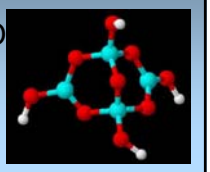
Groups 3, 13, Lanthanoides

B, Al, Ga, In Tl,
Sc, Y, La
Ln

Boron

Borax $Na_2[B_4O_5(OH)_4]8H_2O$
often seen as $Na_2[B_4O_7]10H_2O$



Salt hydrolyses in water:

$[B_4O_5(OH)_4]^{2-} + 5H_2O \rightarrow 2B(OH)_4^- + 2B(OH)_3$

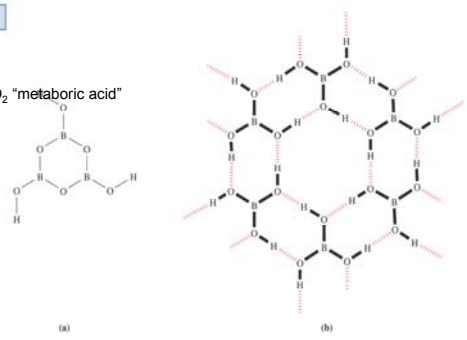
tetraborate anion — borate tetrahedral — boric acid planar

pH in borax = pK (9.1) for boric acid:

$B(OH)_3 + H_2O \leftrightarrows B(OH)_4^- + H^+_{aq}$

13.18

HBO_2 "metaboric acid"



(a) (b)

Fig. 13.17 The structure of metaboric acid, $B_3O_3(OH)_3$. (b) Schematic representation of part of one layer of the solid state lattice of boric acid (orthoboric acid), $B(OH)_3$; covalent bonds within each molecule are highlighted in bold, and intermolecular hydrogen bonds are shown by red hashed lines. The hydrogen bonds are asymmetrical, with O–H = 100 pm and O···O = 270 pm.

Housecroft and Sharpe, *Inorganic Chemistry*, 3rd Edition © Pearson Education Limited 2008

Boric acid analysis

Identification: Planar trimethylborate (ester) volatile, green flame

$B(OH)_3 + 3CH_3OH \rightarrow B(OCH_3)_3 + 3H_2O$

Quantification:

$$B(OH)_3 + \begin{matrix}CH_2OH\\CHOH\\CH_2OH\end{matrix} \rightarrow B(C_3H_6O_3)_2^- + H^+ + 3H_2O$$

bisglycerolatoborate: tetrahedral

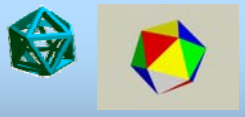
(or other poly-alcohols)

Boron

$2B(OH)_3 \rightarrow B_2O_3 + H_2O$

$3Mg + B_2O_3 \rightarrow 2B + 3MgO$

Silver-gray crystals (amorphous brown), mp~2450°C, hard, isolator – complicated structure: Basic unit B_{12} Icosahedron



B_{84} ($B_{12} + B_{12} + B_{60}$)

Fig 13.7

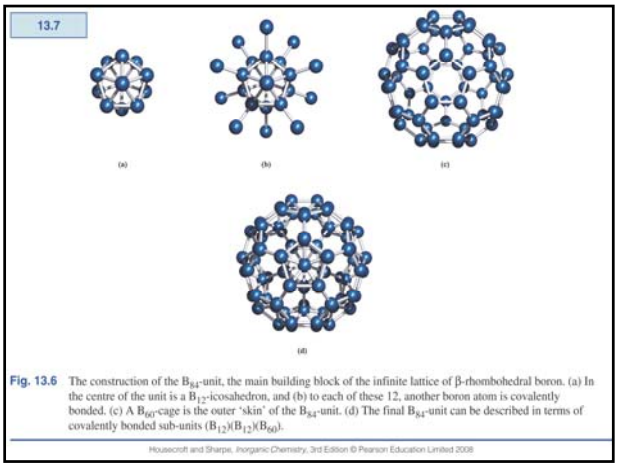


Fig. 13.6 The construction of the B_{84}-unit, the main building block of the infinite lattice of β-rhombohedral boron. (a) In the centre of the unit is a B_{12}-icosahedron, and (b) to each of these 12, another boron atom is covalently bonded. (c) A B_{60}-cage is the outer 'skin' of the B_{84}-unit. (d) The final B_{84}-unit can be described in terms of covalently bonded sub-units (B_{12})(B_{12})(B_{60}).

