Lithium Aluminum Hydride

\[ \text{LiAlH}_4 \]

For the reaction between LiH and AlCl₃ to occur to a noticeable extent, the thick, hard lumps of lithium hydride must be ground to a very fine powder and then sieved. This treatment is performed under nitrogen. A very reactive ether suspension of LiH is obtained if the material is wet-ground with anhydrous ether in a special ball mill (K. Ziegler et al.) and used immediately.

A fresh suspension of 23.5 g. (2.96 moles) of LiH in 200 ml. of ether is introduced (with exclusion of moisture) into a three-neck flask provided with a dropping funnel, a reflux condenser and a stirrer. A solution of 71.2 g. (0.534 mole) of AlCl₃ in 300 ml. of ether is then added in drops with vigorous stirring. The reaction starts immediately, as shown by the boiling of the ether. The rate is kept uniform by adjustment of the addition rate. When all the AlCl₃ solution has been added, stirring is continued until the reaction has subsided, and the mixture is left to stand for some time. The contents of the flask are then filtered, using nitrogen pressure, through a fritted glass filter, and the clear filtrate is concentrated at atmospheric pressure until it has a syrupy consistency. The residual ether may be evaporated in vacuum at 70°C. The yield of LiAlH₄, based on AlCl₃, is about 85%.

Insufficient grinding of the LiH may prevent the reaction from starting spontaneously, or from going to completion, and lead to sudden, explosive bursts of renewed activity; in such cases the reaction is started by adding 200 ml. of ether, followed by a solution of 3 g. of LiAlH₄ in 30 ml. of ether, to the finely divided LiH. The subsequent procedure is the same as described above. According to Wiberg, a slight quantity of iodine may be used as an initiator instead of the LiAlH₄.
According to Wiberg, the difficulties involved in the preparation of sufficiently reactive LiH are not encountered if AlBr₃ is used instead of AlCl₃. In this case, coarse LiH can be used:

An ether solution of AlBr₃ is prepared by adding small portions of the material (total 267 g. = 1 mole) to 750 ml. of extremely pure, dry ether in a flask cooled with ice-salt mixture. A 33-g. portion (4.1 moles) of coarsely ground LiH is placed in a three-neck flask with a reflux condenser, a stirrer and a dropping funnel. The hydride is covered with 250 ml. of ether, and the AlBr₃ solution is allowed to run in; the addition takes one to two hours. The stirred mixture is then heated to the boiling point of ether and kept at this temperature for a few hours. The LiBr and unreacted LiH precipitate on cooling. The solution is rapidly decanted through a layer of glass wool in a funnel. The filtrate obtained consists of an ether solution of LiAlH₄ saturated with LiBr. The solution may be stabilized by storing it over a small quantity of LiH.

**PROPERTIES:**

Colorless solid, stable in dry air at room temperature. The ether solution is used in inorganic and organic chemistry as a reducing and hydrogenating agent.

**REFERENCES:**


**Calcium Aluminum Hydride**

\[
4 \text{CaH}_2 + 2 \text{AlCl}_3 = \text{Ca(AlH}_4)_2 + 3 \text{CaCl}_2
\]

A freshly prepared solution of AlCl₃ in tetrahydrofuran is added to a suspension of finely ground calcium hydride in the same
solvent. A 30% excess of CaH$_2$ should be used. The mixture is refluxed under nitrogen for several hours in a flask provided with a stirrer and a reflux condenser. When the solution has cooled, it is rapidly suction filtered and the solvent is slowly distilled from the filtrate under nitrogen. The solid residue evolves further tetrahydrofuran when heated to 80-90°C in aspirator vacuum. The nearly colorless residue from this treatment still contains about 50-60% tetrahydrofuran, in addition to the Ca(AlH$_4$)$_2$. The hydride content can be raised to 60% by treatment in high vacuum.

Before the CaH$_2$ can be used in the reaction, it should be ground for 8-24 hours in a porcelain ball mill. The grinding and subsequent preparation of the tetrahydrofuran suspension are done in the absence of moisture; this ensures sufficient reactivity of the hydride. Before heating the reaction mixture it is recommended that a few crystals of iodine or, better still, a small quantity of a previously prepared tetrahydrofuran solution of Ca(AlH$_4$)$_2$ be added. The AlCl$_3$ should be sublimed before use. At worst, it may be only slightly yellow.

**PROPERTIES:**

The tetrahydrofuran solution of Ca(AlH$_4$)$_2$ is rapidly decomposed by moisture. Even on storage in a closed vessel, considerable decomposition occurs after some weeks.

**REFERENCE:**


**Polymeric Aluminum Hydride**

\[
\text{(AlH}_3)_n \times \text{O(C}_2\text{H}_5)_2
\]

3 LiAlH$_4$ + AlCl$_3$ = 4/n(AlH$_3$)$_n$ + 3 LiCl

113.9  133.4  120.0  127.2

A solution of 1.137 g. of LiAlH$_4$ in 30 ml. of ether is placed in a small three-neck flask fitted with a nitrogen inlet tube, a reflux condenser and a dropping funnel. The apparatus is thoroughly flushed with dry nitrogen, and a solution of 1.33 g. of AlCl$_3$ in 20 ml. of ether is dropped in. The ensuing reaction is vigorous, but falls off rapidly. A filter tube with a sealed-in fritted disk is substituted for the funnel, and the solution is filtered out of the flask. The ether is partly evaporated from the filtrate by slowly raising the temperature to 90°C in high vacuum. The white residue has the composition \((\text{AlH}_3)_n \times \text{O(C}_2\text{H}_5)_2\), the ratio of AlH$_3$ to ether
depending on the duration and temperature of evaporation; it ranges from 2.8 : 1 to 4.8 : 1. The product cannot be obtained entirely free of ether, since hydrogen slowly splits off at temperatures exceeding 90°C.

Immediately after completion of the reaction, the solute consists of monomeric AlH₃. After a short while, however, a polymer with a high ether content begins to separate.

REFERENCES:

\textbf{Aluminum Chlorohydride}

\[ \text{AlCl}_3 + \text{AlH}_3 = \text{Al}_2\text{Cl}_3\text{H}_3 \]

A fresh ether solution of monomeric AlH₃ is prepared as described in the previous section and the LiCl precipitate is removed by filtration or centrifugation. A solution of AlCl₃ in a small volume of ether is immediately added to the clear AlH₃ solution. The two reactants (AlH₃ and AlCl₃) are added in equimolar amounts. The addition of the AlCl₃ prevents the polymerization of the AlH₃. The ether can then be completely evaporated from the solution, yielding a water-clear liquid, which distills at 80°C without decomposition in high vacuum. It has the composition of Al₂Cl₃H₃.

SYNONYM:
Trichlorodialane.

PROPERTIES:
The ether solution of the compound behaves chemically as a mixture of solutions of AlH₃ and AlCl₃. It has the advantage of being more stable than an ether solution of pure AlH₃.

