Greenwood & Earnshaw
2nd Edition

Chapter 7
Aluminium, Gallium, Indium and Thallium

Observations
➢ Aluminum is the most common metal, 8.3% wt. of the earth’s crust. Ga, In, Tl are relatively rare.
➢ Aluminum is monoisotopic, excellent heat and electrical conductor.
➢ Gallium has anomalous melting point (but not boiling point) and anisotropic electrical resistivity:
a 17.5, b 8.20, c 55.3; liquid is 25.8 $\mu$ohm-cm.
➢ Thallium has a very stable oxidation state of one and is very electropositive, corrodes in moist air. I – III oxidative equilibria dominates its chemistry.

The Trihalides of Aluminum

| Table 7.6 Properties of crystalline AlX3 |
|----------------------|------------------|------------------|------------------|
| Property             | AlF3             | AlCl3            | AlBr3            | AlI3            |
| MP °C                | 1290             | 192.4            | 97.8             | 189.4           |
| Sublimation pt.      | 1272             | 180              | 256              | 382             |
| (1 atm) °C           | 1498             | 707              | 527              | 510             |
| $\Delta H[kJ mol^{-1}]$ | 170              | 120              | 80               | 60              |

Polymeric solids, CN = 6, $\mu$ X || dimeric CN = 4, 2 $\mu$ X

Halides once hydrated cannot be dehydrated. AlF3 alone does not form a hexahydrate.

$\text{AlCl}_3 + 3\text{H}_2\text{O} \rightarrow [\text{Al(H}_2\text{O)}_3]^{3+} + 3\text{Cl}^- \xrightarrow{\text{heat}} \text{Al(OH)}_3\cdot\text{H}_2\text{O} + 3\text{HCl}$

$\text{AlF}_3 + n\text{H}_2\text{O} \rightarrow \text{AlF}_3n\text{H}_2\text{O} \quad n = 1, 3, 9$

$\xrightarrow{\text{heat}} \text{Al}_2\text{O}_3$

the affinity of Al for F ≠ O
Complex Halides – Cryolite Structure

AlF₃ + 3 NaF → Na₃AlF₆

Aluminum Smelting

Synthetic cryolite has the perovskite structure (CaTiO₃)₆ facial-cubic structure. No AlF₆³⁻ ions occur. The is not clearly ionic since the Na-F and Al-F distances are nearly equal. All Al occupy octahedral sites; 1/3 Na occupy octahedral sites, 2/3 occupy 12 coordinate sites.

Trihalides of Ga, In, Tl & Complex Halides

The trihalides of Al resemble those of Ga with some structural differences. The trihalides become less stable as one goes down the group.

InCl₅ → InCl₅⁻

GaCl₄⁻

Other adducts vary between sq. pyd. & trig. bipyd. geometry.

[Tl₂Cl₉]³⁻ Two regular TlCl₆ octahedra sharing a common face.

Hydrates, Hydroxides and Oxides

Acidity of [M(H₂O)₆]³⁺

<table>
<thead>
<tr>
<th>M</th>
<th>Al</th>
<th>Ga</th>
<th>In</th>
<th>Tl</th>
</tr>
</thead>
<tbody>
<tr>
<td>pKₐ</td>
<td>4.95</td>
<td>2.6</td>
<td>3.7</td>
<td>1.15</td>
</tr>
</tbody>
</table>

B(OH)₃  Al(OH)₃  Ga(OH)₃  In(OH)₃  TiOH
Acidic  Amphoteric  Basic  Strongly Basic

MO(OH)
Layer lattice

M₂O₃
Structurally very complex
See p 243 text

Al₂(SiO₃)₃  Al₂O₃  CaO
Acid  Acid  Basic

CaAl₂O₃₂  TiO₂
Basic  Basic
Important Aluminum Oxides

- α-Alumina – Al$_2$O$_3$ – Corundum, Sapphire including very strong optical glass, “Saffil” fibres.
- γ-Alumina – Al$_2$O$_3$ – “Activated alumina”, a defect spinel structure.
- Sodium-β-alumina – NaAl$_{11}$O$_{17}$ - Na$_2$O·0.11Al$_2$O$_3$ – a “solid electrolyte” & Na$^+$ conductor, see Na/S battery applications, p 678 text.
- Tricalcium Aluminate – Ca$_3$Al$_2$O$_6$ – Principal ingredient of “Portland Cement”.