Boron hydrides - boranes

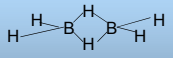
Stock: Nobel prize 1976

$Mg + 2B \rightarrow MgB_2$

$MgB_2 + H_2O \rightarrow MgO + B_xH_y$

$4NaH + B(OCH_3)_3 \rightarrow NaBH_4 + 3NaOCH_3$

$NaBH_4 + BF_3 \rightarrow B_2H_6 + NaBF_4$

B_2H_6 

central H's: 3-center.2-electron bonds
terminal H's:2-center.2-electron bonds

Boron halides

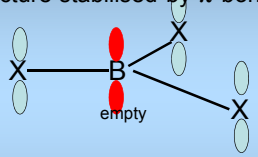
Preparation

- $Na_2B_4O_5(OH)_4 + 12HF \rightarrow Na_2O(BF_3)_4$; + $H_2SO_4 \rightarrow 4BF_3 + 2NaHSO_4 + H_2O$
  not $B(OH)_3 + 4HF \leftrightarrow H_3O^+ + BF_4^- + 2H_2O$
- $B_2O_3 + 3C + Cl_2/Br_2 \rightarrow 6CO + 2BCl_3/2BBr_3$

	BF_3	BCl_3	BBr_3	BI_3
Mp °C	-127	-107	-46	50
Bp °C	-100	12.5	91	210
ΔH_f^o (g)	646	444	368	267
r_{B-X}	1.30	1.75	1.87	2.10
$+H_2O$	$BF_4^- + B(OH)_3$	$HCl + B(OH)_3$	$HBr + B(OH)_3$	$HI + B(OH)_3$

Boron halides

planar structure stabilised by π-bonding



Lewis acid properties

(planar) $X_3B + L \leftrightarrow X_3B{:}L$ (tetrahedral)

$K_{X=F} < K_{X=Cl} < K_{X=Br} < K_{X=I}$

Boron - Nitrogen

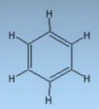
$3BCl_3 + 3NH_3 \rightarrow (BClNH)_3 \rightarrow BN + HCl$

	layers/Å	d/gml^{-1}	X-X/Å
Hexagonal BN	3.33	2.29	1.446
Graphite	3.35	2.26	1.415

	cell constant	hardness
Kubic BN	3.567Å	10
Diamond	3.615	10

Borazine $(BNH_2)_3$

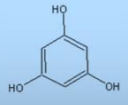
$3B_2H_6 + 6NH_3 \rightarrow 2\ B_3N_3H_6 + 12H_2$



benzene-like (density, liquid, distances)

$B_3N_3H_6 + 3H_2O \rightarrow (BOH)_3(NH)_3 + 3H_2$

$HB{=}NH + HO\text{-}H \rightarrow HOH\overset{-}{B}\text{-}\overset{+}{N}H_2$



$100\ ^oC \rightarrow HOB\text{-}NH + H_2$

Al, Ga, In, Tl

	Al	Ga	In	Tl
Σ Ionisation potentials	5138	5520	5082	5437
Electron configuration	[Ne] $3s^23p^1$	[Ar]$3d^{10}$ $4s^24p^1$	[Kr]$4d^{10}$ $5s^2p^1$	[Xe]$4f^{14}5d^{10}$ $6s^26p^1$
Electric resistivity	2.7	27	8.4	18
$E^o\ M \rightarrow M^{3+}$	-1.66	-0.56	-0.34	0.72
MP ^oC	660	30	157	304