REFERENCE:
**Aluminum Hydride Trimethylaminate**

$$\text{AlH}_3 \cdot 2\text{N(CH}_3\text{)}_3, \text{AlH}_3 \cdot \text{N(CH}_3\text{)}_3$$

$$\text{AlH}_3 \cdot 2\text{N(CH}_3\text{)}_3$$

$$\text{AlH}_3 + 2\text{N(CH}_3\text{)}_3 = \text{AlH}_3 \cdot 2\text{N(CH}_3\text{)}_3$$

As in the preceding two preparations, a fresh ethereal solution of monomeric AlH$_3$ is prepared and its concentration adjusted to 0.5 M. A 15-ml. portion of a 1 M ether solution of anhydrous trimethylamine is added to 15 ml. of the hydride solution. If a slight turbidity results, the mixture should be centrifuged. The clear solution is left to stand for one half hour. The ether is then vacuum distilled, starting at $-78^\circ$C and slowly raising the temperature to $+20^\circ$C. The residue, a white powder, is slowly sublimed in high vacuum into a receiving flask cooled with an ice-salt mixture; the sublimation temperature is $40^\circ$C. The composition of the sublimate is AlH$_3 \cdot 2$ N(CH$_3$)$_3$.

**PROPERTIES:**

Colorless crystals. M.p. 95°C; decomposes above 100°C. Fumes in air and is vigorously hydrolyzed in water. Soluble in tetrahydrofuran, ether and benzene.

$$\text{AlH}_3 \cdot \text{N(CH}_3\text{)}_3$$

The compound is prepared analogously, but using equimolar quantities of the hydride and the amine. The white powder left in the flask after removal of the ether sublimes between 50 and 60°C (1 mm.). The product consists of colorless crystals which have the composition AlH$_3 \cdot$ N(CH$_3$)$_3$.

**PROPERTIES:**

M.p. 76°C. Otherwise similar to AlH$_3 \cdot 2$ N(CH$_3$)$_3$.

**REFERENCE:**


**Diethylaluminum Bromide**

$$\text{Al(C}_2\text{H}_5\text{)_2Br}$$

$$2\text{Al} + \text{Mg} + 4\text{C}_2\text{H}_5\text{Br} = 2\text{Al(C}_2\text{H}_5\text{)_2Br} + \text{MgBr}_2$$

The reaction is carried out in a one-liter, three-neck flask equipped with a stirrer, a reflux condenser and a dropping funnel,
as well as an inlet tube for dry, oxygen-free nitrogen. The flask is filled with 107 g. of turnings obtained from an alloy of 30% magnesium and 70% aluminum. Small quantities of iodine and ethyl bromide are added. After a short time the halide can be observed to react with the metal. The reaction flask is then immersed in an oil bath and a total of 496 g. of ethyl bromide is added dropwise during 2.5 hours. The flask is then heated to 120-140°C and kept at this temperature for one hour to ensure completion of the reaction. The product is separated from the magnesium bromide by vacuum distillation, using an oil pump, and is redistilled in vacuum (2 mm., 75°C). All operations must be carried out under nitrogen. The yield is 370 g. of Al(C₂H₅)₂Br, contaminated with 2% AlC₂H₅Br₂.

REFERENCE:

Triethylaluminum

Al(C₂H₅)₃

Sodium wire (50 g.) is introduced under nitrogen into a three-neck flask fitted with a stirrer, a reflux condenser and a nitrogen inlet tube. Then 150 g. of Al(C₂H₅)₂Br is added dropwise. The flask is heated to 105°C and a vigorous reaction soon begins. The mixture starts to boil and external cooling is necessary. As soon as the reaction quiets down, an additional 186 g. of Al(C₂H₅)₂Br is added. The temperature is slowly raised to 200°C and maintained there for 10 hours, with constant stirring. The flask is then cooled to room temperature and 2 g. of sodium wire is added to ensure completion of the dehalogenation. Stirring is resumed, and the temperature is again raised to 150°C and held for 1.5 hours. The Al(C₂H₅)₃ formed is distilled from the reaction mixture in vacuum (2 mm.). Further purification is achieved by fractionation in a vacuum Podbielniak column; the product boiling between 128 and 130°C and 50 mm. is collected.

PROPERTIES:
Formula weight 114.2. Spontaneously flammable. Immediately hydrolyzed by moisture to Al(OH)₃ and C₂H₆.

REFERENCES:
A. von Grosse, J. M. Mavity, J. Org. Chem. 5, 106 (1940). Recent pressure processes for aluminumtrialkyls starting with Al, H₂ and olefins, as well as their applications to the low-pressure polymerization of ethylene, are given in K. Ziegler et al., Angew. Chem. 67, 424 (1955).
Triethylaluminum Etherate

\[ \text{Al}(	ext{C}_2\text{H}_5)_2 \cdot \text{O(C}_2\text{H}_5)_2 \]

A 24-g. sample of Electron metal turnings (15.1% Al, the remainder Mg and traces of Si) is covered with 400 ml. of ether in a three-neck flask fitted with a reflux condenser, a stirrer and a dropping funnel; 150 g. of ethyl bromide is added by drops. The reaction may be initiated by the addition of a few crystals of iodine. While the reaction is in progress, the ether should be boiling at a uniform rate. When the metal has completely dissolved, the ether is quickly removed, leaving a solid residue from which the triethylaluminum etherate is distilled at 140-180°C into an ice-cooled receiver. The distillation is carried out slowly under nitrogen at 14-16 mm., using an oil bath. The product is re-distilled at 112°C and 16 mm.

PROPERTIES:

Formula weight 188.3. Colorless liquid, sensitive to air and moisture. B.p. 112°C (16 mm.).

REFERENCES:


Diethylaluminum Hydride

\[ \text{Al(C}_2\text{H}_5)_2\text{H} \]

\[ \text{Al(C}_2\text{H}_5)_2\text{Cl} + \text{LiH} = \text{Al(C}_2\text{H}_5)_2\text{H} + \text{LiCl} \]

The ether complex of diethylaluminum chloride is prepared first by adding dropwise one half mole of AlCl₃, dissolved in some ether, to one mole of Al(C₂H₅)₃·O(C₂H₅)₂. When the evolution of heat ceases, the excess solvent is evaporated and the Al(C₂H₅)₃Cl etherate is distilled in vacuum. A 76-g. portion of this product is diluted with 120 ml. of absolute ether and placed in a 500-ml., three-neck flask which has been flushed with dry nitrogen. A suspension of LiH in ether (62 ml., 7 M in LiH) is prepared in a dropping funnel under a nitrogen blanket and allowed to flow into the flask. Lithium chloride separates and the reaction mixture boils. Toward the end of the reaction, stirring is applied and the mixture is heated to 40°C for 15 minutes more. The LiCl
rapidly precipitates when the flask is allowed to cool. The clear supernatant is then sampled with a pipette and tested for halogen. If the test is positive, a few more drops of the LiH suspension are added. The supernatant should be just halogen free but should not contain any appreciable amount of excess Li. The mixture is then centrifuged and the clear solution decanted. The precipitate is washed with a small volume of ether, which is then evaporated in an aspirator vacuum, the last traces being removed at 50°C. The residual Al(C₅H₅)₂H is distilled in high vacuum, holding the flask in a bath maintained at 80°C or lower. It is collected in a receiver cooled to —20°C. The distillate is a water-clear liquid. The entire preparation should be carried out without interruption. The presence of solid deposits during the distillation of the crude product lowers the yield, which otherwise may be as high as 70%.

