ALUMINUM HALIDES AND ALUMINUM NITRATE

1. Introduction

Both the binary and complex fluorides of aluminum have played a significant role in the aluminum industry. Aluminum trifluoride [7784-18-1], AlF_3, and its trihydrate [15098-87-0], $AlF_3{\cdot}3H_2O$, have thus far remained to be the only binary fluorides of industrial interest. The nonahydrate [15098-89-2], $AlF_3{\cdot}9H_2O$, and the monohydrate [12252-28-7, 15621-55-3], $AlF_3{\cdot}H_2O$, are of only academic curiosity. The monofluoride [13595-82-9], AlF, and the difluoride [13569-23-8], AlF_2, have been observed as transient species at high temperatures.

Of the fluoroaluminates known, cryolite, ie, sodium hexafluoroaluminate [15096-52-2], Na_3AlF_6, has been an integral part of the process for production of aluminum. The mixtures of potassium tetrafluoroaluminate [14484-69-6],

$KAlF_4$, and potassium hexafluoroaluminate [13575-52-5], K_3AlF_6, have been employed as brazing fluxes in the manufacture of aluminum parts.

Two new types of aluminates, with far-ranging commercial potential, have been prepared and characterized in the past few years. The first is the tetrafluoroaluminate anion (AlF_4^-) for which a reproducible, high-yield synthesis has been developed. This anion is able to stimulate various guanosine nucleotide binding proteins (G-proteins), and inhibit P-type ATPases by serving as a non-hydrolyzing phosphate mimic. Additionally, tetrafluoroaluminate complexes serve as precursors to aluminum trifluoride, which is used as a catalyst for chlorofluorocarbon isomerizations and fluorinations. The aluminum halides and aluminum nitrates have similar properties with the exception of the fluorides. In this group the chlorides are the most commercially important.

2. Aluminum Monofluoride and Aluminum Difluoride

Significant vapor pressure of aluminum monofluoride [13595-82-9], AlF, has been observed when aluminum trifluoride [7784-18-1] is heated in the presence of reducing agents such as aluminum or magnesium metal, or is in contact with the cathode in the electrolysis of fused salt mixtures. AlF disproportionates into AlF_3 and aluminum at lower temperatures. The heat of formation at 25°C is −264 kJ/mol (−63.1 kcal/mol) and the free energy of formation is −290 kJ/mol (−69.3 kcal/mol) (1). Aluminum difluoride [13569-23-8] has been detected in the high temperature equilibrium between aluminum and its fluorides (2).

3. Aluminum Trifluoride

Aluminum trifluoride trihydrate [15098-87-0], $AlF_3{\cdot}3H_2O$, appears to exist in a soluble metastable α-form as well as a less soluble β-form (3). The α-form can be obtained only when the heat of the reaction between alumina and hydrofluoric acid is controlled and the temperature of the reaction is kept below 25°C. Upon warming the α-form changes into a irreversible β-form which is insoluble in water and is much more stable. The β-form is commercially available.

Aluminum trifluoride trihydrate is prepared by reacting alumina trihydrate and aqueous hydrofluoric acid. The concentration of acid can vary between 15 to 60% (4). In the beginning of the reaction, addition of $Al(OH)_3$ to hydrofluoric acid produces a clear solution which results from the formation of the soluble α-form of $AlF_3{\cdot}3H_2O$. As the addition of $Al(OH)_3$ is continued and the reaction temperature increases, irreversible change takes place and the α-form of $AlF_3{\cdot}3H_2O$ gets converted to the β-form and precipitation is observed. After all the alumina is added, the reaction mixture is continuously agitated for several hours at 90–95°C. After the precipitate settles down, the supernatant liquid is removed using rotary or table vacuum filters and the slurry is centrifuged. The cake is washed with cold water, dried, and calcined in rotating horizontal kilns (5), flash dryers, or fluid-bed calciners to produce anhydrous AlF_3 for aluminum reduction cells. This process is known as a wet process.

Aluminum trifluoride can also be advantageously made by a dry process in which dried $Al(OH)_3$ is treated at elevated temperatures with gaseous hydrogen fluoride. High temperature corrosion-resistant alloys, such as Monel, Inconel, and titanium are used in the construction of fluidized-bed reactors. In one instance, an Inconel reactor is divided into three superimposed compartments by two horizontal fluidizing grid sieve plates. Aluminum hydroxide is fed into the top zone where it is dried by the existing gases. The gases such as HF and SiF_4 are scrubbed from stack gases with water. These gases are recycled or used in the manufacture of cryolite [15096-52-3]. Solids are transported from top to bottom by downcomers while HF enters at the bottom zone getting preheated by heat exchange from the departing AlF_3. The bulk of the reaction occurs in the middle compartment which is maintained at 590°C.

The third process involves careful addition of aluminum hydroxide to fluorosilicic acid (6) which is generated by fertilizer and phosphoric acid-producing plants. The addition of $Al(OH)_3$ is critical. It must be added gradually and slowly so that the silica produced as by-product remains filterable and the $AlF_3{\cdot}3H_2O$ formed is in the soluble α-form. If the addition of $Al(OH)_3{\cdot}3H_2O$ is too slow, the α-form after some time changes into the insoluble β-form. Then separation of silica from insoluble β-$AlF_3{\cdot}3H_2O$ becomes difficult.

$$H_2SiF_6 + 2\,Al(OH)_3 \longrightarrow 2\,AlF_3 \cdot 3H_2O \;+\; SiO_2 \;+\; H_2O$$

Environmentally sound phosphate fertilizer plants recover as much of the fluoride value as H_2SiF_6 as possible. Sales for production of $AlF_3{\cdot}3H_2O$ is one of the most important markets (see FERTILIZERS; PHOSPHORIC ACID AND THE PHOSPHATES).

Dehydration of $AlF_3{\cdot}3H_2O$ above 300°C leads to a partial pyrohydrolysis forming HF and Al_2O_3 which can be avoided by heating the trihydrate gradually to 200°C to remove 2.5 moles of water and then rapidly removing the remainder at 700°C. This latter procedure yields a product having less than 3.5% water content and Al_2O_3 content below 8% (7). This product is a typical material used in aluminum reduction cells. The presence of alumina does not interfere in the process of aluminum reduction because it replaces part of the alumina that is fed to the cells.

The principal use of AlF_3 is as a makeup ingredient in the molten cryolite, $Na_3AlF_6{\cdot}Al_2O_3$, bath used in aluminum reduction cells in the Hall-Haroult process and in the electrolytic process for refining of aluminum metal in the Hoopes cell. A typical composition of the molten salt bath is 80–85% Na_3AlF_6, 5–7% AlF_3, 5–7% CaF_2, 2–6% Al_2O_3, and 0–7% LiF with an operating temperature of 950°C. Ideally fluorine is not consumed in the process, but substantial quantities of fluorine are absorbed by the cell lining and fluorine is lost to the atmosphere. Modern aluminum industry plants efficiently recycle the fluorine values.

Minor uses of aluminum fluoride include flux compositions for casting, welding (qv), brazing, and soldering (see SOLDERS AND BRAZING ALLOYS) (8,9); passivation of stainless steel (qv) surfaces (10); low melting glazes and enamels (see ENAMELS, PORCELAIN OR VITREOUS); and catalyst compositions as inhibitors in fermentation (qv) processes. Table 1 gives typical specifications for a commercial sample of AlF_3.