Al^{3+} - H_2O

$Al(H_2O)_6^{3+} \leftrightarrows Al(H_2O)_5OH^{2+} + H^+$ pK~5.0

Short notation $Al^{3+} \leftrightarrows Al(OH)^{2+} + H^+$

$Al(OH)^{2+} \leftrightarrows Al(OH)_2^{+} + H^+$ pK~5.5

$Al(OH)_2^{+} \leftrightarrows Al(OH)_3 + H^+$ pK~6.5

$Al(OH)_3 \leftrightarrows Al(OH)_4^{-} + H^+$ pK~7.5

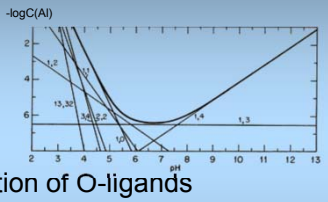
$2Al(OH)^{2+} \leftrightarrows Al(OH)_2Al^{4+}$ K~10^2

$\leftrightarrows Al_3(OH)_4^{3+}$

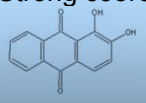
$\leftrightarrows Al_{13}(OH)_{32}^{7+}$

Al^{3+} - H_2O

Equilibrium distribution with solid $Al(OH)_3$



Strong coordination of O-ligands



in base → red insoluble ppt.

Al^{3+} - X^-

$Al_2O_3 + 6HF \rightarrow 2AlF_3(s)$ $+3F^- \leftrightarrows AlF_6^{3-}$

$Al + {}^{3/2}X_2 \rightarrow AlX_3$

$AlCl_3 + RCl \rightarrow AlCl_4^- + R^+$ (Friedel-Craft)

$Na + Al + H_{2\ (3\ atm)} \rightarrow NaAlH_4$

$NaAlH_4 + LiCl \rightarrow {}_{\text{in ether}}\ LiAlH_4 + NaCl$

$LiMH_4$ M=	B	Al	Ga	In	Tl
Dec. temperature	380	100	50	0	0

Tl

$Tl(H_2O)_6^{3+} \leftrightarrows Tl(H_2O)_5OH^{2+} + H^+$ pK~1.1

brown Tl_2O_3 s

Halides as Al: TlF_6^{3-} TlX_4^- X=Cl,Br,I

$Tl_{aq}^{3+} + 2e^- \rightarrow Tl^+$ 1.25 V "inert pair"

TlOH strong base

TlCl insoluble

$Tl_2Na[Co(NO_2)]$ insoluble

Tl_2S black

Tl_2CrO_4 yellow

Tl(I) – Tl(III)

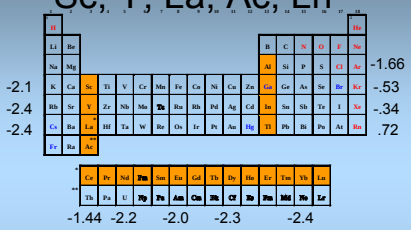
Tl I + I_2 in HI conc. evaporated → Tl I_3

- Same structure as NH_4I_3 (linear I_3^-)
- E^o (Tl^{3+}/Tl^+) = 1.25V ; E^o $(½I_2/I^-)$ = 0.54V

- 2Tl I_3 + $6OH^-$ → Tl_2O_3 + $6I^-$ + $3H_2O$
- I_3^- - top absent in absorption spectrum of Tl I_3 in MeOH
- Tl I_3 + I^- → Tl I_4^-

Sc, Y, La, Ac, Ln

-



$[Ng](ns)^2(n\text{-}1d)^1$

Ln: $[Xe](6s)^2(5d)^1(4f)^y$

+ hard lewis bases

O^{2-}, F^-, OXO^{n-}, NO_3^-

$[Ng](n\text{-}1\ d)^{10}(ns)^2(np)^1$

Tl: $[Xe](4f)^{14}(5d)^{10}(6s)^2(6p)^1$

III hard to moderate

I: soft

M^{3+} (Notes, p4)

