is the Most Abundant Metal of Earth's Crust)

Boron	$Na_2B_4O_7 \cdot 10H_2O$	Borax
Mineral: Borax	$Na_2B_4O_7 \cdot 4H_2O$	Kernite
	$NaCaB_5O_9 \cdot 8H_2O$	Ulexite
Aluminium (alumen)	Al_2O_3	Corundum, sapphire, ruby
Lat.: Alaun	$Al(OH)_3$	Hydrargillite
	$AlO(OH)$	Diaspore, boehmite
	$Al_2(OH)_4[Si_2O_5]$	Kaolinitic clay
	$Na_3[AlF_6]$	Cryolite
Gallium (gallia)	rare, normally accompanied by other elements, e.g. Zn	
Lat.: France	→ limited resources	
Indium	rare, mostly accompanied by Zn (ZnS)	
Indigo spectral line	→ limited resources	
Thallium (thallus)	$TlAsS_2$	Lorandite
Greek: green twig		

3.2 Properties

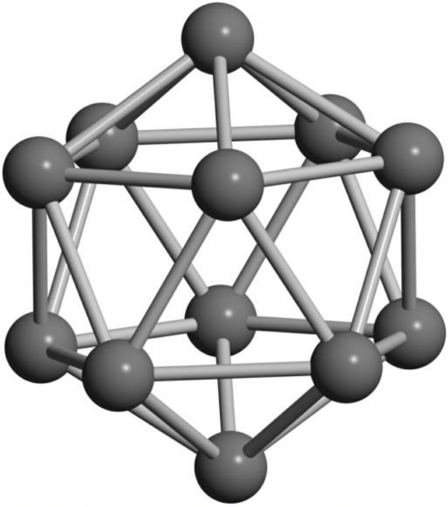
Boron Is the Most Electropositive Non-Metal (More a Semi-Metal). All Other Members of the Group Are Metals

	B	Al	Ga	In	Tl
Atomic number	5	13	31	49	81
Electronic configuration	[He] $2s^22p^1$	[Ne] $3s^23p^1$	[Ar] $3d^{10}4s^24p^1$	[Kr] $4d^{10}5s^25p$	[Xe]$4f^{14}$ $5d^{10}6s^26p^1$
Electronegativity	2.0	1.5	1.8	1.5	1.4
Ionisation energy [eV]	8.3	6.0	6.0	5.8	6.1
Standard potential Me/Me^{3+} [V]	-0.87	-1.68	-0.53	-0.34	+0.72
Oxidation states	+3	+3	(+1), +3	(+1), +3	+1, +3
Melting point T_m [°C]	2080	660	30	157	304
Boiling point T_b [°C]	3860	2518	2200	2080	1457
Density [g/cm³]	2.34	2.70	5.91	7.31	11.85

- The most stable oxidation state of B, Al, Ga and In is +3 as one would expect
- Ga^+ and In^+ are strong reducing agents
- Tl^{3+} is a strong oxidising agent

3.3 Boron - Elemental Structures

Four Crystalline Modifications of Boron Are Known, Wherein The Common Structural Unit Consists of B_{12}-Icosahedrons (20 Facets)



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α-rhombohedral boron

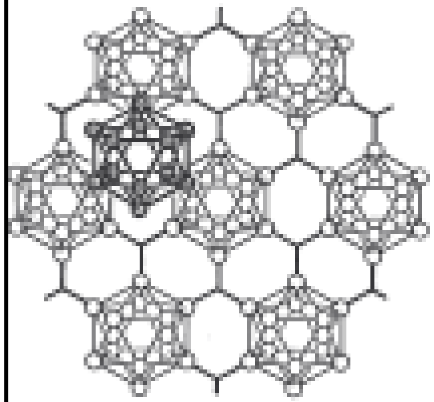
Cubic closed packing of B_{12}-icosahedrons

α-tetragonal boron

Hexagonal closed packing of B_{12}-icosahedrons + individual boron atoms

ß-rhombohedral boron

Complex structure with 105 B atoms per unit cell



ß-tetragonal boron

Complex structure with 190 B atoms per unit cell

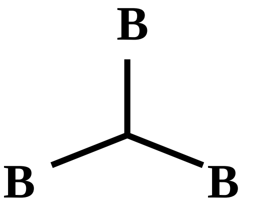
The complexity of the structures is a result of the shortage of electrons of boron which possess 4 valence orbitals but only 3 electrons

⇒ open and closed 2-electrons-3-center bonds (2e3c)

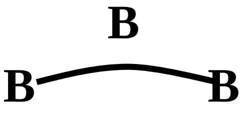
3.3 Boron – Elemental Structures

Typical For the Structures of the Allotropic Boron Modifications and For the Boranes Are Two- and Three-Center-Bonding

