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 μ 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 AlX_3

Property	AlF_3	$AlCl_3$	$AlBr_3$	AlI_3
MP/°C	1290	192.4	97.8	189.4
Sublimation pt (1 atm)/°C	1272	180	256	382
$\Delta H_f^\ominus$/kJ mol^{-1}	1498	707	527	310

polymeric solids, CN = 6, μ X || dimeric CN = 4, 2 μ X

Halides once hydrated cannot be dehydrated. AlF_3 alone does not form a hexahydrate.

$AlCl_3 \xrightarrow{H_2O} [Al(H_2O)_6]^{3+}\ 3\ Cl^- \xrightarrow{heat} AlO(OH)\bullet H_2O + 3HCl$

$\xrightarrow{heat} Al_2O_3$

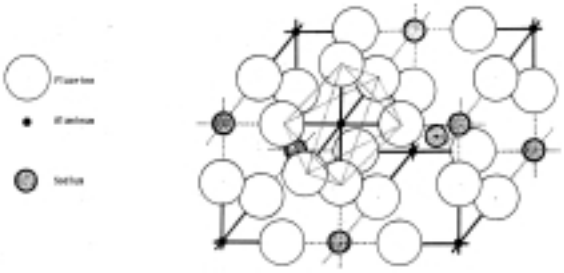
$AlF_3 \xrightarrow{H_2O} AlF_3\bullet nH_2O$ n = 1, 3, 9

the affinity of Al for F ≅ O

Complex Halides – Cryolite Structure

$AlF_3 + 3\,NaF \longrightarrow Na_3AlF_6$ Aluminum Smelting

Synthetic cryolite has the perovskite structure ($CaTiO_3$) a face-centered cubic structure. No AlF_6^{3-} 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 trichloride of Al is important as Friedal Crafts & isomerization Catylist.
The trihalides of Ga resemble those of Al with some structural differences.
The trihalides become less stable as one goes down the group.

$GaCl_4^-$, $InCl_4^-$ } T_d $\quad InCl_5^{2-}$ square pyramidal (103.9°, 242 pm, 246 pm)

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

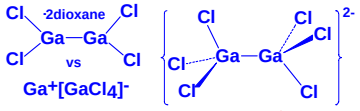
The trihalides of Tl are chemically quite distinct from the rest of the group.

$TlF_3 \xrightarrow{H_2O} Tl(OH)_3 + 3\,HF$ $\quad NaTlF_4$ Fluorite Str. $\quad Na_3TlF_6$ Cryolite Str.

mp_d 550 C $\quad$ hydrolyses rapidly

$[Tl_2Cl_9]^{3-}$ Two regular $TiCl_6$ octahedra sharing a common face.

Ga(II) ~ In(II) vs. Ga(I)Ga(III)



$Tl(I) \rightleftharpoons Tl(III)$ $\quad Ga^+[GaCl_4]^-$

TlI_3 is $Tl^+ I_3^-$ but TlI_4^- is Tl(III); Tl_2I_4 is $Tl^+ TlI_4^-$

Hydrates, Hydroxides and Oxides

Acidity of $[M(H_2O)_6]^{3+}$	M	Al	Ga	In	Tl *
	pK_a	4.95	2.6	3.7	1.15

* Needs "non-coordinating anion"

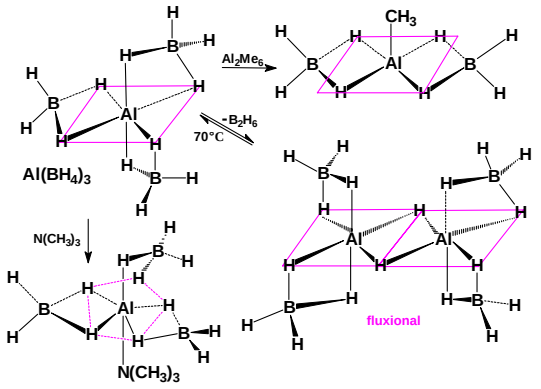
$B(OH)_3$	$Al(OH)_3$	$Ga(OH)_3$	$In(OH)_3$	TlOH
Acidic	Amphoteric		Basic	Strongly Basic ~KOH
	~100 C	100-1500 atm, H_2O, 250-400 C		~100 C
	MO(OH) layer lattice		InO(OH) ~Rutile Str.	Tl_2O black platelets
	~150 C			$-O_2$ ~1000 C
	M_2O_3 structurally very complex See p 243 text		In_2O_3 Basic	Tl_2O_3
				OH^-
				Tl^{3+}

$Al_2(SiO_3)_3 \xleftarrow{SiO_2}$ Acid Oxide Acceptor $\quad Al_2O_3 \xrightarrow{CaO}$ Base Oxide Donor $\quad Ca(AlO_2)_2$