Table 1. **Specification for Commercial Aluminum Trifluoride**

Parameter	Specification
assay as AlF_3, %	90–92
Al_2O_3, typical, %	8–9
SiO_2, max, %	0.1
iron as Fe_2O_3, %	0.1
sulfur as SO_2, %	0.32
bulk density, g/cm^3	
loose	1.3
packed	1.6
screen analysis, % retained	
105 μm (140 mesh)	20
74 μm (200 mesh)	60
44 μm (325 mesh)	90

Other hydrates of aluminum trifluoride are the nonahydrate [15098-89-2], $AlF_3 \cdot 9H_2O$, which is stable only below 8°C, and aluminum trifluoride monohydrate [12252-28-7], [15621-55-3], $AlF_3 \cdot H_2O$, which occurs naturally as a rare mineral, fluellite found in Stenna-Gwyn Cornwall, U.K. (11).

3.1. High Purity Aluminum Trifluoride. High purity anhydrous aluminum trifluoride that is free from oxide impurities can be prepared by reaction of gaseous anhydrous HF and $AlCl_3$ at 100°C, gradually raising the temperature to 400°C. It can also be prepared by the action of elemental fluorine on metal/metal oxide and subsequent sublimation (12) or the decomposition of ammonium fluoroaluminate at 700°C.

Relatively smaller amounts of very high purity AlF_3 are used in ultra low loss optical fiber–fluoride glass compositions, the most common of which is ZBLAN containing zirconium, barium, lanthanum, aluminum, and sodium (see FIBER OPTICS). High purity AlF_3 is also used in the manufacture of aluminum silicate fiber and in ceramics for electrical resistors (see CERAMICS AS ELECTRICAL MATERIALS; REFRACTORY FIBERS).

Anhydrous aluminum trifluoride, AlF_3, is a white crystalline solid. Physical properties are listed in Table 2. Aluminum fluoride is sparingly soluble in water (0.4%) and insoluble in dilute mineral acids as well as organic acids at ambient temperatures, but when heated with concentrated sulfuric acid, HF is liberated, and with strong alkali solutions, aluminates are formed. AlF_3 is slowly attacked by fused alkalies with the formation of soluble metal fluorides and aluminate. A series of double salts with the fluorides of many metals and with ammonium ion can be made by precipitation or by solid-state reactions.

3.2. Health and Safety Factors. Owing to very low solubility in water and body fluids, AlF_3 is relatively less toxic than many inorganic fluorides. The toxicity values are oral LD_{LO}, 600 mg/kg; subcutaneous, 3000 mg/kg. The ACGIH adopted (1992–1993) TLV for fluorides as F^- is TWA 2.5 mg/m^3. Pyrohydrolysis and strong acidic conditions can be a source of toxicity owing to liberated HF.

Table 2. **Physical Properties of Anhydrous Aluminum Trifluoride**

Property	Value
mol wt	83.977
mp, °C	1278[a]
transition point, °C	455
density, g/cm^3	3.10
dielectric constant	6
heat of transition at 455°C, kJ/mol[b]	0.677
heat of sublimation for crystals at 25°C, kJ/mol[b]	300
ΔH_f at 25°C, kJ/mol[b]	−1505
ΔG_f at 25°C, kJ/mol[b]	−1426
S at 25°C, J/(mol·K)[b]	66.23
C_p at 25°C J/(mol·k)[b]	
α-crystals	74.85
β-crystals	100.5

[a] Sublimes.

[b] To convert J to cal, divide by 4.184.

4. Fluoroaluminates

The naturally occurring fluoroaluminates are listed in Table 3.

The common structural element in the crystal lattice of fluoroaluminates is the hexafluoroaluminate octahedron, AlF^{3}_{6}. The differing structural features of the fluoroaluminates confer distinct physical properties to the species as compared to aluminum trifluoride. For example, in AlF_3 all corners are shared and the crystal becomes a giant molecule of very high melting point (13). In $KAlF_4$, all four equatorial atoms of each octahedron are shared and a layer lattice results. When the ratio of fluorine to aluminum is 6, as in cryolite, Na_3AlF_6, the AlF^{3-}_{6} ions are separate and bound in position by the balancing metal ions. Fluorine atoms may be shared between octahedrons. When opposite corners of each octahedron are shared with a corner of each neighboring octahedron, an infinite

Table 3. **Naturally Occurring Fluoroaluminates**

Name	Cas Registry Number	Molecular formula
cryolite	[15096-52-2]	Na_3AlF_6
chiolite	[1302-84-7]	$Na_5Al_3F_{14}$
cryolithionate	[15491-07-3]	$Na_3Li_3(AlF_6)_2$
thomsenolite, hagemannite	[16970-11-9]	$NaCaAlF_6{\cdot}H_2O$
ralstonite	[12199-10-9]	$Na_{2x}(Al_{2x},Na_x)\ (F,OH)_6{\cdot}yH_2O$
prosopite	[12420-95-0]	$CaAl_2(F,OH)_8$
jarlite, *meta*-jarlite	[12004-61-4]	$NaSr_3Al_3F_{16}$
weberite	[12423-93-7]	Na_2MgAlF_7
gearksutite	[12415-96-2]	$CaAl(F,OH)_5{\cdot}H_2O$
pachnolite	[15489-46-0]	$NaCaAlF_6{\cdot}H_2O$

chain is formed as, for example, in Tl_2AlF_5 [33897-68-6]. More complex relations exist in chiolite, wherein one-third of the hexafluoroaluminate octahedra share four corners each and two-thirds share only two corners (14).

4.1. Cryolite. Cryolite constitutes an important raw material for aluminum manufacturing. The natural mineral is accurately depicted as $3NaF\cdot AlF_3$, but synthetic cryolite is often deficient in sodium fluoride. Physical properties are given in Table 4.

Table 4. **Physical Properties of Cryolite**

Property	Value
mol wt	209.94
mp, °C	1012
transition temperature, °C	
monoclinic-to-rhombic	565
second-order	880
dimensions of unit cell, nm	
a	0.546
b	0.561
c	0.780
vapor pressure of liquid at 1012°C, Pa[a]	253
heat of fusion at 1012°C, kJ/mol[b]	107
heat of vaporization at 1012°C, kJ/mol[b]	225
heat of transition, kJ/mol[b]	
monoclinic-to-rhombic at 565°C	8.21
second-order at 880°C	0.4
heat capacity, J/(mol·K)[b]	
monoclinic crystal at 25°C	215
cubic crystal at 560°C	281
liquid at 1012°C	395
S, J(mol·K)[b,c]	238
ΔH_f^0 at 25°C,[c] kJ/mol[b]	−3297
ΔG_f^0 at 25°C,[c] kJ/mol[b]	−3133
density, g/cm^3	
monoclinic crystal at 25°C	2.97
cubic crystal from x-ray	2.77
solid at 1012°C	2.62
liquid at 1012°C	2.087
hardness, Mohs'	2.5
refractive index	
α-fom	1.3385
β-fom	1.3389
τ-fom	1.3396
electrical conductivity, $(\Omega\cdot cm)^{-1}$	
solid at 400°C	4.0×10^{-6}
liquid at 1012°C	2.82
viscosity, liquid at 1012°C, mPa·s(= cP)[a]	6.7
surface tension, liquid in air, mN/m(= dyn/cm)	125
activity product constant in water at 25°C	1.46×10^{-34}
solubility in water, g/100 g	
at 25°C	0.0042
at 100°C	0.0135

[a] To convert Pa to mm Hg, multiply by 7.

[b] To convert J to cal, divide by 4.184.

[c] Monoclinic crystal.

Cryolite derives its name from its resemblance to ice when immersed in water as a result of the closely matched refractive indexes. The only commercially viable source of cryolite deposits has been found in the south of Greenland at Ivigtut (15). Minor localities, not all authenticated, are in the Ilmen Mountains in the former USSR; Sallent, in the Pyrenees, Spain; and Pikes Peak, Colorado (16). For the most part the ore from Ivigtut is a coarse-grained aggregate carrying 10–30% of admixtures, including siderite, quartz, sphalerite, galena, chalcopyrite, and pyrite, in descending order of frequency.