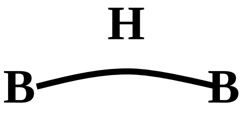
Three-Center-Bonding



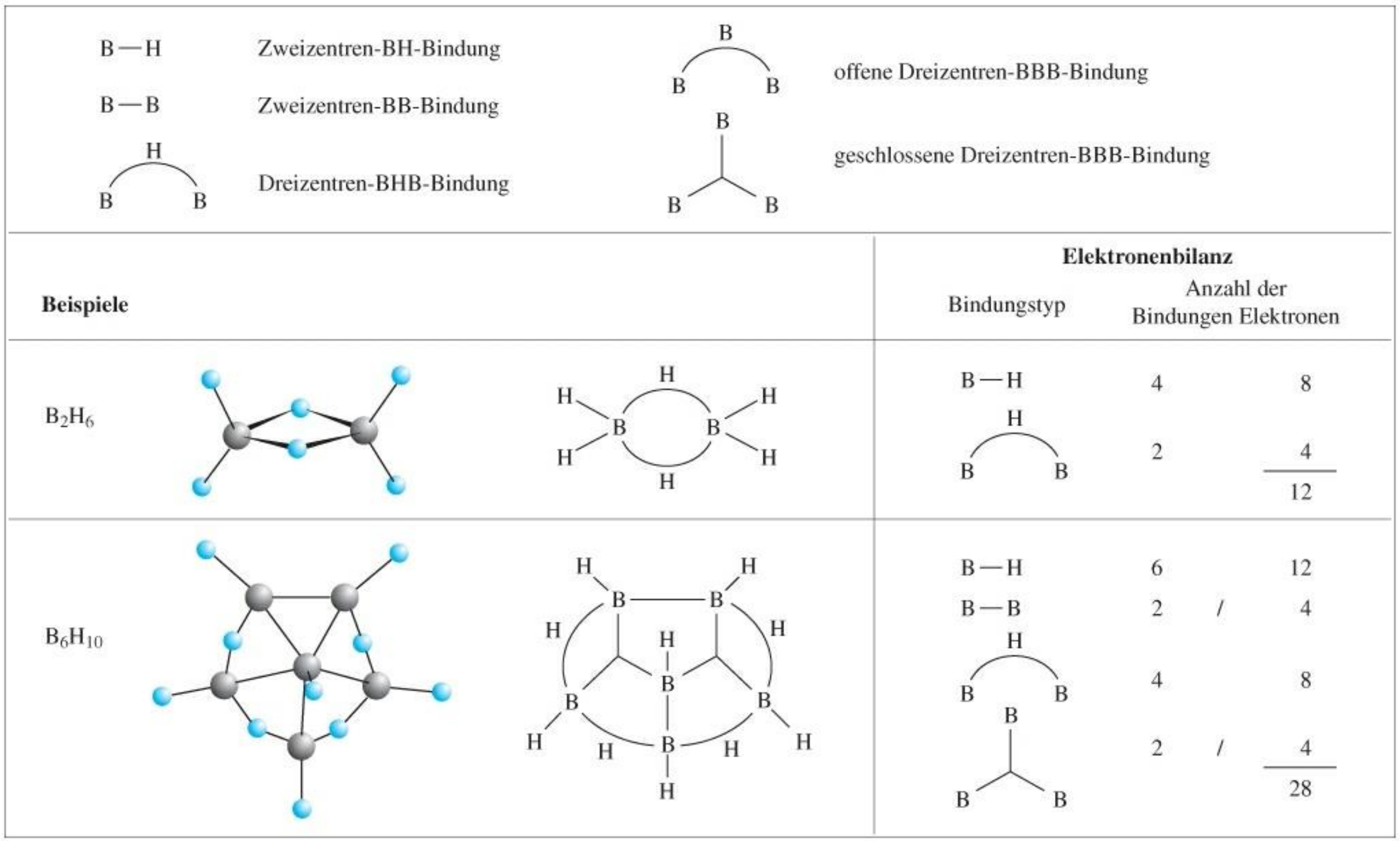
sp^3 sp^3 sp^3



sp^3 p sp^3



sp^3 s sp^3



B—H	Zweizentren-BH-Bindung
B—B	Zweizentren-BB-Bindung
$B \overset{H}{\frown} B$	Dreizentren-BHB-Bindung
$B \overset{B}{\frown} B$	offene Dreizentren-BBB-Bindung
$\overset{B}{\underset{B \quad B}{\curlywedge}}$	geschlossene Dreizentren-BBB-Bindung

Beispiele	Elektronenbilanz		
	Bindungstyp	Anzahl der Bindungen	Elektronen
B_2H_6	B—H	4	8
	$B \overset{H}{\frown} B$	2	4
			12
B_6H_{10}	B—H	6	12
	B—B	2 /	4
	$B \overset{H}{\frown} B$	4	8
	$\overset{B}{\underset{B \quad B}{\curlywedge}}$	2 /	4
			28

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3.4 Synthesis and Chemical Behaviour

Boron

Synthesis

- Reduction of boron halides: $2\ BCl_3(g) + 3\ H_2(g) \rightarrow 2\ B(s) + 6\ HCl(g)$
- Metallothermal reduction of boron oxide: $B_2O_3 + 3\ Mg \rightarrow 2\ B + 3\ MgO$

Chemical behaviour

- At room temp. B reacts sluggishly and solely oxidising acids can oxidise it to boric acid
- Formation of metal borides: Mn_4B, CrB, TiB_2, MgB_2, WB_4, CaB_6, YB_{66}

Aluminium

Synthesis (annual production 1990: $18.5 \cdot 10^6$ t, 2002: $25.5 \cdot 10^6$ t, 2014: $53.9 \cdot 10^6$ t)

- F. Wöhler 1827: $AlCl_3(s) + 3\ K(s) \rightarrow Al(s) + 3\ KCl(s)$
- 1. Step: Al_2O_3-Formation from bauxite ($AlO(OH) + Fe_2O_3$) by Bayer-process

  $AlO(OH)(s) + Fe_2O_3(s) + NaOH(s) \rightarrow Na[Al(OH)_4](aq) + Fe_2O_3(s)$ → "Red mud"

  $2\ Na[Al(OH)_4] + Al(OH)_3$-Seed cystal $\rightarrow 2\ NaOH + 2\ Al(OH)_3 \xrightarrow{\Delta T} Al_2O_3(s) + 3\ H_2O(l)$

  2. Step: Fused-salt electrolysis of Al_2O_3 with the addition of cryolite (Na_3AlF_6) as a flux (eutectic at 18.5 mol-% Al_2O_3: $T_m = 935\ °C$)