PROPERTIES:

Air- and moisture-sensitive liquid. B.p. 55-56°C (10⁻³ mm.).

REFERENCE:


**Aluminum Chloride**

\[ \text{Al} + 3 \text{HCl} = \text{AlCl}_3 + 1\frac{1}{2} \text{H}_2 \]

I. One end of a large diameter Vycor tube (25 to 40 mm.) is inserted through one of two holes bored in a cork closing a wide-neck flask. The second hole holds a tube leading to the hood. The cork can be dispensed with if the reaction tube can be made to fit tightly into the neck of a long-neck, round-bottom flask. The reaction tube is placed in an electric furnace. The distance between the hot zone and the receiver flask should not be longer than 8 cm., to prevent plugging of the tube by the sublimate. The cork is protected from the heat by an asbestos wrapping. A porcelain boat containing aluminum turnings or powder is inserted in the reaction tube. Gaseous HCl is then passed through from the end opposite the receiver. The rubber tubing connections should be as short as possible. When the air has been completely displaced by the HCl, the furnace is slowly heated until a white mist begins to appear. The flow of HCl is then increased and the temperature raised to
prevent premature condensation of the sublimate. The reaction is then allowed to continue until the aluminum has been completely consumed.

II. Commercial AlCl₃, which usually contains iron and traces of oxygen due to hydrolysis, may be purified by the following procedure. The crude material is mixed with about 10% by weight of aluminum turnings and the mixture is placed in a sublimation flask with a side arm through which a moderate stream of dry HCl is fed during the sublimation. A short, wide, curved tube connects the sublimation flask with the receiving flask and the entire system is protected against moisture by a drying tube. Further purification is by resublimation in a nitrogen atmosphere, using the receiver of the first step as a sublimation flask; the rest of apparatus is similar.

**PROPERTIES:**


**REFERENCES:**


**Aluminum Bromide**

AlBr₃

I. \[ \text{Al} + \frac{1}{2} \text{Br}_2 = \text{AlBr}_3 \]

27.0 239.7 266.7

Very pure AlBr₃ may be prepared in the apparatus shown in Fig. 244. The bottom of the reaction flask is covered with a layer of glass wool, and the desired quantity of very pure, degreased dry aluminum turnings is placed on top. Nitrogen, dried over P₂O₅, is introduced at e and escapes at f. When the last traces of moist air have been flushed out, stopcock e is closed and the stream of nitrogen is passed from g to f. Dry bromine is then added from the dropping funnel into flask a. The rate of addition is adjusted so that the heat of reaction maintains the resulting AlBr₃ at a temperature sufficient for refluxing in the middle section of the air condenser. A considerable excess of Al should remain after all the bromine has been added. The reaction flask is then heated until the liquid flowing down from b is colorless.
The direction of the nitrogen stream is reversed, a drying tube filled with $P_2O_5$ is attached at $g$, and the AlBr$_3$ is distilled from $a$ into receiver $c$. When the distillation is complete, the receiver is disconnected without interrupting the nitrogen flow and immediately closed tightly.

II. When colorless AlBr$_3$ is not required, the procedure described in I may be carried out in a regular distillation flask with a dropping funnel for bromine. The bottom of the flask is again covered with glass wool and the aluminum placed on top. The flask is preheated over an open flame to about 100°C. The dropwise addition of Br$_2$ is then carried out at such a rate that it is rapidly consumed. The temperature should remain below the boiling point of AlBr$_3$. When the addition is complete the product is distilled through a descending tube into a receiver.

**PROPERTIES:**

Colorless, shiny lamellae. Hydrolyzes in moist air. Reacts violently with water (caution!). Soluble in many organic solvents. M.p. 97.5°C, b.p. 255°C; d (18°C) 3.205, d (100°C, liq.) 2.64.

**REFERENCES:**


**Aluminum Iodide**

\[ \text{Al} + \frac{1}{2} \text{I}_2 = \text{AlI}_3 \]

I. Aluminum turnings and a few crystals of iodine are placed in a $CO_2$-filled flask and heated until reaction begins. More I$_2$ is then added until only a small amount of aluminum remains. The
reaction product is kept a little longer in the molten state and then transferred under nitrogen into an Anschütz distillation flask, where it is slowly distilled in an oil pump vacuum. The pump is protected against iodine vapor by two wash bottles filled with activated charcoal.

II. A 20-g. portion of dried and sublimed iodine is dissolved in 80 ml. of CS$_2$ and heated with 3.5 g. of sheet aluminum in a flask provided with a reflux condenser. When the reaction is over, the mixture is filtered, the filtrate is heated over a water bath (caution: do not use an open flame!) to distill off most of the CS$_2$, and the concentrated residue is cooled. Aluminum iodide crystallizes out. The crystals are suction-filtered, washed with hexane and dried at 100°C. The product retains a slight yellow-brown tinge.

**PROPERTIES:**


**REFERENCES:**

II. W. Nespital, Z. phys. Chem. (B) 16, 164 (1932).

**Aluminum Chloride Hydrate**

$\text{AlCl}_3 \cdot 6 \text{H}_2\text{O}$

At 0°C, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ is slightly soluble (21 mg./100 ml.) in saturated aqueous HCl and is therefore easily isolated from such a solution. The aluminum is dissolved in concentrated HCl and the solution is transferred into a three-neck flask fitted with a stirrer, an inlet tube for HCl gas and an outlet tube. The flask is cooled to 0°C and HCl gas is introduced into the continuously stirred and cooled solution until it is saturated. The inlet tube should not dip into the solution, since it might become clogged with salt, but sufficient absorption of the HCl is ensured by vigorous stirring. A wash bottle with concentrated H$_2$SO$_4$ connected to the outlet of the flask serves to indicate the progress of the saturation. The precipitated hydrate is rapidly suction-filtered and, while still cold, washed with some ether and dried on a clay plate.

**REFERENCE:**

Sodium Tetrachloroaluminate

$\text{NaAlCl}_4$

\[
\text{NaCl} + \text{AlCl}_3 = \text{NaAlCl}_4
\]

The reaction is carried out in a Pyrex vessel (Fig. 245), which should be as compact as possible. The stoichiometric amounts of C.P. NaCl and freshly sublimed AlCl$_3$ are introduced into the pear-shaped part of the reaction vessel. The filling is done under nitrogen and the vessel should be very clean and dry. A melting point capillary is then affixed underneath the ground joint; the apparatus is evacuated to a high vacuum and torch-sealed. It is then immersed as deeply as possible in an oil bath at 200-240°C. The AlCl$_3$, which tends to sublime onto the cool parts of the wall, is driven back by passing a luminous flame over the condensate spots. When the flask contents have become a nearly clear melt, they are poured hot into the side flask of the vessel. The product solidifies on cooling.