The mineral cryolite is usually white, but may also be black, purple, or violet, and occasionally brownish or reddish. The lustre is vitreous to greasy, sometimes pearly, and the streak is white. The crystals are monoclinic, differing only slightly from orthorhombic symmetry, and have an axial angle of $90°11$. The space group is $P2_1/m$. The [001] and [110] axes are usually dominant, giving the crystals a cubic appearance. Twinning is ubiquitous, and because the lamellae tend to be perpendicular, cleavage appears to be cubic. The fracture of individual crystals, however, is uneven. Because its refractive indexes are close to that of water, powdered cryolite becomes nearly invisible when immersed in water, but because the optical dispersion is different for the two materials the suspension shows Christiansen colors.

Upon heating the crystallographic angles approach 90° and the transition to the cubic form at 565°C is accompanied by a small heat change. The transition also involves a substantial change in density as evidenced by a characteristic decrepitation (17). The second transformation occurs at 880°C as indicated by the slope of the heating curve. It is also accompanied by a sharp rise in electrical conductivity. The heat change is very small and the transitions with rising temperatures probably mark the onset of a lattice disorder. The more plastic character of the solid near the melting point seems to corroborate this view (18).

Liquid cryolite is an equilibrium mixture of the products of the dissociation:

$$Na_3AlF_6 \longrightarrow 2\,NaF + NaAlF_4$$

The composition to the melting point is estimated to be 65% Na_3AlF_6, 14% NaF, and 21% $NaAlF_4$ [1382-15-3]. The ions Na^+ and F^-; are the principal current carrying species in molten cryolite whereas the AlF^{4-}; is less mobile. The structural evidences are provided by electrical conductivity, density, thermodynamic data, cryoscopic behavior, and the presence of $NaAlF_4$ in the equilibrium vapor (19,20).

Molten cryolite dissolves many salts and oxides, forming solutions of melting point lower than the components. Figure 1 combines the melting point diagrams for cryolite–AlF_3 and for cryolite-NaF. Cryolite systems are of great importance in the Hall-Heroult electrolysis process for the manufacture of aluminum (see ALUMINUM AND ALUMINUM ALLOYS). Table 5 lists the additional examples of cryolite as a component in minimum melting compositions.

The vapor from molten cryolite is largely $NaAlF_4$, the vapor pressures of Na_3AlF_6, NaF, and $NaAlF_4$ near the melting point are about in the ratios 5:1:30. Therefore, the liquid tends to become depleted in AlF_3, and the composition of the aluminum cell electrolyte has to be regularly adjusted by the addition of AlF_3 (20,22).

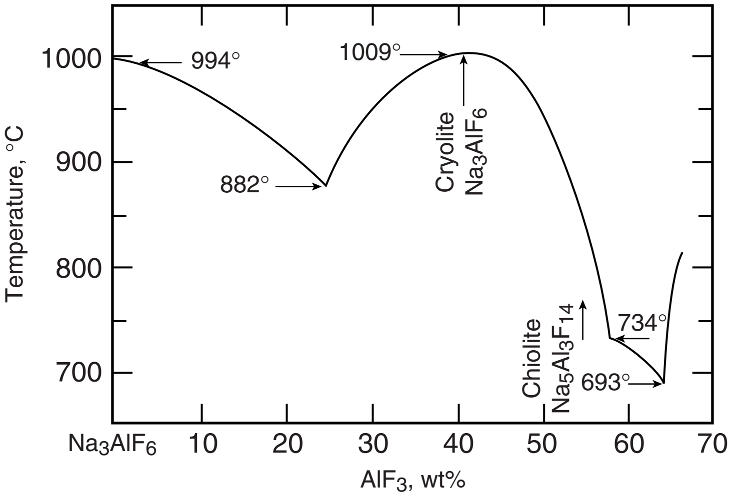

Fig. 1. Liquidus curves in the system NaF–AlF_3 (21).

In contact with moist air, molten cryolite loses HF and is depleted in AlF_3.

$$2\ Na_3AlF_6 + 3\ H_2O \longrightarrow 6\ NaF + 6\ HF\ +\ Al_2O_3$$

The more electropositive metals react with cryolite, liberating aluminum or aluminum monofluoride (22,23). The reduction of cryolite by magnesium is a current

Table 5. **Minimum Melting Compositions Containing Cryolite**

NaF	24.5	882
AlF_3	64	693
Al_2O_3	10.5	962
Li_3AlF_6	62	710
CaF_2	25.8	945
ZrO_2	14	969
MgO	7.5	902
CaO	11.3	896
ZnO	2.4	974
CdO	6.0	971
TiO_2	4.0	970
BaF_2	62.5	835
PbF_2	40	730
feldspar	70	830
NaF	34.0	870
Al_2O_3	12.0	
CaF_2	23.0	867
Al_2O_3	17.7	
CaF_2	37.8	675
AlF_3	6.2	
SiO_2	17	ca 800
Al_2O_3	50	

method for removal of magnesium in the refining of aluminum. Upon contact with strong acids cryolite liberates hydrogen fluoride.

4.2. Synthetic Cryolite. The supply of cryolite is almost entirely met by synthetic material which possesses the same properties and composition with a minor difference in that it is deficient in NaF. Millions of tons of cryolite are used per year. Synthetic cryolite also commonly contains oxygen, hydroxyl group, and/or sulfate groups. The NaF deficiency does not interfere for most applications but the presence of moisture leads to the fluorine losses as HF on heating. Because synthetic cryolite is lighter than the natural mineral, losses by dusting are also higher.

There are several processes available for the manufacture of cryolite. The choice is mainly dictated by the cost and quality of the available sources of soda, alumina, and fluorine. Starting materials include sodium aluminate from Bayer's alumina process; hydrogen fluoride from kiln gases or aqueous hydrofluoric acid; sodium fluoride; ammonium bifluoride, fluorosilicic acid, fluoroboric acid, sodium fluosilicate, and aluminum fluorosilicate; aluminum oxide, aluminum sulfate, aluminum chloride, alumina hydrate; and sodium hydroxide, sodium carbonate, sodium chloride, and sodium aluminate.

The manufacture of cryolite is commonly integrated with the production of alumina hydrate and aluminum trifluoride. The intermediate stream of sodium aluminate from the Bayer alumina hydrate process can be used along with aqueous hydrofluoric acid, hydrogen fluoride kiln gases, or hydrogen fluoride-rich effluent from dry-process aluminum trifluoride manufacture.

$$NaAlO_2 + Na_2CO_3 + 6\,HF \longrightarrow Na_3AlF_6 + 3\,H_2O + CO_2$$

The HF and Na_2CO_3 give a sodium fluoride solution. Bayer sodium aluminate solution is added in the stoichiometric ratio. Cryolite is precipitated at 30–70°C by bubbling CO_2, until the pH reaches 8.5–10.0. Seed crystals are desirable. The slurry is thickened and filtered, or settled and decanted, or centrifuged. The resulting product is calcined at 500–700°C. The weight ratio of fluorine to aluminum in the product should exceed 3.9. The calculated value is 4.2 (24). Cryolite can also be made by passing gaseous HF over briquettes of alumina hydrate, sodium chloride, and sodium carbonate at 400–700°C, followed by sintering at 720°C (25).

In addition, there are other methods of manufacture of cryolite from low fluorine value sources, eg, the effluent gases from phosphate plants or from low grade fluorspar. In the former case, making use of the fluorosilicic acid, the silica is separated by precipitation with ammonia, and the ammonium fluoride solution is added to a solution of sodium sulfate and aluminum sulfate at 60–90°C to precipitate cryolite (26,27):

$$12\,NH_4F + 3\,Na_2SO_4 + Al_2(SO_4)_3 \longrightarrow 2\,Na_3AlF_6 + 6\,(NH_4)_2SO_4$$

The ammonia values can be recycled or sold for fertilizer use. The most important consideration in this process is the efficient elimination of the phosphorus from the product, because as little as 0.01% P_2O_5 in the electrolyte causes a 1–1.5% reduction in current efficiency for aluminum production (28).