  Cathode: $Al^{3+} + 3\ e^- \rightarrow Al(l)$

  Anode: $2\ O^{2-} + C(s) \rightarrow CO_2(g) + 4\ e^-$

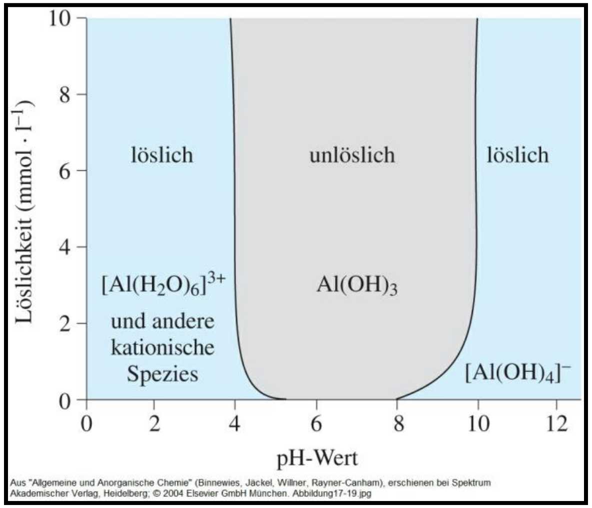
3.4 Synthesis and Chemical Behaviour

Aluminium

Chemical behaviour

- **Oxidation:** $4\ \text{Al(powder)} + 3\ \text{O}_2\text{(g)} \rightarrow 2\ \text{Al}_2\text{O}_3\text{(s)} : \Delta H°_R = -3352\ \text{kJ/mol}$
  $\Rightarrow$ **flash lamp for photography**
- **With diluted acids:** $2\ \text{Al(s)} + 6\ \text{H}_3\text{O}^+\text{(aq)} \rightarrow 2\ \text{Al}^{3+}\text{(aq)} + 3\ \text{H}_2\text{(g)} + 6\ \text{H}_2\text{O(l)}$
- **With oxidising acids:** **Passivation through oxidation of the surface**
- **In alkaline solution:** $2\ \text{Al(s)} + 2\text{OH}^-\text{(aq)} + 6\ \text{H}_2\text{O(l)} \rightarrow 2\ [\text{Al(OH)}_4]^-\text{(aq)} + 3\ \text{H}_2\text{(g)}$
- **In diluted aqueous solutions Al^{3+} forms a hexaaqua aluminate ion which reacts as an acid:**
  $[\text{Al(H}_2\text{O)}_6]^{3+}\text{(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons [\text{Al(OH)(H}_2\text{O)}_5]^{2+}\text{(aq)} + \text{H}_3\text{O}^+\text{(aq)}$
- **Solubility of Al^{3+}:**

$\text{pH} < 4$	$[\text{Al(H}_2\text{O)}_6]^{3+}$
$4 < \text{pH} < 9$	Al(OH)_3
$\text{pH} > 9$	$[\text{Al(OH)}_4]^-$



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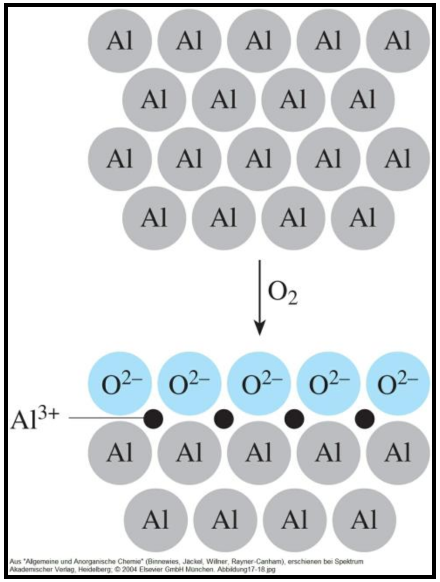

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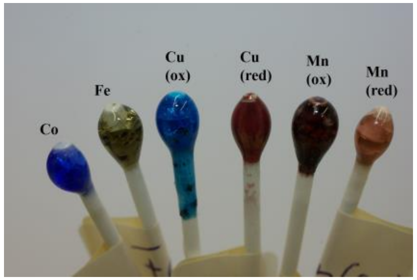
3.5 Applications

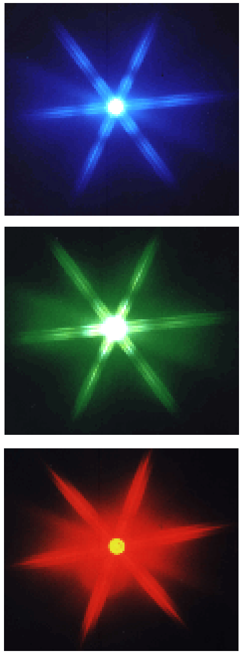
Boron

- ^{10}B exhibits high neutron capturing cross-section ⇒ moderator in nuclear power plants
- Deoxidising agent in metallurgy
- Ferroboron for the tempering of steel
- Borax as flux: Solid state chemistry, borax pearls



Aluminium

- Low density (2.7 g/cm^3): aviation/automotive industry, engineering, containers, pack.
- High thermal conductivity: frying pans and cookware
- Moderate electronic conductivity: high voltage cable



Gallium, Indium

- Form semi-conducting III/V-compounds: (In,Ga)N, (In,Ga)P, (In,Ga)As LEDs
- Alloying constituent in babbit metal
- Indium halides as blue emitter in discharge lamps: In^{3+} lines/InX band
- For transparent semiconductors, e.g. SnO_2:In (ITO) or SnO_2:Sb (ATO)

Thallium

- Of some importance in forensics (Tl-verification in case of intoxication)
- Tl/Hg alloys with 8.7% Tl freezes at -60 °C: low-temperature thermometer