PROPERTIES:

Colorless, crystalline material. M.p. 156°C.

REFERENCES:


Tetrachloroaluminic Acid Dietherate

$\text{HAICl}_4 \cdot 2 \text{O(C}_2\text{H}_5)_2$

\[
\text{HCl} + \text{AlCl}_3 + 2 \text{O(C}_2\text{H}_5)_2 = \text{HAICl}_4 \cdot 2 \text{O(C}_2\text{H}_5)_2
\]

Dry HCl gas is passed through absolute ether until a concentrated solution is obtained. Slightly less than the stoichiometric amount of anhydrous AlCl$_3$ is added with cooling and shaking. A
clear oil separates and slowly forms white crystals when the mixture is cooled to $-20^\circ C$ with stirring. The crystals are filtered under nitrogen on a sintered glass filter and washed with ether. The compound is stable on storage if moisture is excluded.

Analogously, $\text{AlBr}_3$ and $\text{HBr}$ may be reacted to form $\text{HAlBr}_4 \cdot 2 \text{O(C}_2\text{H}_5)_2$, which is obtained in the form of an oil.

REFERENCE:

**Aluminum Chloride Ammoniate**

$$\text{AlCl}_3 \cdot \text{NH}_3$$

$$\text{AlCl}_3 + \text{NH}_3 = \text{AlCl}_3 \cdot \text{NH}_3$$

Thoroughly dried ammonia is passed over freshly sublimed $\text{AlCl}_3$ in a long, 20–40 mm. diameter glass tube. Higher ammoniates are formed as the contents melt. The reaction tube is swept with nitrogen and slowly heated in a furnace from $190^\circ C$ to $360^\circ C$ at which temperature the monoammoniate $\text{AlCl}_3 \cdot \text{NH}_3$ is obtained. It is purified by vacuum distillation at 2 mm., with the flask on an oil bath at 205–210$^\circ C$.

**PROPERTIES:**
Moisture-sensitive, colorless substance. M.p. 130$^\circ C$.

**REFERENCES:**

**Aluminum Chloride-Sulfur Dioxide Adduct**

$$\text{AlCl}_3 \cdot \text{SO}_2$$

$$\text{AlCl}_3 + \text{SO}_2 = \text{AlCl}_3 \cdot \text{SO}_2$$

A combustion tube is charged with $\text{AlCl}_3$, which should be pure and free of iron. An excess of $\text{SO}_2$ is condensed on the chloride.
No moisture should be present during the reaction. The tube is
torch-sealed and heated to 50°C for about half an hour. The excess
SO₂ is then allowed to escape by heating the sealed end of the tube.
The residue is a viscous, colorless liquid, which gradually solidi­
fies. Its composition is AlCl₃·SO₂.

REFERENCES:
H. Gerding and E. Smit, Z. phys. Chem. (B) 51, 204 (1942).

**Aluminum Chloride-Thionyl Chloride Adduct**

\[ \text{AlCl}_3 \cdot \text{SOCl}_2 \]

\[
2\text{AlCl}_3 + \text{SOCl}_2 \rightarrow \text{Al}_2\text{Cl}_6 \cdot \text{SOCl}_2
\]

Anhydrous AlCl₃ is dissolved at room temperature in excess
SOCl₂. When large quantities are to be prepared, the solubility of
the AlCl₃ can be increased by heating the solution. The excess
SOCl₂ is distilled from the red-brown solution and the tempera­
ture of the bath in which the flask is immersed is then slowly
raised. The first fraction is discarded. The Al₂Cl₆·SOCl₂ distills
over at 212 to 216°C in the form of oily droplets which solidify
in the receiving flask. The product is purified by fractionation,
b.p. 214-215°C.

REFERENCE:

**Aluminum Chloride-Phosphorus Pentachloride Adduct**

\[ \text{AlCl}_3 \cdot \text{PCl}_5 \]

\[
\text{AlCl}_3 + \text{PCl}_5 \rightarrow \text{AlCl}_3 \cdot \text{PCl}_5
\]

1. Aluminum chloride and more than the stoichiometric amount of
PCl₅ are placed in a thick-wall tube sealed at one end. The tube
is evacuated using an oil pump and the other end is sealed. The
tube is then heated until the solid turns into a clear melt. After
cooling, the tube is opened under nitrogen and the contents are
poured into a small distillation flask. Vacuum is applied and the
temperature slowly raised to 300°C to remove the excess PCl₅.
II. A precipitate of $\text{AlCl}_3 \cdot \text{PCl}_5$ is produced on mixing a chloroform solution of $\text{PCl}_5$ and $\text{AlCl}_3$.

**PROPERTIES:**

Colorless powder. M.p. 380°C (383°C, II). Soluble in nitrobenzene. This solution conducts a current and probably contains the ions $\text{AlCl}_4^-$ and $\text{PCl}_4^+$.

**REFERENCES:**


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**Aluminum Bromide-Hydrogen Sulfide Adduct**

$\text{AlBr}_3 \cdot \text{H}_2\text{S}$

$\text{AlBr}_3 + \text{H}_2\text{S} = \text{AlBr}_3 \cdot \text{H}_2\text{S}$

266.7 34.1 300.8

Aluminum bromide is dissolved in liquid $\text{H}_2\text{S}$ with exclusion of moisture. When solution is complete, the excess $\text{H}_2\text{S}$ is evaporated. Alternatively, dry $\text{H}_2\text{S}$ gas may be introduced into a solution of $\text{AlBr}_3$ in CS$_2$ and the precipitated crystals filtered with exclusion of moisture.

**PROPERTIES:**

Colorless, moisture-sensitive crystals. M.p. 103°C in a closed tube. Structure: Al tetrahedrally surrounded by 3 Br and 1 S.

**REFERENCES:**


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**Aluminum Iodide-Hexammoniate**

$\text{AlI}_3 \cdot 6\text{NH}_3$

$\text{AlI}_3 + 6\text{NH}_3 = \text{AlI}_3 \cdot 6\text{NH}_3$

407.7 102.2 509.9

Approximately 1 g. of coarsely ground, pure $\text{AlI}_3$ is placed in a tared dry flask and weighed. A slow nitrogen stream is passed
through a trap containing dry, liquid ammonia at $-40^\circ$C, and is then introduced into the flask with the AlI$_3$, which is kept at $-70^\circ$C throughout the reaction. The ammonia is absorbed by the iodide, and a fine, white powder forms. Periodic weighing is used as a check for the quantitative absorption of six moles of NH$_3$ for each mole of AlI$_3$ present.

If the concentration of ammonia in the nitrogen is too high, or if the cooling is not efficient enough, the reaction may become so vigorous that the iodide will melt and partially sublime. Partial ammonolysis of the AlI$_3$ may also occur.