Significant amounts of cryolite are also recovered from waste material in the manufacture of aluminum. The carbon lining of the electrolysis cells, which may contain 10–30% by weight of cryolite, is extracted with sodium hydroxide or sodium carbonate solution and the cryolite precipitated with carbon dioxide (28). Gases from operating cells containing HF, CO_2, and fluorine-containing dusts may be used for the carbonation (29).

The specifications for natural cryolite include 95% content of sodium aluminum fluorides as Na_3AlF_6, 4% of other fluorides calculated as CaF_2, and 88% of the product passing through 44 μm sieve (325 mesh). Product for the ceramic industry contains a small amount of selected lump especially low in iron. The following is a typical analysis for commercial-grade cryolite: cryolite as Na_3AlF_6, 91%; fluorine, 48–52%; sodium, 31–34%; aluminum, 13–15%; alumina, 6.0%; silica (max), 0.70%; calcium fluoride, 0.04–0.06%; iron as Fe_2O_3, 0.10%; with moisture at 0.05–0.15%, bulk density at 1.4–1.5 g/cm^3, and screen analysis passing through 74 μm (200 mesh) at 65–75%.

In spite of the fact that cryolite is relatively less soluble, its fluoride toxicity by oral routes are reported to be about the same as for soluble fluorides: LD_{50} = 200 mg/kg; for NaF, 180 mg/kg; KF, 245 mg/kg (30). Apparently, stomach fluids are acid enough to bring the solubility of cryolite up to values comparable with other fluorides. Chronic exposure may eventually lead to symptoms of fluorosis. The toxicity to insects is in many cases high enough for control. Because of its variable composition, synthetic cryolite may show physiological activity greater than the natural mineral (31).

The effective dissolution of Al_2O_3 by molten cryolite to provide a conducting bath has spurred the need for its use in manufacture of aluminum. Additives enhance the physical and electrical properties of the electrolyte, for example the lowering of melting point by AlF_3 (Fig. 1). Figure 2 illustrates the effect of various additives on the electrical conductivity of liquid cryolite. AlF_3 has the

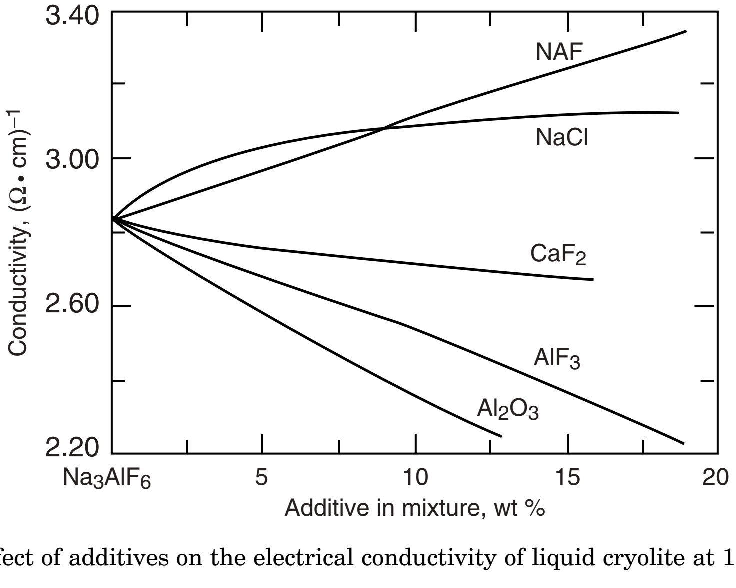

Fig. 2. Effect of additives on the electrical conductivity of liquid cryolite at 1009°C (32).

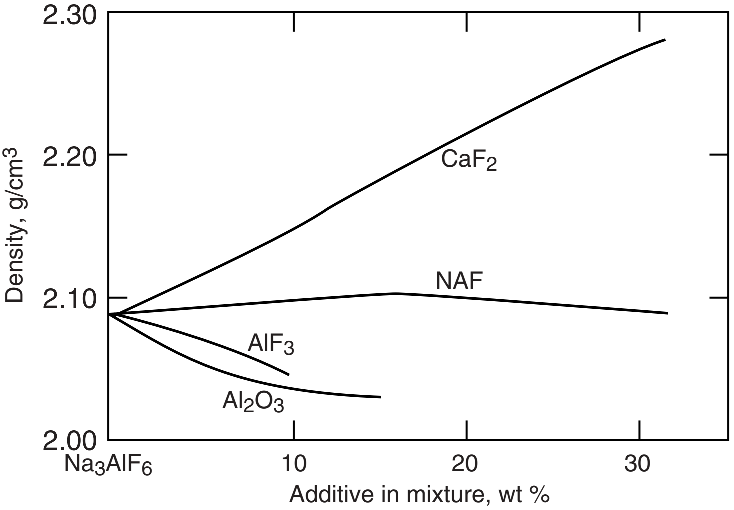

Fig. 3. Effect of additives on the density of liquid cryolite at 1009°C.

adverse effect of decreasing the electrical conductivity. Calcium fluoride is better in this regard but again too much of it can lead to rise in density of the melt close to that of aluminum (ca 2.28 g/cm^3), inhibiting the separation of metal and electrolyte as indicated in Figure 3. Sodium fluoride has the disadvantage of reducing the current efficiency while increasing density and conductivity. Small amounts of lithium fluoride may also improve density and conductivity. Compromises on all of these factors have led to the following composition of the electrolyte: 80–85% cryolite, 5–7% AlF_3, 5–7% CaF_2, 0–7% LiF, and 2–8% Al_2O_3.

Another use for cryolite is in the production of pure metal by electrolytic refining. A high density electrolyte capable of floating liquid aluminum is needed, and compositions are used containing cryolite with barium fluoride to raise the density, and aluminum fluoride to raise the current efficiency.

Other applications of cryolite include use in reworking of scrap aluminum as flux component to remove magnesium by electrochemical displacement; as a flux in aluminizing steel as well as in processing a variety of metals; in the compounding of welding-rod coatings; as a flux in glass manufacture owing to its ability to dissolve the oxides of aluminum, silicon, and calcium, and also because of the low melting compositions formed with the components; for lowering the surface tension in enamels and thereby improving spreading (33); as a filler for resin-bonded grinding wheels for longer wheel life, reducing metal buildup on the wheel, and faster and cooler grinding action; and in insecticide preparations making use of the fines residue from the refining operation of the cryolite.

4.3. Potassium Tetrafluoroaluminate.

Potassium tetrafluoroaluminate, $KAlF_4$, an important fluoroaluminates, mainly because of developments in the automotive industry involving attempts to replace the copper and solder employed in the manufacture of heat exchangers. The source mineral for aluminum radiator manufacture, bauxite, is highly abundant and also available in steady supply. Research and developmental work on the aluminum radiators started in the 1960s using chloride salt mixtures for brazing. The resulting products and the process itself could not compete with conventional radiators because these processes were comparatively uneconomical. This led to the development of an all fluoride-based flux which confers corrosion-resistant features to the product as well as to the process. Potassium tetrafluoroaluminate in mixtures with other fluoroaluminates, potassium hexafluoroaluminate [13775-52-5], K_3AlF_6, and potassium pentafluoroaluminate monohydrate [41627-26-3], $K_2AlF_5{\cdot}H_2O$, has emerged as a highly efficient, noncorrosive, and nonhazardous flux for brazing aluminum parts of heat exchangers. Nocolok 100 Flux (Alcan Aluminum Corp.) developed by Alcan (Aluminum Co. of Canada) has been the first commercial product. Its use and mechanistic aspects of the associated brazing process have been well documented (33–37).