3.6 Boron-Oxygen Compounds

Boric Acids and Boron Trioxide

Ortho-boric acid H_3BO_3

- $B(OH)_3(aq) + H_2O(l) \rightarrow H^+(aq) + [B(OH)_4]^-$
- Acts as mono-protonic acid
- reacts with alcohols and sugars to esters
  $B(OH)_3(s) + 3\ MeOH(l) \rightarrow B(OMe)_3(l) + 3\ H_2O(l)$
- T = 150 °C: $H_3BO_3(s) \rightarrow HBO_2(s) + H_2O(g)\uparrow$
- T = 300 °C: $4\ HBO_2(s) \rightarrow H_2B_4O_7(s) + H_2O(g)\uparrow$

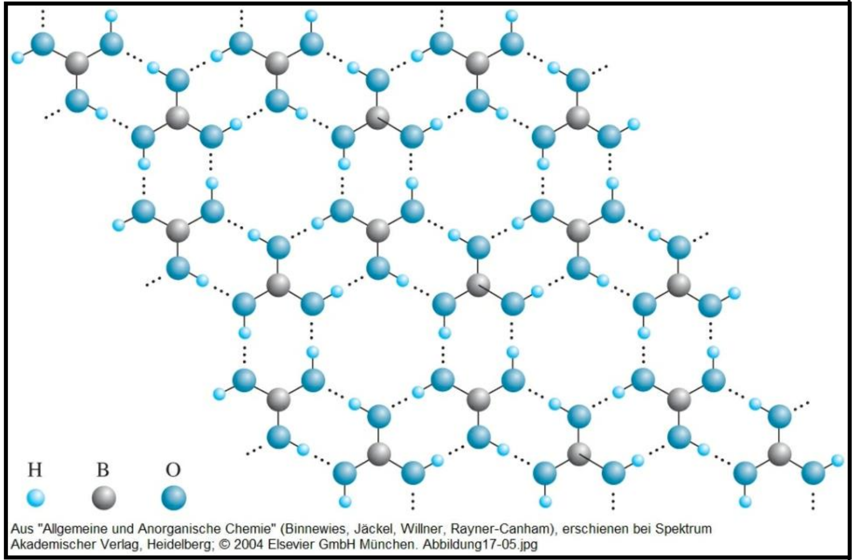
Meta-boric acid HBO_2

- Hydrolysis leads to H_3BO_3
- T = 500 °C: $2\ HBO_2(s) \rightarrow B_2O_3(s) + H_2O(g)\uparrow$

Boron oxide B_2O_3

- Hydrolysis leads to H_3BO_3
- $B_2O_3 + MO \rightarrow M(BO_2)_2$
- $B_2O_3 + Ln_2O_3 \rightarrow 2\ LnBO_3$ (Ln = Sc, Y, La-Lu)
- $SrO + 2\ B_2O_3 \rightarrow SrB_4O_7$
- $Gd_2O_3 + 2\ MgO + 5\ B_2O_3 \rightarrow 2\ GdMgB_5O_{10}$

Structure of crystalline ortho-boric acid



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Dotierung	Applications
$Co^{2+/3+}$, Fe^{2+}, etc.	Borax pearls
Eu^{3+}, Tb^{3+}, Tm^{3+}	Plasma displays
Eu^{2+}	UV (λ = 366 nm)
Ce^{3+}, Tb^{3+}	Fluorescent lamps

3.6 Boron-Oxygen Compounds

Borates

Ortho-borates

- Isolated trigonal planar $[BO_3]^{3-}$-units
- Polymorph $LnBO_3$-phases are isomorph to $CaCO_3$-modifications (calcite, vaterite, aragonite)

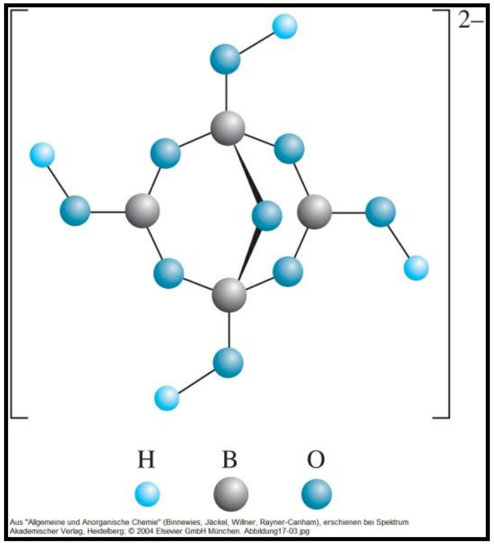
Meta-borates

- BO_3-units are combined to rings by oxygen atoms
- Hydroxo borates such as $[B_3O_3(OH)_5]^{2-}$ and $[B_4O_5(OH)_4]^{2-}$ are hydrolysed meta-borates

Per-borates

- Contain $[B_2(O_2)_2]$-units
- Application as sodium per-borate in detergents (→ presentations)

Structure of $[B_4O_5(OH)_4]^{2-}$



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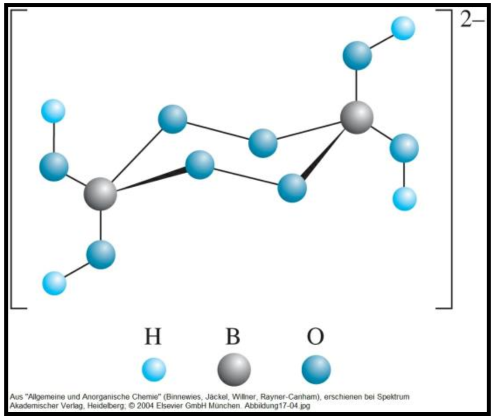
Structure of $[B_2(O_2)_2(OH)_4]^{2-}$