**REFERENCE:**


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**Aluminum Hydroxide**

$\alpha$-Al(OH)$_3$ (HYDRARGILLITE)

I. Aluminum hydroxide (C.P. or better) is dissolved with moderate heating in sodium hydroxide solution (saturated in the cold) until saturation is attained. The solution is diluted with water to a density of 1.1, suction-filtered through hard filter paper, and stored for two weeks in a closed vessel. The mother liquor is decanted from the precipitate of Al(OH)$_3$ formed. The residue is digested for several days with cold water and then washed with hot water until no alkaline reaction is detectable with litmus. The product is dried first over CaCl$_2$, then over P$_2$O$_5$. The entire preparation is carried out in Pyrex glassware.

II. Aluminum hydroxide is precipitated from solution by a cold solution of (NH$_4$)$_2$CO$_3$; the crystals are thoroughly washed on a leaf filter and added in small portions to a 50% NaOH solution until no further solution occurs. The greater part of the solution is filtered. The remainder, which contains a small quantity of undissolved aluminum hydroxide, is used to seed the filtrate. Well-developed crystals of hydrargyllite form in about eight days. They are then washed free of alkali.

**PROPERTIES:**

Poor adsorptivity. Converted into boehmite (AlOOH) at 180 to 200°C. $d$ (20°C) 2.424.

**REFERENCES:**


15. ALUMINUM

β-Al(OH)₃ (BAYERITE)

I. Aluminum hydroxide (C.P. or better) is dissolved with moderate heating in sodium hydroxide solution (saturated in the cold) until saturation is attained. The solution is diluted with water to a density of 1.15 and suction-filtered through hard filter paper. Carbon dioxide is then bubbled through the filtrate for three days. The mother liquor is decanted from the resulting precipitate; the subsequent treatment is identical to that described for hydargillite (I). The thoroughly washed and dried residue is pure bayerite.

II. Pure aluminum ribbon is cut into strips, degreased and rinsed with freshly distilled acetone. The pieces are covered with a layer of amalgam by a short dip in a 0.1 M solution of HgCl₂ and thoroughly washed with distilled water, followed by a final rinsing with double-distilled water. The pieces are then transferred to a Pyrex flask closed off with a soda-lime tube, and covered with double-distilled water. White flakes of bayerite form after a few days.

Initially, the product obtained by procedure II is amorphous according to its x-ray pattern; however, after 25-30 hours, the bayerite lines begin to appear in the powder pattern.

PROPERTIES:

Hexagonal crystals. Considered to be a metastable modification of Al(OH)₃. Industrial Al(OH)₃, which is made by stirring seeded aluminum hydroxide solutions, is chiefly hydargillite. Precipitation from acid solution, on the other hand, yields exclusively an amorphous product when carried out in the cold, and chiefly boehmite (α-AlOOH) when hot solutions are used.

REFERENCES:
R. Fricke, Z. anorg. allg. Chem. 166, 244 (1927); 175, 249 (1928).

α-AlOOH (BOEHMITE)

I. As described in method II for preparation of bayerite, C.P. aluminum is coated with a layer of amalgam and thoroughly rinsed with double-distilled water in a ground glass flask with a riser tube. When the water is brought to a boil, a violent reaction ensues which, however, dies down before the aluminum has been entirely consumed. The boehmite obtained is separated by decantation and dried over CaCl₂, followed by drying over P₂O₅.
II. Aluminum hydroxide precipitated in the cold with ammonia solution is covered with water in an autoclave and heated for two hours at 200°C. Pure boehmite is formed.

**Properties:**

Boehmite is the chief constituent of bauxite. It is converted into diaspore by heating it in the presence of NaOH for several days at 350°C in an autoclave. Natural diaspore is added as a seeding material [V. K. Drushinida, Doklady Akad. Nauk SSSR, N.S., 88, 133 (1953)].

**Reference:**


**Aluminum Oxide**

\(\alpha-\text{Al}_2\text{O}_3\) (CORUNDUM)

The compound is prepared by heating aluminum hydroxide or \(\alpha-\text{Al}_2\text{O}_3\) to above 1100°C. Diaspore undergoes rapid conversion above 500°C.

**Properties:**

Rhombohedral crystals. M.p. 2050°C.

\(\beta-\text{Al}_2\text{O}_3\)

The \(\beta\) form crystallizes from molten aluminum oxide containing up to 5% of an alkali oxide. The transition takes place at a temperature not much below the melting point of cryolite (1020°C) when a mixture of cryolite and \(\alpha-\text{Al}_2\text{O}_3\) is annealed. The \(\alpha\) form is converted into \(\beta-\text{Al}_2\text{O}_3\) after annealing a mixture containing 15-20% cryolite for 20 hours.

**Properties:**

Always contains a small amount of alkali. It is therefore occasionally considered to be a very aluminum-rich alkali aluminate. Hexagonal crystals.

**Reference:**

Recent investigations have established that annealing of aluminum hydroxides (with the exception of diaspore) at temperatures between 400 and 1000°C yields not only $\gamma$-$\text{Al}_2\text{O}_3$, but a series of various phases (χ, η, κ, δ-$\text{Al}_2\text{O}_3$), all of which probably contain some residual water to stabilize the respective lattices. As far as range of existence and preparative conditions for these modifications is concerned, the original papers should be consulted.

REFERENCES:

Aluminum Sulfide

$\text{Al}_2\text{S}_3$

I.  
$2\text{Al} + 3\text{H}_2\text{S} = \text{Al}_2\text{S}_3 + 3\text{H}_2$

54.0  102.2  150.2

Aluminum turnings are placed in a corundum boat inserted in a quartz or hard porcelain tube. One end of the tube is connected to a generator of pure, dry $\text{H}_2\text{S}$; the other end leads to the hood. The tube is placed in a furnace and $\text{H}_2\text{S}$ is passed through. The temperature during the first five hours is 600-630°C, and for the following 12 hours, 1000°C. The product consists of 90-94% aluminum sulfide which still contains some unreacted aluminum and 1-3% oxygen. Higher reaction temperatures lead to a higher oxygen content, because the product reacts with the corundum of the boat.

II.  
$2\text{Al} + 3\text{S} = \text{Al}_2\text{S}_3$

54.0  96.2  150.2

A stoichiometric mixture of aluminum filings and sulfur powder is placed in a graphite crucible and covered with some excess sulfur. The reaction is started by a short circuit between the bottom of the crucible and a carbon electrode immersed in the
crucible. The reaction may also be initiated with a burning mag­
nesium strip. After the reaction is over, the product is placed in
a carbon boat or crucible and heated in vacuum for six hours to
1150°C to remove excess aluminum. The molten mass is then
allowed to cool slowly. Crystals 1-3 mm. thick are obtained. See
also the procedure for deuterium sulfide, p. 134.

PROPERTIES:
Yellowish powder or crystals; excess aluminum gives the
compound a gray tinge. Hydrolyzed by water to H₂S and Al(OH)₃.

REFERENCES:
allg. Chem. 255, 288 (1948); cites earlier references.