The important task performed by all brazing processes is the removal of oxide films lying on the surfaces of metals to be joined. The process should also permit wetting and flow of the molten filler metal at the brazing temperature (38). The fluxes employed should melt and become active for a successful brazing action. Thus if the flux melts at a temperature higher than that of the filler metal, it leads to the development of thick oxide films on the liquid filler metal inhibiting the flux action. The system $KF{\cdot}AlF_3$ (Fig. 4) (39) provides the most suitable flux for this applications. The system presents a eutectic mixture of $KAlf_4$ and K_3AlF_6 which melts at $559 \pm 2°C$ (40). This is just below the eutectic temperature of the Al-Si filler metal, which is 577°C. The melting point of pure $KAlF_4$ is $574 \pm 1°C$ and that of K_3AlF_6 is 990°C (40).

Both $KAlF_4$ and K_3AlF_6 are white solids. The former is less soluble (0.22%) in water than the latter (1.4%). The generally cubic form of $KAlF_4$ inverts to the orthorhombic modification between −23 and 50°C. On heating the cubic form is stable to its congruent melting temperature. The materials are generally inert and infinitely stable under ambient conditions. At melting temperatures and more significantly at temperatures above 730°C they react with water releasing hydrogen fluoride (41). Dissolution in strong acids is also slow but is enhanced at higher temperatures leading to the evolution of HF. Several possible interactions of $KAlF_4$ and the metal oxides in the brazing processes have been proposed as part of the mechanism for the latter (34).

An early method of preparation of $KAlF_4$ (42) involved combining aqueous solutions of HF, AlF_3, and KHF_2 in stoichiometric proportions and evaporating the suspension to a dry mixture. The product was subsequently melted and recrystallized. Some of the other conventional technical methods comprise reacting hydrated alumina, hydrofluoric acid, and potassium hydroxide followed by separation of the product from the mother liquor; concentrating by evaporation, a suspension obtained by combining stoichiometric amounts of components; and melting together comminuted potassium fluoride and aluminum fluoride at 600°C and grinding the resulting solidified melt.

Several other proprietary methods have been reported, which in general have the aim of producing lower melting products thereby aiming more at the preparation of a eutectic mixtures of the fluoroaluminates as discussed in the beginning of this section. One process (42) describes the making of $KAlF_4$, melting below 575°C, by addition of potassium hydroxide to the aqueous solution of fluoroaluminum acid. The fluoroaluminum acid is prepared from a reaction of

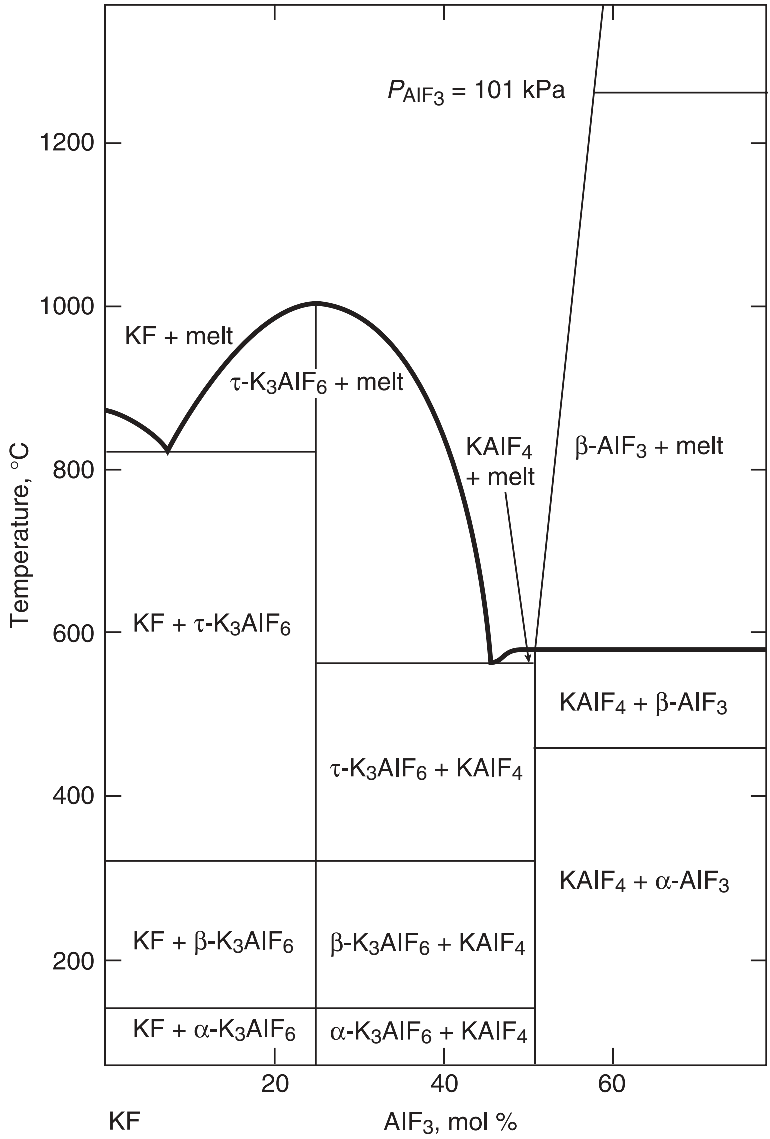

Fig. 4. KF–AlF_3 phase diagram.

hydrofluoric acid and hydrated alumina. A fairly similar method has been reported in making a flux mixture comprising of K_2AlF_5 or $K_2AlF_5 \cdot H_2O$ and $KAlF_4$, wherein a potassium compound is added to the mixed aqueous fluoroaluminic acid ($HAlF_4$, H_2AlF_5, and H_2AlF_6) solution (43).

4.4. Tetrafluoroaluminate. *Synthesis. Aqueous.* Historically, many methods have been used to synthesize the tetrafluoroaluminate (TFA) anion (44). Indeed, aluminofluoride complexes are formed spontaneously in water containing fluoride and trace amounts of aluminum. These methods, however, produce mixtures of aluminates. This partially explains why most applications employing this anion have utilized *in situ* syntheses. Not surprisingly, there was some controversy over the actual products obtained from early syntheses of TFA (45). The first of these methods involved the neutralization of H_3 at 70–80°C (eq. 1) (46). The product was found to be soluble in water. A second proposed method involved the combination of AlF_3 and NaF at 80°C (eq.2) (47). This reaction did not produce TFA but two other products, $AlF_3(H_2O)_3$ and 1.5 $NaF{\cdot}AlF_3$ (chiolite). In an effort to explain this earlier work, and to determine the water solubility of NaTFA, a more tightly controlled synthesis was devised (48). Thus, HTFA was prepared in situ at 80°C (higher temperatures drive the equilibrium towards more HFTA)(49) and then neutralized to a residual acidity of ~0.2% HF (eq. 3). The resulting NaTFA precipitate was isolated by filtration, washed with alcohol, and dried at 105°C. It was subsequently determined that NaTFA decomposes to chiolite and other species when dissolved in water at 25°C. However, at 75°C, the equilibrium is shifted toward the maintenance of TFA and decomposition does not occur. The solubility in water at this temperature is 0.133%.

$$H_3[AlF_6]\ (aq) + NaOH(aq) \longrightarrow Na\ [AlF_4] \cdot H_2O \qquad (1)$$

$$NaF\ (aq) + AlF_3\ (aq) \longrightarrow AlF_3(H_2O)_3\ +\ 1.5NaF \cdot AlF_3 \qquad (2)$$

$$HF\ +\ Al(OH)_3\ +\ Na_2CO_3 \longrightarrow Na\ [AlF_4](s) \qquad (3)$$

Ammonium TFA has been prepared in a number of ways. In one method an inorganic acid such as H_2SO_4 is added to an aqueous slurry of $(NH_4)_3AlF_6$ and either $Al(OH)_3$ or Al_2O_3 leading to the precipitation of $[NH_4^+]\ [AlF_4^-]$ (50). The reaction system was kept under atmospheric pressure and at 70 to 100°C. To neutralize the free ammonia in the slurry and maintain the solubility of the ammonium tetrafluoroaluminate, the inorganic acid was added in such an amount that the pH of the slurry after completion of the reaction was 4 to 7. Varying the method in which the inorganic acid is added to the slurry can control the particle size of the NH_4AlF_4. When the total amount of the acid is poured into the slurry at one time, the particle size of the crystalline NH_4AlF_4 is in the range from about 10 to 20 μm. The particle size increases to the range 20–50 μm when the acid is added intermittently.