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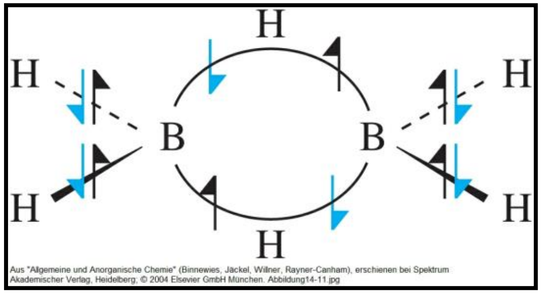
3.7 Boranes

Boron Hydrogen Compounds consist of Three-Center-Bondings (Octet Rule) Since They Suffer from Electron Deficiency and Are Thus Highly Reactive



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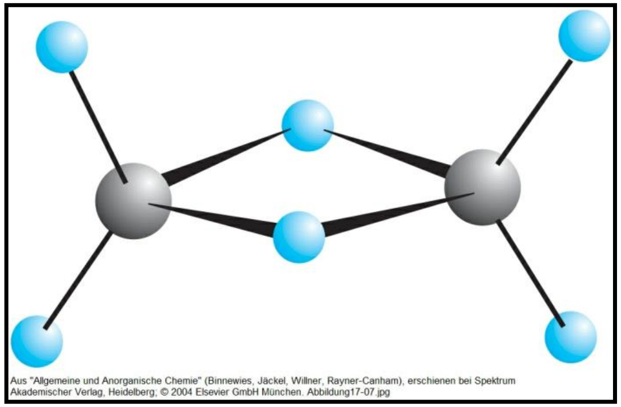
Diborane B_2H_6

- Synthesis: $2\ BF_3(g) + 6\ NaH(s) \rightarrow B_2H_6(g) + 6\ NaF(s)$
- Hydrolysis: $B_2H_6(g) + 6\ H_2O(l) \rightarrow B_2O_3(s) + 3\ H_2(g)$
- Oxidation: $B_2H_6(g) + 3\ O_2(g) \rightarrow B_2O_3(s)$
- Structure: Dimer



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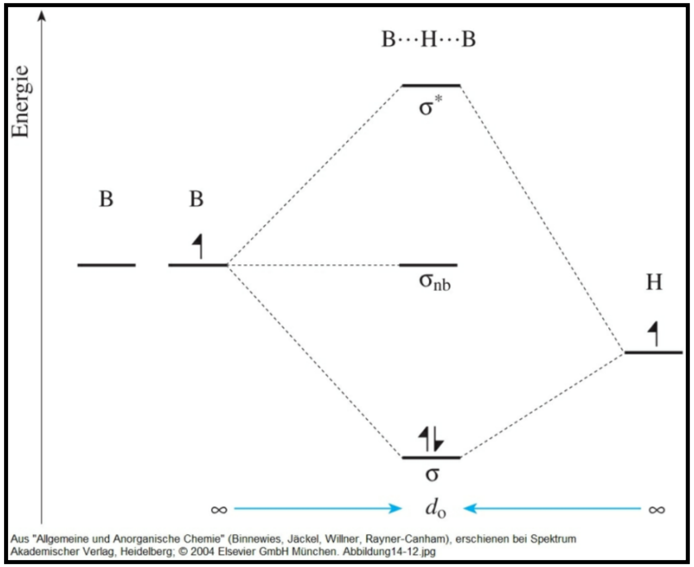

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Sodium tetrahydridoborate $NaBH_4$

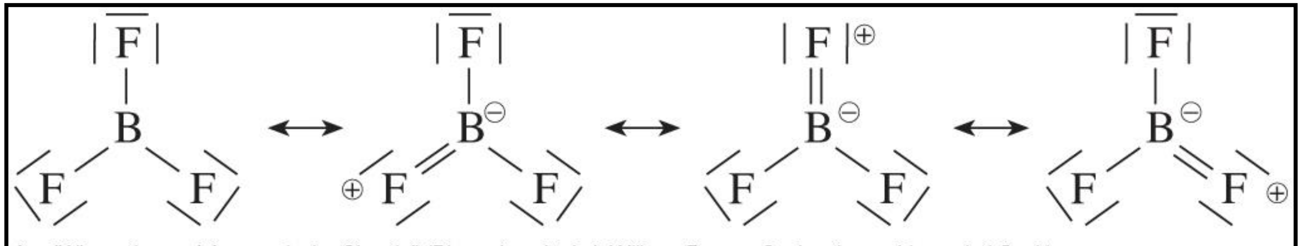
- $4\ NaH(s) + B(OH)_3(s) \rightarrow NaBH_4 + 3\ NaOCH_3$
- Only borane that is used on greater scale
- Reducing agent in organic chemistry:

aldehydes → primary alcohols
ketones → secondary alcohols

3.8 Boron Halides

Boron Halides Are Electron Deficiency Compounds As Well and Form π-Bonds

⇒ Monomers and Trigonal Planar Built



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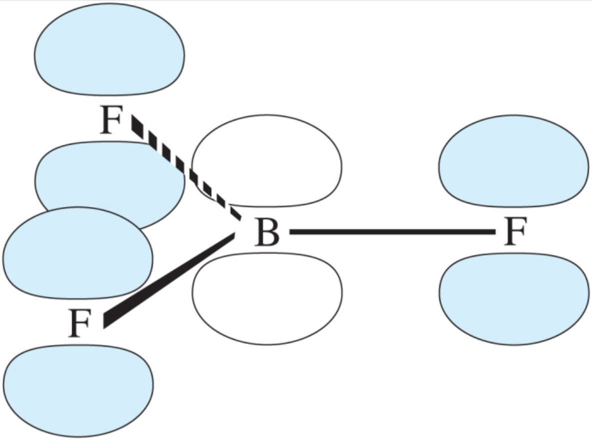