Atom	Me^{3+}	r(6) /Å	E^0 /V	n	$E^0(M^{3+}/M^{n+})$	pK(Maq_6^{3+})		$logK_{EDTA}$
Al	[Ne]	.51	-1.66			5.1		16.1
Ga	$[Ar]3d^{10}$	.62	-0.53					20.3
In	$[Kr]4d^{10}$	.81	-0.34	1	-.43	4.4		25.0
Tl	$[Xe]4f^{14}5d^{10}$	.95	0.72	1	1.21	1.1		
Sc	[Ar]	.73				4.8		23.1
Ti	$[Ar]3d^1$	.67	-1.19	2	-.37	2.2	Violet	
V	$[Ar]3d^2$	.64	-0.87	2	-.25	2.8		25.9
Cr	$[Ar]3d^3$	.62	-0.74	2	-.41	3.8	Violet blue	23.4
Mn	$[Ar]3d^4$	.65	-0.12	2	1.54			
Fe	$[Ar]3d^5$	.65	- .04	2	.77	2.2	Light red	25.5
Co	$[Ar]3d^6$	.61	0.43	2	1.84	0.8	Blue	
Ni	$[Ar]3d^7$	.60		2	high			
Cu	$[Ar]3d^8$			2:	2.4			

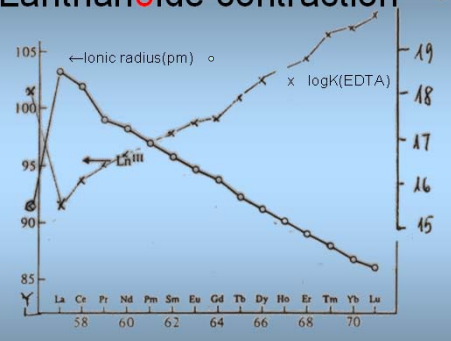
Ln

	Sc	Y	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
d,f	1,0	1,0	1,0	1,1	0,3	0,4	0,5	0,6	0,7	1,7	0,9	0,10	0.11	0,12	0,13	0,14	1,14
n+	3	3	3	4 3	4 3	3	3	2 3	2 3	3	3	4 3	3	3	3	2 3	3
pK M^{3+} aq	4.8	7.7	8.5	8.3	8.1	8.0		7.9		8.0	7.9	8.0	8.0	7.9	7.7	7.7	7.6
E^o ions				1.5	2.9			- 1.56	- 0.43							- 1.15	

$Ce(IV)_{aq} \leftrightarrows Ce(OH)^{3+}_{aq} + H^+$ pk~-1.1 strong acid

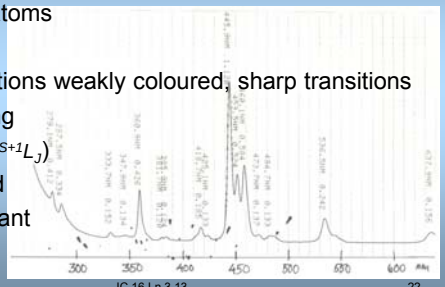
$Ce(OH)^{3+} \leftrightarrows Ce(OH)_2^{2+} + H^+$ pk~ 0.8

Lanthanoide contraction



Lanthanoides

Hard lewis acids – prefer hard lewis bases : small anionic atoms



Ln(III)-solutions weakly coloured, sharp transitions

L-S coupling

Important($^{2S+1}L_J$)

Ligand field

less important

Sc^{3+} - H_2O

$Sc^{3+} \leftrightarrows Sc(OH)^{2+} + H^+$ pK~4.3

$Sc(OH)^{2+} \leftrightarrows Sc(OH)_2^{+} + H^+$ pK~5.6

$Sc(OH)_2^{+} \leftrightarrows Sc(OH)_3 + H^+$ pK~6.5

$Sc(OH)_3 \leftrightarrows Sc(OH)_4^{-} + H^+$ pK~9.5

$2Sc(OH)^{2+} \leftrightarrows Sc(OH)_2Sc^{4+}$ $K \sim 10^{2.6}$

$3Sc(OH)^{2+} \leftrightarrows Sc_3(OH)_5^{5+} + H^+$

Equilibrium distribution with solid $Sc(OH)_3$