$[(CH_3)_4N]$TFA has also been prepared by neutralization of an aqueous solution of hydrated aluminum trifluoride in 40% HF with $N(CH_3)_4OH$ (51). Dehydration of the resulting precipitate at <120°C produced hygroscopic $[(CH_3)_4N^+]\ [AlF_4^-]$. $KAlF_4$ can be prepared from aluminum hydroxide, hydrogen fluoride, and potassium hydroxide. The salt could be isolated as a precipitate and dried under vacuum at 80°C. It was found to have a melting point of 546–550°C by differential scanning calorimetry.

$$4\ (NH_4)_3AlF_6\ +\ 2\ Al(OH)_3\ +\ 3\ H_2SO_4 \longrightarrow 6\ NH_4AlF_4\ +\ 3\ (NH_4)_2SO_4\ +\ 6H_2O \qquad (4)$$

$$AlCl_3 \cdot N(C_2H_5)_3\ +\ 2\ NH_4HF_2 \longrightarrow NH_4AlF_4 + (C_2H_5)_3N \cdot HCl\ +\ HCl \qquad (5)$$

$$Al(OH)_3\ +\ 5\ HF\ +\ 2\ KOH \longrightarrow [K^+]\ [AlF_4^-]\ +\ 5\ H_2O\ +\ KF \qquad (6)$$

Fluoroaluminates with organic base counter-cations can be prepared by evaporating a mixture of $Al(OH)_3$ dissolved in HF and the organic base (52). The organic bases used were hydroxylamine, pyridine, quinoline, morpholine, 2-aminopyridine, and α,α′-bipyridyl. The fluoroaluminates were highly hygroscopic solids. Thermal decomposition produced a mixture of aluminum fluoride and oxide, indicating the presence of either hydrated $[baseH^+]$ $[AlF_4{}^-]$ or a mixed fluoro/aquo/hydroxo compound. TFA can be extracted from mixtures of aluminum and sodium fluoride into dimethylsulfoxide (DMSO) and acetonitrile (AN) solutions containing benzo-15-crown-5 (B15C5) (53). This solubilizes, and apparently stabilizes, salts having the general formula [M(B15C5)]+[TFA]− (with M═Na and 1,8-bis(dimethylamino)napthalene). Varying the concentration of B15C5 from 0.2 to 0.7 M both in DMSO and AN solutions, and the ratio of NaF/Al from 4-50, had no significant effect on the extraction. However in DMSO, six-coordinate aluminum fluoride complexes were also present. The (27) Al NMR data was consistent with quintets ~49 ppm, and sextets for the ^{19}F NMR in the range, −188.1 to −194.2 ppm.

$$2\,NH_4F\cdot HF + Al(NO_3)_3 \longrightarrow NH_4AlF_4 + NH_4{}^+ + 2\,H^+ + 3\,NO_3{}^- \tag{7}$$

Preparation of NH_4AlF_4 can be simplified by using equation 7. Mixing of the solutions to form a precipitate follows solvation of each reactant in water. The precipitate is then filtered and dried with acetone. There is no need to heat the precipitate as it dries out in a short amount of time at room temperature.

Cation exchange has not proven to be a useful method to vary the cation paired with TFA. For example, it is not possible to replace a univalent cation with a divalent cation (for two $AlF_4{}^-$ units) since the divalent anion ($AlF_5{}^{2-}$) is readily formed. This is demonstrated in the synthesis of $Mg[AlF_5]\cdot 2.2\,H_2O$ (54).

$$NaF\,(aq) + AlF_3\,(aq) \longrightarrow [M^+]\,[AlF_4{}^-] \text{ where } M = \text{group I metal, Tl, } NH_4 \tag{8}$$

$$Al(NO_3)_3\,(aq) + 4\,NaF\,(aq) \longrightarrow [Na^+]\,[AlF_4{}^-]\,(aq) + 3\,NaNO_3\,(aq) \tag{9}$$

Anhydrous. The addition of trimethylaluminum to pyridinium fluoride produced the first anhydrous TFA product (eq. 10) (55). This compound could subsequently be used to prepare other anhydrous salts through cation exchange. Thus, the compound $[PS]+$ $[AlF_4]-$ (PS = 1,8-bis(dimethylamino)naphthalene) was prepared in a glove box by slurring $[pyridineH^+]$ $[AlF_4{}^-]$ into a solution containing excess PS dissolved in dry acetomtrile (56). Likewise, slurring the pyridinium derivative in neat collidine (collidine = 2,4,6-trimethylpyridine) in a glove box, and heating to 120°C for 30 minutes produced $[collidineH^+]$ $[AlF_4{}^-]$.

$$(CH_3)_3Al + 4\,HF\cdot pyridine \longrightarrow 4\,CH_4 + [pyridineH^+]\,[AlF_4^-] \tag{10}$$

The compound, $[tetraphenylphosphonium^+]$ $[AlF_4{}^-]$, was prepared by cation exchange with the collidine salt dissolved in methanol and $(C_6H_5)_4PBr$. The product was recrystallized from hot acetone or acetonitrile. The arsonium derivative $[(C_6H_5)_4As^+]$ $[AlF_4{}^-]$ was prepared (using $(C_6H_5)_4AsCl$) and characterized in a similar manner. Another synthesis using the collidine salt involved mixing with $N(CH_3)_4C1$ in dry methanol (57). The by-product collidine HCl was sublimed away in flowing nitrogen at <200°C, and the $[(CH_3)_4N^+]$ $[AlF_4^-]$ left behind.

The ordinarily aqueous salt, NH_4AlF_4, could be prepared anhydrous by adding an alkylamine·aluminum trichloride complex to a bifluoride (eg, NH_4HF_2 or $NaHF_2$) in toluene (58). After completion of the reaction the toluene was distilled off and the product was purified by washing with water (to remove NH_4Cl) and then dried in an oven. The beta phase of NH_4AlF_4 could be obtained by heating pyridine$HAlF_4$ (under N_2) to about 180°C in formamide (59). Pyridine is evolved from the solution and $HAlF_4$ remains behind. The $HAlF_4$ reacts with the formamide solvent eliminating CO gas (eq. 11).

$$C_6H_5NH\,AlF_4 + NH_2CHO \longrightarrow NH_4AlF_4 + C_6H_5N + CO \qquad (11)$$

Characterization. *Spectroscopic.* The IR spectra for these compounds showed a sharp band at 785 cm^{-1} attributed to the Al-F stretching frequencies. The Raman spectra showed a sharp band at 635 cm^{-1}. Mixtures, presumably also containing some TFA have IR values in the range of 410–675 cm^{-1}. In the author's laboratory IR values of 567–825 cm^{-1} for hydrated tetrafluoroaluminate anions with inorganic cations (Na^+, Li^+, K^+, Rb^+, Cs^+, and Ti^+) have been obtained.