Complex Metal Hydrides

- $\text{Al(BH}_4\text{)}_3$  
- $\text{Al(H}2\text{BH}_3\text{)}_3$  
- $\text{Al} + \frac{3}{2}\text{H}_2 \rightarrow \text{no reaction}$

- $\text{AlCl}_3 + 3\text{LiAlH}_4 \rightarrow 4\text{AlH}_2\text{(Et}_2\text{O)}_n + 3\text{LiCl}$
- $\text{AlH}_3$ has 6 O_{3c-2e} μ-H’s, 6 d_{Al-Al} = 324 pm, 6 d_{Al-Al} = 445 pm, $\nu_{\text{AsAl}} = 141$, no Al-Al bonding.
- $\text{LiGaH}_4 + \text{Me}_3\text{NCl} \rightarrow \text{GaH}_2\text{NMe}_3+\text{BF}_3$
- $\text{LiMH}_4 + 3\text{Me}_3\text{NCl} \rightarrow \text{GaH}_2\text{NMe}_3$ for M = B, Al, Ga, In, Tl
- $\nu_{\text{AsH}} = 380^\circ, 100^\circ, 50^\circ, 0^\circ$

Hydrides: Al, Ga, In, & Tl
Al, Ga, In, & Tl -- Alkyls & Hydrides

\[ \text{Al} + \frac{3}{2} \text{H}_2 + 2 \text{AlR}_3 \rightarrow 3 \text{AlR}_2\text{H} \]

\[ \text{AlEt}_2\text{H} + \text{H}_2\text{C}==\text{CH}_2 \rightarrow \text{AlEt}_3 \text{ dimeric} \]

\[ 2 \text{Al} + 3 \text{H}_2 + 2 \text{Al}_2\text{Et}_6 \rightarrow 6 \text{Et}_2\text{AlH} \]

\[ 2 \text{Al} + 3 \text{H}_2 + 6 \text{(CH}_3\text{)}_2\text{C}==\text{CH}_2 \rightarrow 2 \text{Al}[(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{Al}] \]

\[ 2 \text{Al}[(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{Al}] \rightarrow (\text{CH}_3\text{CH}==\text{CH}_2)_2\text{Al} \rightarrow \text{Al}[(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{Al}]_2 \]

\[ \text{TlX}_3 + 2 \text{RMgX} \rightarrow \text{R-Tl-R} + \text{X}^- \]

Aluminum Alkyls -- The "Growth" Reaction

Aluminum Alkyls -- Ziegler-Natta Catalysis

\[ \text{TiCl}_4 + \text{Al}_4\text{Et}_6 \rightarrow \text{TiCl}_3 \text{Et}_2\text{Al} \rightarrow \text{TiCl}_3 \text{Et}_n \rightarrow \text{L}_n\text{Ti-Et} \]

Classical Mechanism:
Aluminum Alkyls – Ziegler-Natta Catalysis

- Classical mechanism requires chain transfer of an ever increasing length chain, entropy consideration as polymer chains become very long.
- The “concerted pathway” was invoked to counter the entropy troubles above.
- Polypropylene is only “head-to-tail”, most valuable polymer produced by Z-N catalysis. The methyl groups alternate along the chain.
- Reactivity: terminal > geminal > internal olefins. Only homopolymerization feasible.

Some Interesting Organometallics

\[ \text{TiOH}_{(aq)} + \text{C}_2\text{H}_6 \rightarrow \text{Ti} \text{gas phase crystalline phase} \]

Trialkyl derivatives of Ga, In, Tl are all monomeric. Those of Ga & Tl tend to be liquids or low mp.

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\[ \text{TlOH}_{(aq)} + \text{C}_5\text{H}_6 \rightarrow \text{In} \text{gas phase crystalline phase} \]

Indium compound has similar structure

- \( d_{\text{ring}} = 285 \text{ & } 309 \text{ pm}; J_{\text{ring}} 128^\circ; \gamma_{\text{ring}} 177^\circ \)

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\[ \text{Ga Br} \text{BrBr} \]

\[ \text{Ga Br} \text{O} \text{O} \text{O} \]

\[ \text{MeAlMe}^{+} \]

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\[ \text{Tl}^{+} \]

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\[ \text{in} \text{gas phase crystalline phase} \]

Indium compound has similar structure

- \( d_{\text{ring}} = 285 \text{ & } 309 \text{ pm}; J_{\text{ring}} 128^\circ; \gamma_{\text{ring}} 177^\circ \)