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Synthesis

- $B_2O_3(s) + 6\ HF(g) \rightarrow 2\ BF_3(g) + 3\ H_2O(l)$
- $Ph\text{-}N{\equiv}N^+ + BF_4^- \rightarrow Ph\text{-}F + BF_3 + N_2$
- $B_2O_3 + 3\ C + 3\ Cl_2 \rightarrow 2\ BCl_3 + 3\ CO$

Reactions with water

- $4\ BF_3 + 3\ H_2O \rightarrow HBF_4 + 3\ H_3BO_3$
- $BX_3 + 3\ H_2O \rightarrow 3\ HX + H_3BO_3$

The σ-bonding system in BF_3 is formed by linear combination of the three atomic orbitals of boron, 2s, $2p_x$ and $2p_y$, and three 2p -orbitals of the fluorine atoms. Additionally, 4 π-MOs are formed through the interaction between the $2p_z$-orbital of boron with the three $2p_z$-orbitals of the fluorines.

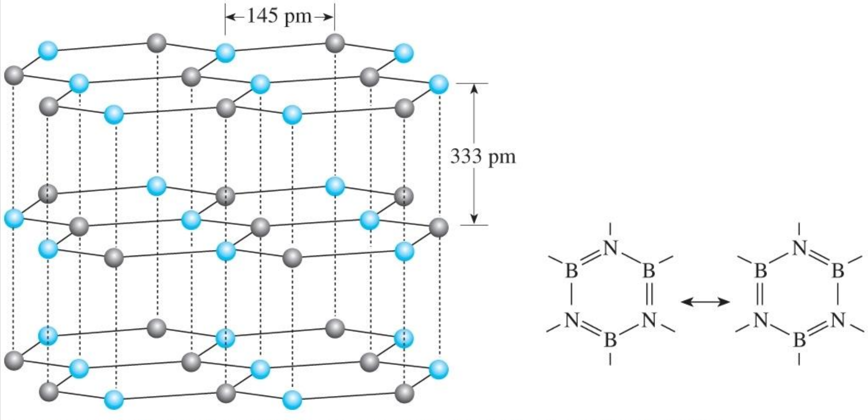
3.9 Boron-Nitrogen Compounds

Boron Nitride

$2\,BBr_3 + 6\,NH_3 \rightarrow 2\,B(NH_2)_3 \rightarrow 2\,B(NH)_{1.5} \rightarrow (BN)_x$ „polymeric boron nitride“

Technical synthesis

• $B_2O_3 + 2\,NH_3 \rightarrow 2\,BN + 3\,H_2O$	800 – 1200 °C in $Ca_3(PO_4)_2$ - matrix
• $B_2O_3 + 3\,C + N_2 \rightarrow 2\,BN + 3\,CO$	1800 – 1900 °C



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Structures

• α-BN	hexagonal (similar to graphite)
• ß-BN	cubic (diamond-like structure)
• γ-BN	meta-stable (wurtzite structure)

Properties

- colourless
- no electronic conductor (in contrary to graphite)
- thermally extremely stable (T_m = 3270 °C)

⇒ high-temperature lubricant, fire-proof coatings/linings

3.9 Boron-Nitrogen Compounds

Borazine

Borazine is sometimes also called “inorganic benzene”

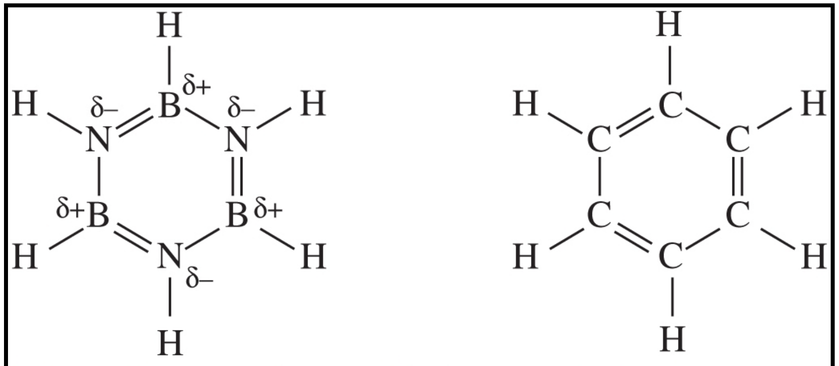
Synthesis

From diborane and NH_3 at 250-300 °C

$$3\ B_2H_6 + 6\ NH_3 \rightarrow 6\ H_3B\text{-}NH_3 \xrightarrow[-6\ H_2]{} 6\ H_2B\text{=}NH_2 \xrightarrow[-6\ H_2]{} 6\ HB\equiv NH \xrightarrow[\text{trimerisation}]{} 2\ (HB\equiv NH)_3$$

(diborane) (borazane) (borazene) (borazine)