NMR peaks at −187 to −194 ppm (^{19}F NMR) and 49 to 52 ppm ($^{27}A1$ NMR) were observed for the PSH, collidineH, (17), $(CH_3)_4N$, $(CH_3)_4P$, $(CH_3)_4As$, and $(CH_3CH_2)_4P$ tetrafluoroaluminate species. Similar NMR data was observed for the AlF_4^- anion stabilized by benzo-15-crown-5 in solutions of donor solvents. The coupling for $[PSH^+][AlF^{4-}]$ in CD_3CN was observed as a sextet from ^{19}F-^{27}Al in the ^{19}F NMR, and a quintet from ^{27}Al- ^{19}F in the ^{27}Al NMR.

In aqueous solutions, there is a rapid, pH dependant exchange between H_2O, OH^-, and F^- ligands binding to the aluminum cation. The solution behavior of fluoroaluminate complexes in aqueous solutions has been studied using ^{27}Al and ^{19}F NMR.

The question of coordination of the fluoroaluminate species in aqueous solutions has also been investigated. The coordination of the fluoroaluminate species is an important one with regards to its ability to interfere with the activities of nucleoside-binding proteins. As noted before, the tetrafluoroaluminate anion has been proposed to stimulate 6-proteins and P-type ATPases by assuming a geometry that is similar to a γ-phosphate. The AlF_4^--nucleoside diphosphate (NDP) complex is thought to mimic the size and shape of a nucleoside triphosphate (60). However, theoretical studies have ruled out any tetracoordination for AlF_x in aqueous solutions (61), although it is possible that ternary species such as $AlOH_yF_x$ may be tetrahedra. A reversible equilibria exist between the different fluoroaluminate species. The proportions of multifluorinated species, such as $AlF_x(H_2O)_{6-x}{}^{(3-x)+}$ (where $x = 3$–6) or $AlF_xOH(H_2O)_{5-x}{}^{(2-x)+}$ (where $x = 3$–5), depend on the excess concentration of free fluoride ions and on the pH of the solution (62).

Structures. There are several examples of tetrahedral $[AlX_4^-]$ species when X=Cl, Br, I. The $[AlF_4^-]$ species has however been controversial due to lack of structural proof, malthough there is indirect evidence, including IR Raman (in molten salts) and NMR data. Tetrahedrally coordinated AlF_4^- compounds had been proposed to exist in a hot melt or in vapor phase, but upon cooling reassembled into six-coordinate forms. In the structure of $[PSH^+][AlF_4^-]$ (where PS = Proton Sponge) the expected tetrahedral anion was confirmed. Accordingly, the F-Al-F angles were ~109° (with Al-F distances of ~1.62 Å). The closest contact between the coordinated fluoride and the chelated proton of the cation was 2.77 Å, which could be considered a long hydrogen bond. (check H bonds to F, add sum of the Van der Waals for H and F=). The crystal structure of [tetraphenylphosphonium$^+$] $[AlF_4^-]$ and [tetraphenylarsonium$^+$] $[AlF_4^-]$ has also been reported. Both structures are similar to that of [PSH] $[AlF_4^-]$ with discrete cations and anions.

The structure of [collidineH$^+$] $[AlF_4^-]$ contains $[AlF_4^-]\infty$ chains, with six-coordinate aluminum. The collidinium cations form strong hydrogen bonds to the terminal fluoride ions of the chain, effectively forming a sheath around these chains. In between the chains and residing in a hydrophobic region defined by the collidinium ions are two independent, discrete, tetrahedral $[AlF_4^-]$ species. As before, the $[AlF_4^-]$ anions have no contact, other than Van der Waals, with other species in the lattice. In the structure of a related compound, $AlF_3(NH_3)_2$ (bridging F), only octahedral aluminum is observed (63). Indeed, there is evidence for octahedral coordination in the tetrafluoroaluminate complex in the active sites of proteins such as the G-protein $Gi\alpha_1$, (64) transducin (65) NDP kinase (66) nitrogenase (67) the Ras-RasGAP complex (68) and the G-protein RhoA (69).

Commercial Production. The commercially utilized Al-F compounds are inorganic and synthetic in origin. Tetrafluoroaluminate salts, $M[AlF_4]$ can be prepared by many different methods. These preparations are mostly *in situ* due to the small amounts of the material needed for the various applications. AlF_3 is a catalyst for various reactions and is prepared by the thermolysis of the $[AlF_4]^-$ anions (70). This must take place at elevated temperatures (between 700 and 900 K) since the enthalpy of this reaction is +66.9 kJ. As an example, the beta phase of $[NH_4^+][AlF_4^-]$ can be thermolyzed at 550°C to form the kappa phase of AlF_3 (59). Fluoroaluminum catalysts can also be prepared by pyrolysis of precursors obtained from aqueous solution, treatment of Al_2O_3 with HF at elevated temperatures, and treatment of $AlCl_3$ with HF or chlorofluorocarbons. One advantage of the $[AlF_4]$- route, however, is that the AlF_3 is produced without any oxide or hydroxide contamination.

Health and Safety Factors. In view of the ubiquity of phosphate in cell metabolism together with the dramatic increase in the amount of aluminum and fluoride now found in our ecosystem, aluminofluoride complexes represent a strong potential danger for living organisms, including humans (71). One area of important research will be the investigation of the long-term pharmacological and toxicological effects of exposure to tetrafluoroaluminate complexes on animals and plants. Another area of future research will be the determination of the relationship, if any, between aluminum in everyday products (cooking utensils, deodorants, antacids, food and beverage packaging), the increasing use of fluoride (water fluoridation, dental products, industrial fertilizers), and the health of humans.

The toxicity of these fluoroaluminates is mainly as inorganic fluorides. The ACGIH adopted (1992–1993) values for fluorides as F^- is TLV 2.5 mg/m^3. The oral toxicity in laboratory animal tests is reported to be LD_{50} rat 2.15 mg/kg (41). Because of the fine nature of the products they can also be sources of chronic toxicity effects as dusts.

Uses. Catalysis. Tetrafluoroaluminates are used in the preparation of AlF_3. Aluminum trifluoride is important in the industrial production of aluminum metal, as it increases the conductivity of electrolytes in the electrolysis process. Aluminum trifluoride is also used as a catalyst for chlorofluorocarbon isomerization and fluorination. High surface area AlF_3 dispersed onto carbon, organic, or inorganic supports may be a useful catalyst for these or other reactions (72). For example, a fluoroaluminum species (obtained from ammonium bifluoride in anhydrous methanol slurried with calcined alumina) generated on a support of alumina was treated with chromium to obtain active olefin polymerization catalysts (73).

$$5\ NaAlF_4\ (s) \longrightarrow Na_5Al_3F_{14}\ (s) + 2\ AlF_3\ (s) \qquad (12)$$

Biological Activity. Aluminum fluoride complexes, especially tetrafluoroaluminates [AlF_4^-], are currently receiving intense scrutiny because of their ability to act as phosphate analogues and thereby stimulate various guanosine nucleotide binding proteins (G-proteins) (74) and inhibit P-type ATPases (75) (See Fig. 5). G-proteins take part in an enormous variety of biological signaling systems, helping to control almost all important life processes. As a result of the ubiquitous nature of G-proteins, tetrafluoroaluminates are used in laboratory studies to investigate the physiological and biochemical changes caused in cellular systems by aluminofluoride complexes.

For most of the biochemical and physiological studies involving the putative AlF_4^- anion, the fluoride source is usually sodium fluoride, and the aluminum source is aluminum nitrate or aluminum chloride. Solutions are usually prepared with millimolar concentrations of sodium fluoride, and micromolar concentrations of the aluminum source.