Important Aluminum Oxides

- **α-Alumina – Al_2O_3 – Corundum, Sapphire including very strong optical glass, "Saffil" fibres.**
- **γ-Alumina – Al_2O_3 – "Activated alumina", a defect spinel structure.**
- **Sodium-β-alumina – $NaAl_{11}O_{17}$ - $Na_2O \cdot 0.11Al_2O_3$ –a "solid electrolyte" & Na^+ conductor, see Na/S battery applications, p 678 text.**
- **Tricalcium Aluminate – $Ca_3Al_2O_6$ – Principal ingredient of "Portland Cement".**

Complex Metal Hydrides



Hydrides: Al, Ga, In, & Tl

$Al + {}^3/_2 H_2 \longrightarrow$ no reaction

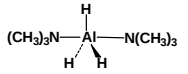
$4\ AlCl_3 + 3\ LiAlH_4 \longrightarrow 4\ AlH_3(Et_2O)_n + 3\ LiCl$

α-AlH_3 has 6 O_h 3c-2e μ-H's
6 d_{Al-Al} = 324 pm, 6 d_{Al-Al} = 445 pm,
$\angle_{AlHAl}$ = 141°, no Al-Al bonding.

benzene reflux

$4\ AlH_3$ T_d 150-200°C

2 $N(CH_3)_3$



$LiGaH_4 + Me_3N{\cdot}HCl \longrightarrow GaH_3{\cdot}NMe_3 \xrightarrow{BF_3} GaH_3$

Viscous liq.
T_{mp} -15°C
T_{dec} –25°C

Hydrides of In, Tl too unstable to isolate

$LiMH_4$ M =	B	Al	Ga	In	Tl
°C T_{dec} =	380°	100°	50°	O°	

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

$Al + {}^{3}/_{2}\,H_2 + 2\,AlR_3 \longrightarrow 3\,AlR_2H$

$AlEt_2H + H_2C{=}CH_2 \longrightarrow AlEt_3$ (dimeric) — *cf.* Hydroboration; AlH_3 ineffective

$2\,Al + 3\,H_2 + 2\,Al_2Et_6 \longrightarrow \{6\,Et_2AlH\} \xrightarrow{6\,H_2C{=}CH_2} 3\,Al_2Et_6$

$2\,Al + 3\,H_2 + 6\,(CH_3)_2C{=}CH_2 \xrightarrow[\text{cat. amts. } Al[CH_2CH(CH_3)_2]_3]{200\text{ atm}\ 100^\circ C} 2\,Al[CH_2CH(CH_3)_2]_3$ monomeric

$2\,Al(CH_2CH(CH_3)_3 \xrightarrow{Na} \{(CH_3)_3CHCH_2)_3Al{-}Al[CH_2CH(CH_3)_2]_3\}^{2-}$

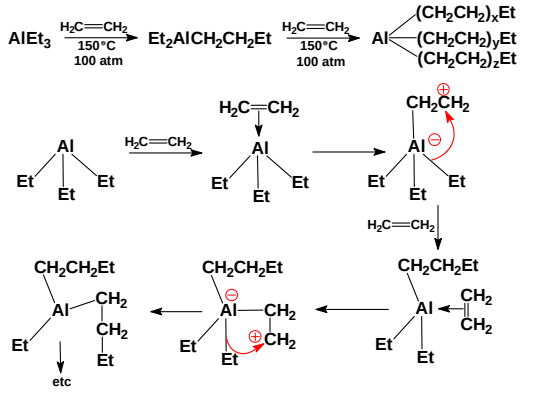
mp 40 °C, diamagnetic

$TlX_3 + 2\,RMgX \longrightarrow [\,R{-}Tl{-}R\,]^{+}\,X^{-}$

linear cation, isoelectronic with R_2Hg

R = Me, soluble and stable in water.

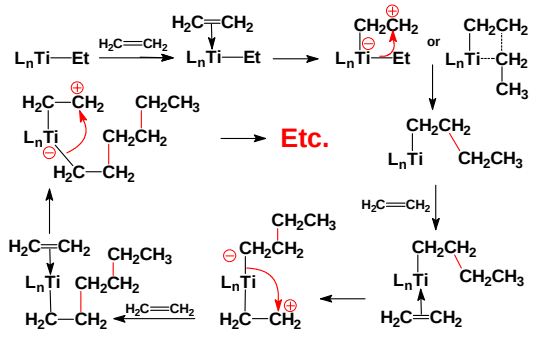
Aluminum Alkyls – The "Growth" Reaction



Aluminum Alkyls – Ziegler-Natta Catalysis

$TiCl_4 + Al_2Et_6 \xrightarrow[\text{solvent}]{\text{alkane}} \{\text{Ti(III)}Et_nCl_{3-n}\}$ (brown suspension) $\equiv L_nTi\text{-}Et$

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