Aluminum Sulfite

BASIC ALUMINUM SULFITE, Al₂O₃ · 2SO₂ · H₂O

Sulfur dioxide is introduced into a suspension of Al(OH)₃ in
water until a clear solution is obtained. The latter is then placed
in a flask closed with a Bunsen valve. The flask is heated to
76-80°C with constant shaking. A magnetic stirrer may be used.
Sulfur dioxide is evolved in the process, a slight positive pressure
being maintained by the valve. Crystallization sets in suddenly
and is essentially complete after four hours. The solid product is
filtered and dried under vacuum. It consists of Al₂O₃ · 2 SO₂ · 3 H₂O.
Heating to 68 to 90°C under vacuum liberates water until the
composition Al₂O₃ · 2 SO₂ · 1 H₂O is attained.

PROPERTIES:
Formula weight 248.08. Heating above 100°C causes decompo­
sition with evolution of SO₂ and water.

REFERENCE:
(1936).

NEUTRAL ALUMINUM SULFITE, Al₂O₃ · 3SO₂ · xH₂O

A concentrated aqueous solution of aluminum sulfite is prepared
according to the directions in the preceding method and evaporated
over P₂O₅ in a desiccator. The P₂O₅ should be renewed several times. Sulfur dioxide is passed through the desiccator during the entire drying process, which takes about 10-14 days.

**PROPERTIES:**

White powder with variable water content.

**REFERENCE:**


### Aluminum Selenide

[^2Al + 3Se = Al₂Se₃]

54.0 236.9 290.9

I. Pure, dry aluminum powder (30 g.) is ground together with 50 g. of finely divided, dry precipitated selenium. Then 5 g. of the mixture is transferred into a thick-wall, 200-ml. clay crucible provided with a lid. The crucible is placed in the hood and a small piece of burning magnesium strip is dropped in to ignite the mixture. The crucible is immediately covered again. At intervals of a few seconds the lid is raised a little and about 3 g. of the starting mixture is added until the entire mixture is used up. When the crucible has cooled down, the product is crushed and stored in a closed container.

II. A stoichiometric mixture of aluminum powder and red selenium is placed in a combustion tube, which is evacuated and sealed off. The end of the tube at which the mixture is situated is carefully heated over an open flame until the onset of the reaction, which occurs at the beginning of red heat. The reaction progresses slowly throughout the entire mass and is accompanied by incandescence.

III. Aluminum turnings are placed in a carbon boat inserted in a Pyrex reaction tube. One end of the tube is connected to a source of high vacuum, the other end to a storage tube containing red selenium. The system is evacuated and the selenium is driven into the reaction tube by heating. The reaction tube itself is heated to 600-650°C for 36 hours, which is the time required for complete conversion.

**PROPERTIES:**

Yellow; slowly hydrolyzed in moist air to H₂Se and Al(OH)₃.
REFERENCES:
H. G. Grimm and A. Metzger, Ber. dtsch. chem. Ges. 69, 1356 (1936).

Aluminum Telluride

\[ \text{Al}_2\text{Te}_3 \]

\[ 2\text{Al} + 3\text{Te} = \text{Al}_2\text{Te}_3 \]

I. A corundum crucible is placed in a quartz tube sealed at one end. A narrow glass tube is inserted deep into the quartz tube, and is used for introduction of a slow stream of nitrogen during the reaction. The Te is placed in the crucible with the help of a small long-stem funnel and then fused into a solid mass by heating the quartz tube. The calculated amount of aluminum powder is then added in small portions. If the usually vigorous reaction does not occur, it may be started by mixing the melt briefly with an iron wire. When the reaction is over, the product is annealed by heating for half an hour at 800–900°C.

II. A Pyrex tube (12-mm. diameter) is torch-sealed at one end and is slightly constricted 10 cm. from the sealed end. The lower, sealed part of the tube is charged with tellurium, and a porcelain boat containing somewhat less than the calculated amount of aluminum powder is made to slide down into the tube until it is stopped by the constriction. A second constriction is then made at the open end. The tube is evacuated with an aspirator; the aluminum is heated to a light red glow (caution, the glass may warp) and the tellurium melts. The evaporating tellurium reacts with the aluminum. A small fraction of the tellurium condenses on the colder walls above the aluminum. When all the tellurium has evaporated from the lower end of the tube, the latter is sealed and the condensed tellurium is evaporated from the walls and made to pass several times over the aluminum until its quantity appears to remain constant.

PROPERTIES:
Brown-black, metallic sheen, quite hard; hydrolyzes in moist air.
Aluminum Nitride

\( \text{AIN} \)

I. \( \text{Al} + \frac{1}{2} \text{N}_2 = \text{AIN} \)
\[
\begin{array}{ccc}
27.0 & 14.0 & 41.0 \\
\end{array}
\]

A nickel boat is filled with very pure aluminum powder which has been degreased and dried either by extraction with ether or by heating to 150°C in a stream of nitrogen. The boat is placed in a quartz or porcelain tube and heated in an electric furnace while purified nitrogen is passed over it. Even though the nitride starts to form on the surface below 650°C, the reaction proper begins only at 820°C, when the entire mass begins to glow. At this point the flow of nitrogen should be increased to prevent the \( \text{N}_2 \) pressure from decreasing owing to the rapid reaction. When the reaction is essentially complete, the mass is allowed to cool in a stream of nitrogen. Since the product still contains some unreacted metal, it is pulverized and reheated under nitrogen for 1-2 hours at 1100-1200°C. The product obtained is nearly white and has a nitrogen content not far below theoretical.

II. \( \text{Al} + \text{NH}_3 = \text{AlN} + \frac{3}{2} \text{H}_2 \)
\[
\begin{array}{ccc}
27.0 & 17.0 & 41.0 \\
\end{array}
\]

To obtain silicon-free AIN, aluminum powder pretreated as above is placed in a trough of molybdenum sheet inside a nickel reaction tube, and \( \text{NH}_3 \) is led through while the tube is heated to 1300°C in an electric furnace.

III. \( \text{AlCl}_3 \cdot \text{NH}_3 = \text{AlN} + 3 \text{HCl} \)
\[
\begin{array}{ccc}
150.4 & 41.0 & 109.4 \\
\end{array}
\]

The reaction is performed in the apparatus shown in Fig. 246, which consists essentially of a thick-wall Pyrex tube with an enlargement in the middle and four necks at the top. A thin glass tube (nitrogen inlet) passes through the middle neck and reaches nearly to the bottom. The two side necks contain silver wire leads to a tungsten heating coil suspended in the reaction tube at the level of the bulb. The fourth neck is an outlet for the gas. The reaction tube is thoroughly dried and \( \text{AlCl}_3 \cdot \text{NH}_3 \), prepared
according to the procedure on p. 817, is placed at the bottom. The nitrogen flow is turned on, coil $w$ is heated to about 1000°C, and the AlCl$_3$·NH$_3$ is evaporated at 400°C into the upper chamber of the tube, where it is remelted by the second heating element $h$ and made to flow down again. The decomposition takes place on the tungsten coil, AlN being deposited. When the reaction is complete, the product is scraped off and freed of residual chlorine by heating to incandescence in a nitrogen atmosphere.

**PROPERTIES:**

Slowly hydrolyzed in moist air. Dry O$_2$ and HCl attack the compound only above 800°C, M.p. 2150–2200°C; d (25°C) 3.05. Crystallizes in a wurtzite lattice.