Structure ⇒



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Properties

Polar B-N bond leads to higher reactivity in comparison to benzene

⇒ Ready addition of Br_2 or HCl

3.10 Boron-Oxygen Compounds

Aluminium Oxide and Aluminates

Synthesis: see production of aluminium

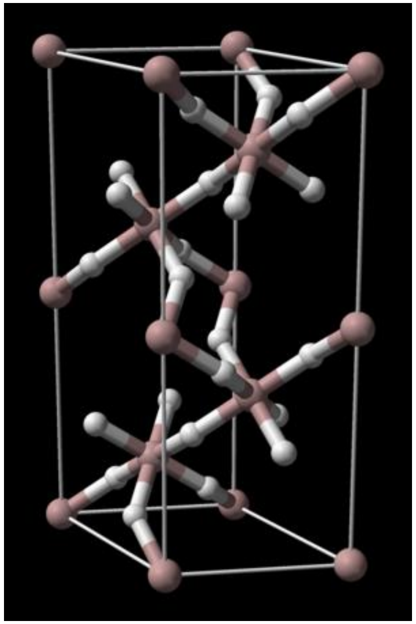
Al_2O_3 modifications

γ-Al_2O_3	forms from $Al(OH)_3$ at 400 °C
	insoluble in water, soluble in strong acids and bases
	catalyst, catalyst substrate, $T < 600$ °C, OH groups
α-Al_2O_3	forms during tempering of γ -Al_2O_3 at $T > 1000$ °C
(corundum)	abrasive, polishing agent, fire-resistant material ($T_m = 2055$ °C)
	artificial gemstone (ruby: α-Al_2O_3 + 0.2% Cr_2O_3 at $T > 2200$ °C)
ß-Al_2O_3	= $NaAl_{11}O_{17}$ „layered structure with good Na^+-ion conductivity“

Alum	$M^IM^{III}(SO_4)_2{\cdot}12H_2O$, e.g. $KAl(SO_4)_2{\cdot}12H_2O \Rightarrow$ shaving stone
Aluminates	$MeO + Al_2O_3 \rightarrow MeAl_2O_4$ (Me = Mg, Zn, Fe, Co) $\Rightarrow$ spinels
	$MeO + Al_2O_3 \rightarrow MeAl_2O_4$ (Me = Ca, Sr, Ba)
	$\Rightarrow$ „Afterglow“ phosphors: $CaAl_2O_4{:}Eu^{2+},Tm^{3+}$ 440 nm
	$SrAl_2O_4{:}Eu^{2+},Dy^{3+}$ 525 nm

3.11 Aluminium Hydrides

Alane and Alanates



Alane AlH_3

Synthesis: $3\ LiAlH_4 + AlCl_3 \rightarrow 3\ LiCl + 4\ AlH_3$ (in ether)

Properties: white powder, because it is polymeric $((AlH_3)_x)$

CN 6 $AlH_{6/2}$

highly air and moisture sensitive!

three-center-two-electrons-bonding

Alanates $MeAlH_4$

Synthesis: $AlX_3 + 4\ LiH \rightarrow LiAlH_4 + 3\ LiX$ (X = Cl, Br)

Properties: strong reducing agent

strong hydration agent

storage of hydrogen?

3.12 Aluminium Halides

The Properties of the Aluminium Halides Are Defined by the Polarisability of the Anions

Ionic charge density Al^{3+} = 370 C/mm³ ⇒ strong polarising effect!

AlX_3	T_m [°C]	Structure
X = F	1290	lattice made of AlF_6-octahedrons
X = Cl	183 (sublimed)	solid: lattice, fluid and gaseous phase: Al_2Cl_6-dimers
X = Br	97.5	Al_2Br_6-dimers
X = I	190	Al_2I_6-dimers

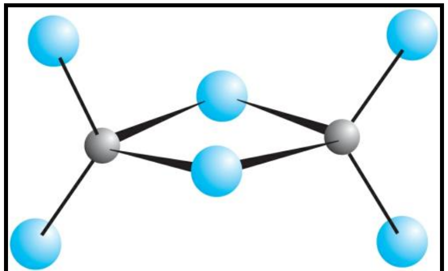
$AlF_3 + x\ MeF \rightarrow Me[AlF_4], Me_2[AlF_5], Me_3[AlF_6]$ Me = Na „cryolite“

$AlCl_3 + H_2O \rightarrow Al(OH)_3 + 3\ HCl$

$AlCl_3 + R\text{-}Cl \rightarrow R^+ + [AlCl_4]^-$

$R^+ + Ar\text{-}H \rightarrow Ar\text{-}R + H^+$ „Friedel-Crafts-Alkylation“

structure of Al_2X_6



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3.13 Gallium and Indium

Gallium and Indium Are Metals With Low Melting Points and High Ductility

Formation of III/V-semi conductors (W = wurtzite, hexagonal ZnS; S = sphalerite, cubic ZnS)

	GaN	GaP	GaAs	GaSb	InN	InP	InAs	InSb
Structure	W	S	S	S	W	S	S	S
T_m [°C]	>1050	1465	1238	712	>300	1070	942	525
E_G [eV]	3.7	2.3	1.5	0.7	1.9	1.4	0.4	0.2
E_G [nm]	370	520	830	1800	660	900	3100	6200

Formation of gallates and indates (analogous to aluminates)

$SrO + Me_2O_3 \rightarrow SrMe_2O_4$ (Me = Ga, In)

$SrS + Me_2S_3 \rightarrow SrMe_2S_4$ (Me = Ga, In) „thiogallate and thioindate“

$SrGa_2S_4$:Eu (λ_{max} = 525 nm) is a prominent phosphor in electro luminescence displays

Stability of the monovalent oxidation state increases:

Formation of I/III-compounds: $MeCl_2 = Me^I[Me^{III}Cl_4]$ (Me = Ga, In)

Of technical importance is ITO = Indium-Tin-Oxide: $SnO_2:In^{3+}$ for transparent electrodes

3.14 Thallium and the Inert-Pair Effect

Tl(III)-Compounds Are Strong Oxidising Agents, while Tl(I)-Compounds Are Stable

Ionisation enthalpy [MJ/mol]	$X(g) \rightarrow X^+(g) + e^-$	$X^+(g) \rightarrow X^{2+}(g) + e^-$	$X^{2+}(g) \rightarrow X^{3+}(g) + e^-$
Aluminium	0.58	1.82	2.75
Thallium	0.60	1.98	2.88

Explanation:
The 6s-electrons are strongly bound at the nucleus due to the high nucleus charge
⇒ shrinkage of the 6s-orbital ⇒ stable s^2-ions (Tl^+, Pb^{2+}, Bi^{3+})

Chemical Properties

- $4\ Tl + O_2 \rightarrow 2\ Tl_2O$
- $Tl_2O + H_2O \rightarrow 2\ TlOH$
- $2\ TlOH + CO_2 \rightarrow Tl_2CO_3 + H_2O$
- **Tl^+ forms hardly soluble halides: $Tl^+ + X^- \rightarrow TlX\downarrow$ (X = Cl, Br, I)**
- **Strong resemblance to lead!**

3.15 Biological Aspects

Aluminium

- The cation is toxic to humans and animals
- $5 \cdot 10^{-6}$ mol/l in water suffices to kill fish
- Decrease in pH-value of waters leads to increasing Al^{3+}-concentrations
- Tea contains a rather high amount of Al^{3+}-ions, which can be masked through complexation by the addition of milk or lemon
- Acidosis of soils leads to the release of Al^{3+}-ions

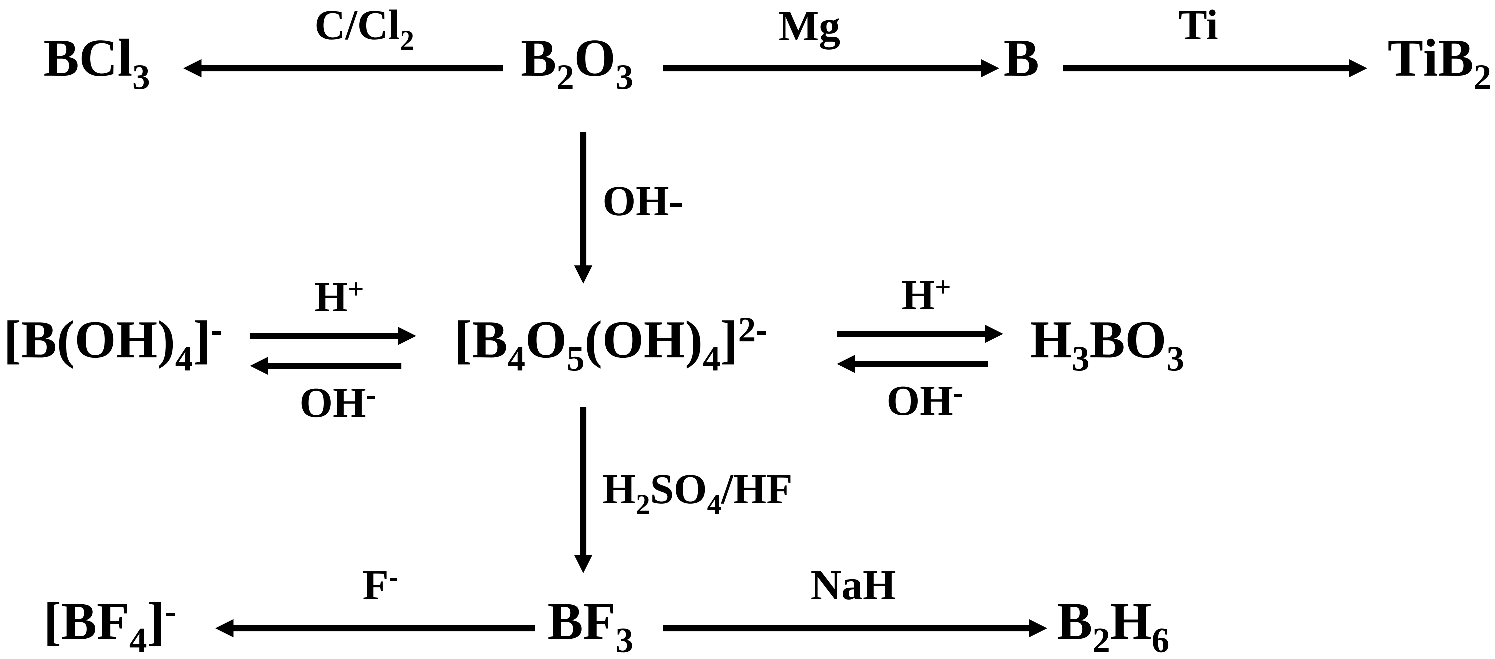
$\Rightarrow$ some plants can grow even on acidic soil, due to their ability to synthesise citric or malic acid

Thallium

- Highly toxic, due to its similarity to K^+ as a big water soluble ion, that can easily penetrate cells and disturb enzymatic processes there
- Tl_2SO_4 is used as rat poison
- Tl-salts are popular toxins in Agatha Christies (1890-1976) novels

Overview Boron Chemistry

Oxidation States: +III, 0, -II, -III



$$\begin{tikzcd}
BCl_3 & B_2O_3 \arrow[l, "C/Cl_2"'] \arrow[r, "Mg"] \arrow[d, "OH-"] & B \arrow[r, "Ti"] & TiB_2 \\
{[B(OH)_4]^-} \arrow[r, shift left, "H^+"] & {[B_4O_5(OH)_4]^{2-}} \arrow[l, shift left, "OH^-"] \arrow[r, shift left, "H^+"] \arrow[d, "H_2SO_4/HF"] & H_3BO_3 \arrow[l, shift left, "OH^-"] & \\
{[BF_4]^-} & BF_3 \arrow[l, "F^-"'] \arrow[r, "NaH"] & B_2H_6 &
\end{tikzcd}$$

Overview Aluminium Chemistry

Oxidation States: +III, 0