**REFERENCES:**

I. F. Fichter, Z. anorg. allg. Chem. 54, 322 (1907); 82, 194 (1912).
J. Wolf, Z. anorg. allg. Chem. 83, 159 (1913); 87, 123 (1914).


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**Lithium Aluminum Nitride**

$$\text{Li}_3\text{AlN}_2$$

A stoichiometric mixture of Li$_3$N and cleaned and degreased aluminum bronze (99.3% Al) is placed in a molybdenum boat, which is then inserted in an iron tube and heated to 630°C in a stream of nitrogen. A vigorous reaction ensues and the nitrogen is absorbed. The temperature is raised to 750°C for a short time and the product is then cooled under nitrogen.

**Alternative procedures:** The compound is also formed when AlN is annealed with Li$_3$N or when an alloy of 3 Li and 1 Al is heated in a stream of N$_2$. 
PROPERTIES:

White powder, hydrolyzed by humid air. Thermally stable up to 1000°C. Crystallizes in the cubic system in a CaF$_2$ superstructure.

REFERENCE:


**Aluminum Azide**

Al(N$_3$)$_3$

\[
\text{AlH}_3 + 3 \text{HN}_3 = \text{Al(N}_3\text{)}_3 + 3 \text{H}_2
\]

An ether solution of AlH$_3$ is prepared from LiAlH$_4$ and AlCl$_3$, and is then filtered and frozen in a liquid-nitrogen-cooled trap. (cf. p. 807). An excess of anhydrous HN$_3$ dissolved in ether is added, and the contents of the trap are allowed to melt slowly by gradually removing the Dewar flask. The evolution of hydrogen starts at -116°C. The trap is then allowed to warm to room temperature; vacuum is applied and the ether and excess HN$_3$ are distilled off with renewed cooling. The product Al(N$_3$)$_3$ remains as a white powder.

PROPERTIES:

Very moisture sensitive. The compound may be shock detonated. Soluble in tetrahydrofuran.

REFERENCE:


**Aluminum Phosphide**

AlP

\[
\text{Al} + \text{P} = \text{AlP}
\]

Very pure, finely divided aluminum powder (1.8 g.) and 2.9 g. of purified, dried red phosphorus are ground together in a mortar.
The mixture is placed in a Vycor reaction tube (diameter 20 mm; a little less at the ends), one end of which is connected to a distillation flask containing additional red P, and the other end to a receiving flask. The apparatus is flushed with pure hydrogen. The distillation flask is heated in a continuous stream of H₂ until some phosphorus condenses on the aluminum–phosphorous mixture in the reaction tube. The mixture is then ignited by means of a small but extremely hot flame. The ensuing reaction is short but vigorous. When it is over, the excess P is driven into the receiving flask by heating the entire reaction tube. The tube is then cut at the site of the reaction and the AlP is ground under H₂ and stored in a closed container. The product contains 92–94% AlP.

II. A somewhat less pure product is obtained when a mixture of 27 g. of aluminum powder and 31 g. of red P is ignited with a burning magnesium strip (use safety goggles!) in an iron crucible. The crucible should not be more than half full, since the mass expands during the reaction and may overflow. In any case, the crucible should be covered with a lid. The yellowish to gray-black reaction mass is ground in a heated mortar.

**PROPERTIES:**

Yellowish-gray to dark, crystalline. Reacts with water to form PH₃. Crystallizes in the zinc blende structure.

**REFERENCES:**

V. M. Goldschmidt, Ber. dtsch. chem. Ges. 60, 1289 (1927).

**Lithium Aluminum Phosphide**

\[ \text{Li₃AlP₂} \]

First, Li₃Al is prepared by melting together pieces of Li and Al turnings in a 3:1 atomic ratio. The melting process is carried out at 600–700°C under argon. The alloy is ground under CO₂ in an agate mortar and, as was described for AlP, placed in a Vycor tube, one end of which is connected to a distillation flask containing red P. Instead of placing the alloy in direct contact with the tube,
it is better to pour it into a boat made of sintered corundum or, preferably, ZrO₂. The tube is heated in an atmosphere of phosphorus vapor until the reaction starts.

**PROPERTIES:**

Chemical behavior similar to that of AlP. Crystallizes in a rhombically distorted superstructure of the CaF₂ lattice.

The arsenide Li₃AlAs₂ may be prepared by an entirely analogous procedure; its properties are identical to those of Li₃AlP₂.

**REFERENCE:**


**Aluminum Orthophosphate**

\[ \text{AlP}_4 \]

A concentrated sodium aluminate solution is mixed with concentrated \( \text{H}_3\text{PO}_4 \) until the solution is strongly acidic. It is then transferred into a combustion tube, and the tube is sealed and heated to 250°C for several hours. The white, crystalline product usually contains other phosphates in addition to AlP₄. These, however, can be removed because of their solubility in 1:5 aqueous HCl.

**PROPERTIES:**

Formula weight 121.95. M.p. above 1460°C; d (23°C) 2.56. Very slightly soluble in concentrated HCl and HNO₃. Isomorphous with quartz, the silicon atoms in the lattice being regularly replaced by Al and P atoms. Used for special glasses.

**REFERENCES:**


The arsenate AlAsO₄ is isomorphous with AlP₄. For the preparation see F. Machatschki and A. Moser, Z. Kristallogr. (A) 90, 314 (1935); 94, 212 (1936).

**Aluminum Arsenide**

\[ \text{AlAs} \]

\[ \text{Al} + \text{As} = \text{AlAs} \]

Equimolar amounts of the elements are fused together in an evacuated quartz tube at 800°C. Alternatively, the compound may
be prepared in a way similar to that described for AlP, by passing
As vapors in a stream of hydrogen over finely divided aluminum
powder at about 500°C.

PROPERTIES:
Slowly hydrolyzed by cold water, rapidly by hot water. M.p.
above 1200°C. Crystallizes in the zinc blende structure lattice
type.

The antimonide AlSb may be prepared in the same manner as
AlAs, by fusing the elements in an evacuated quartz vessel.

REFERENCES:

Aluminum Carbide

Al₄C₃

\[ 4\text{Al} + 3\text{C} = \text{Al₄C₃} \]

107.9 36.0 143.9

The purest available aluminum powder is mixed with the
stoichiometric quantity of pure, finely divided carbon; the mixture
is placed in a carbon crucible sealed with a carbon stopper and
heated to 2000°C in an atmosphere of H₂. The heating is discon­
tinued after 30 minutes. The product is orange and contains, in
addition to Al₄C₃, a small amount of Al metal. The carbide is
ground to a powder and the metallic impurity removed by treatment
with ice-cold concentrated HCl. The excess carbon floats on the
surface and may be skimmed off. The purity of the product is
directly related to that of the starting material. The presence of
nitrogen results in the formation of nitrogenous compounds.

The conversion may also be achieved by heating in hydrogen
for three hours to 1500°C. A bright yellow, microcrystalline
carbide results.

PROPERTIES:
Golden yellow, hexagonal leaflets. M.p. 2100°C, decomposes
above 2200°C. Methane is evolved on hydrolysis.

REFERENCES:
M. von Stackelberg et al., Z. phys. Chem. (A) 175, 127, 140 (1936).
Lithium Aluminum Cyanide

$\text{LiAl(CN)}_4$

\[\text{LiAlH}_4 + 4\text{HCN} = \text{LiAl(CN)}_4 + 4\text{H}_2\]

Anhydrous HCN is condensed in vacuum onto a frozen ether solution of LiAlH$_4$ and the mixture is allowed to melt slowly. The theoretical amount of H$_2$ is evolved and LiAl(CN)$_4$ precipitates. If an excess of HCN is used, it may be removed by evacuation, together with the ether. The LiAl(CN)$_4$ residue is a white powder.

PROPERTIES:

Hydrolyzes readily. Decomposes after some time even in the absence of oxygen and moisture.

Aluminum cyanide Al(CN)$_3$ may be prepared in a similar manner, by condensing anhydrous HCN onto a freshly prepared ether solution of monomeric AlH$_3$. The product precipitates out with one mole of ether of crystallization. It may be stored for some time in the absence of oxygen and moisture.

REFERENCE:


Aluminum Methoxide

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

\[\text{AlCl}_3 + 3\text{CH}_3\text{OH} + 3\text{NH}_3 = \text{Al(OCH}_3\text{)}_3 + 3\text{NH}_4\text{Cl}\]

A 45-g. portion of freshly sublimed AlCl$_3$ is dissolved at 0°C in 750 ml. of anhydrous methanol. The solution is allowed to warm up to 5°C and an excess of dry NH$_3$ is slowly bubbled through the flask. The Al(OCH$_3$)$_3$ precipitate is suction-filtered, washed with methanol and dried over P$_2$O$_5$.

REFERENCE:

Aluminum Ethoxide

\[
\text{Al} + 3 \text{C}_2\text{H}_6\text{OH} = \text{Al(OC}_2\text{H}_5)_3 + \frac{3}{2}\text{H}_2
\]

I. Aluminum turnings (27 parts) are covered in a round-bottom flask with 276 parts of anhydrous ethanol. Then HgCl\(_2\) (0.2 part) and a trace of iodine are added to start the reaction. The evolution of hydrogen usually begins after a few seconds. If it fails to occur, the flask may be carefully heated on a water bath. If necessary, the aluminum should be slightly etched with dilute NaOH before use and then rinsed with alcohol.

When the reaction slows down, the flask is heated on the water bath for several hours, until the contents become dry and leafy. The excess alcohol is distilled off on an oil bath at 210–220°C, and the hot, liquid residue is quickly poured into a Claisen flask with a wide, short air condenser. The ethoxide is distilled at 10 mm. and 210–220°C. After a short time, the distillate solidifies to a snow-white mass, which is stored in a well-closed container. The yield is 90%.

II. A 100-g. portion of aluminum turnings is covered with 650 ml. of xylene in a flask equipped with a reflux condenser and a dropping funnel, and the mixture is heated to the boiling point of xylene. Absolute ethanol (440 ml.), containing 0.5 g. of KgCl\(_2\) and a trace of iodine, is added dropwise. The reaction starts immediately, and the heat source may soon be removed. When 320 ml. of ethanol has been added, the reaction slows down and heating is again required. The addition of the alcohol should take about \(1\frac{3}{4}\) hours. Heating is continued somewhat longer, and the mixture is filtered hot through a heated fluted filter. The xylene is completely removed from the filtrate, first by distillation and finally under vacuum. About 400 g. of pure, colorless aluminum ethoxide is left in the flask.

PROPERTIES:


REFERENCES:

I. German patent 286,596.
Aluminum Triethanolaminate

\[
\text{Al}(\text{OC}_2\text{H}_4)_3\text{N}
\]

\[
\text{Al}(\text{OC}_2\text{H}_7)_3 + \text{N}((\text{C}_2\text{H}_4\text{OH})_3 = \text{Al}(\text{OC}_2\text{H}_4)_3\text{N} + 3\text{C}_3\text{H}_7\text{OH}
\]

204.2 149.2 173 2 180.3

Aluminum isopropoxide is fused at 150–160°C with an equimolar quantity of triethanolamine. The solidified melt is recrystallized from dioxane, yielding an adduct of \(\text{Al}(\text{OC}_2\text{H}_4)_3\text{N}\) containing one mole of dioxane. Then the adduct is heated for a considerable time at 140°C, dioxane splits off and the solvent-free product is obtained.

**PROPERTIES:**

Cubic crystals hydrolyzed by water. Soluble in chloroform, benzene and other solvents. Sublimes at above 280°C (13 mm.).

**REFERENCE:**


Aluminum Acetate

\[
\text{Al}(\text{O}_2\text{C}_2\text{H}_5)_3
\]

\[
\text{Al}(\text{OC}_2\text{H}_7)_3 + 3\text{CH}_3\text{COOCOCH}_3 = \text{Al}(\text{O}_2\text{C}_2\text{H}_5)_3 + 3\text{CH}_3\text{COOC}_2\text{H}_5
\]

162.2 306.3 204.1 264 3

A 2.81-g. portion of Al ethylate is placed in a small flask equipped with reflux condenser and 15 ml. of acetic anhydride is dropped in. The reaction requires heat. The flask is then heated in an oil bath at 150–160°C for another five hours. After the mixture has cooled, a white product precipitates and is then decanted from the liquid phase. The solid residue is dried at 5 mm. and 100°C for about three hours. The yield is 3.4 g.

**PROPERTIES:**

Insoluble in benzene. Soluble in water, hydrolyzing to form a gellike precipitate.

**REFERENCE:**

**Aluminum Acetylacetonate**

\[ \text{Al}(C_5H_7O_2)_3 \]

\[ \text{Al}([\text{NO}_3]_3 + 3 \text{CH}_3\text{COCH}_2\text{COCH}_3 + 3 \text{NH}_3 = \text{Al}(C_5H_7O_2)_3 + 3 \text{NH}_4\text{NO}_3 \]

I. A small excess of acetylacetone is added to an aqueous solution of \( \text{Al}([\text{NO}_3]_3 \). Then a dilute solution of \( \text{NH}_4\text{OH} \) is added very slowly. This procedure gives pure \( \text{Al} \) acetylacetonate in quantitative yield.

\[ \text{II. } \text{AlCl}_3 + 3 \text{CH}_3\text{COCH}_2\text{COCH}_3 = \text{Al}(C_5H_7O_2)_3 + 3 \text{HCl} \]

Anhydrous \( \text{AlCl}_3 \) is dissolved in chloroform, and a slight excess of acetylacetone is added.

**PROPERTIES:**

Brilliant plaques or prisms, similar to mother of pearl. M.p. 192–194°C. Sublimes at 140°C (10 mm.). \( d \) (20°C) 1.27. Decomposes when heated in air. Insoluble in water; slightly soluble in alcohol, ether and benzene. Can be recrystallized from acetone.

**REFERENCE:**