Transfer of phosphate groups is the basic mechanism in the regulation of the activity of numerous enzymes, including energy metabolism, cell signaling, movement, and regulation of cell growth. Phosphate is an important component of phospholipid in the cell membranes. AlF_4^- acts as a high affinity analog of the γ-phosphate (76,77). AlF_4^- mimics the role of γ-phosphate only if the β-phosphate

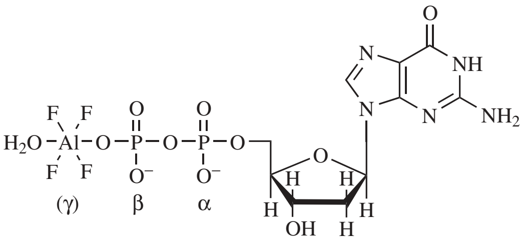

Fig. 5. AlF_4^--GDP binding. AlF_4^- binds strongly to the β-phosphate.

is present and remains unsubstituted. The effect is more readily seen with G proteins because guanosine diphosphate (GDP) is always tightly bound at the site afier the hydrolysis of guanosine triphosphate (GTP).

The tetrafluoroaluminate complex was proposed to act as an analogue of the terminal phosphate of GTP because the Al-F bond length is close to the P-O phosphate bond length, and the AlF_4^- and PO_4^{3-} structures are both tetrahedral. Fluorine and oxygen have nearly the same size and the same valence orbitals. Aluminum and phosphorus have their valence electrons in the same third shell. However, the two bonding schemes differ in that the former is more ionic while the latter is more covalent. In phosphate, oxygen is covalently bound to the phosphorus and does not exchange with oxygen from the solvent. In $[AlF_4^-]$ the bonding between the electropositive aluminum and the highly electronegative fluorine is more ionic in character. The reaction of a bound phosphate compound with orthophosphate is endergonic and slow, whereas the corresponding reaction with $[AlF_4^-]$ is rapid and spontaneous. Fluorides in the bound complex can also exchange with free fluoride ions in solution.

G protein-mediated cell responses are of key importance in the processes of neurotransmission and intercellular signaling in the brain (78) and AlF_4^- acts as an active stimulatory species (79). Aluminofluoride complexes mimic the action of many neurotransmitters, harmones, and growth factors. Exposure of osteoclasts to AlF_4^- resulted in a marked inhibition of bone resorption (80). Brief exposure to aluminum fluoride complexes induced prolonged enhancement of synaptic transmission (81) and can affect the activity of many other ion channels and enzymes in the kidney (82). Rapid and dynamic changes of the actin network are of vital importance for the motility of human neutrophils. AlF_4^- induction expressed a pronounced and sustained increase in a filamentous form of actin in intact human neutrophils (83).

It should be noted that the human body does posses natural barrier systems to aluminum intake. There are various physiological ligands, such as transferrin, citrate, and silicilic acid, which are efficient buffers in preventing the intake of aluminum under natural conditions (84). However, the formation of AlF_4^- only requires trace amounts of aluminum, and the increased bioavailability of aluminum in the environment will certainly lead to increased absorption of aluminum by living organisms.

It should be noted that there is some uncertainty over the identity of the biologically active aluminum compound. Species with four fluorines, six fluorines, and with the fluorines replaced by hydroxide appear possible. For example, multinuclear NMR spectroscopy was used to study the ternary system Al^{3+}, F^-, and NDP in aqueous solutions ($pH = 6$) without protein (85,86). Ternary complexes (NDP) AlF_x ($x = 1-3$) were found, but no (NDP)AlF_4^- was detected. Further multinuclear NMR studies of fluoroaluminate species in aqueous solutions over a wider pH range (2–8) with varying [F]/[Al] concluded that all the fluoroaluminate complexes observed in aqueous solution are hexacoordinated with an octahedral geometry (87). Further research specifically targeted to elucidate the nature of the aluminum phosphate interaction will certainly provide the answer in the near future.

As Flux Material. Potassium tetrafluoroaluminate can be used as a flux when soldering aluminum. A flux is added in order to remove oxides and other disruptive covering films on the metal surface (88). A mix of fluoroaluminates (including $KAlF_4$ and $KAlF_6$) can be used as a flux in the brazing of aluminum and aluminum alloy parts. The flux containing the mix of fluoroaluminates allows brazing of aluminum at temperatures lower than what could be accomplished with fluoride fluxes, thus saving heating energy (89). Another method utilizes a flux-coated soldering rod that is used to deliver a solder alloy and a flux compound to the region to be repaired. The flux compound has a higher melting temperature than the solder alloy, and is present as a coating that thermally insulates the alloy to cause the flux compound and the solder alloy to melt nearly simultaneously during the soldering operation. The solder alloy is preferably a zinc-aluminum alloy, while the flux coating preferably contains a cesium-aluminum flux compound such as potassium cesium tetrafluoroaluminate, dispersed in an adhesive binder that will readily volatilize or cleanly bum off during the soldering operation. The flux compound and binder form a hard coating that adheres to and thermally insulates the solder alloy until the flux compound melts. By controlling the relative amounts of flux compounds and binders, the flux coating remains protective and insulating on the alloy until melting of the flux compound begins (90).

Other. $LiAlF_4$ can be incorporated into the carbon cathode current collector of non-aqueous lithium batteries. $LiAlF_4$ is also used as the non-aqueous electrolyte, which can be dispersed throughout the cathode collector (91).

Future Considerations. Industrially, continued AlF_4^- research will be seen in the development of better AlF_4^- precursors, which provide for cleaner decomposition at lower temperatures to AlF_3. The deposition of AlF_4^- onto organic or inorganic supports for subsequent decomposition to AlF_3 continues to be investigated. Future research will also be conducted with the view of preparing more pure $M^+ AlF_4^-$ (M = metal or organic cation) with less dangerous starting materials, lower temperatures, and better cost effectiveness. Preparation of better fluxes containing AlF_4^- for the soldering of aluminum and aluminum alloys will also be a continuing area of research and development.

All of these applications will benifit from fundamental synthetic and structural results. Thus, there will be a clear connection between laboratory research and commercial applications.

5. Aluminum Chloride

The chemistry of aluminum chloride is influenced significantly by hydration. Aluminum chloride hexahydrate [7784-13-6], $AlCl_3{\cdot}6H_2O$, is a crystalline solid that dissolves easily in water forming ionic species. Heating the hydrate results in the loss of hydrogen chloride [7647-01-0], HCl, and formation of aluminum oxide [1344-28-1], Al_2O_3. On the other hand, anhydrous aluminum chloride [7466-70-0] reacts violently with water evolving heat, a gas consisting of hydrogen chloride and steam, and aluminum oxide particulates. Anhydrous aluminum chloride sublimes at 180°C leaving no residue. The uses of anhydrous aluminum chloride and the hydrated form are also very different. The anhydrous material is a Lewis acid used as an alkylation catalyst. The hydrate is used principally as a flocculating aid.

Table 6. **Physical Properties of Anhydrous Aluminum Chloride**[a]

Property	Value
molecular weight	133.34054
density at 25°C[b], g/mL	2.46
sublimation temperature[b], °C	180.2
triple point, °C, 233 kPa[c]	192.5 ± 0.2
heat of formation, 25°C, kJ/mol[d]	-705.63 ± 0.84
heat of sublimation of dimer, 25°C, kJ/mol[d]	115.52 ± 2.3
heat of solution, 20°C, kJ/mol[d]	−329.1
heat of fusion, kJ/mol[d]	35.35 ± 0.84
entropy, 25°C, J/(K·mol)[d]	109.29 ± 0.42
heat capacity, 25°C, J/(K·mol)[d]	91.128

[a] Ref. 92.

[b] Ref. 93.

[c] To convert kPa to psi, multiply by 0.145.

[d] To convert J to cal, divide by 4.184.

Commercially, aluminum chloride is available as the anhydrous $AlCl_3$, as the hexahydrate, $AlCl_3 \cdot 6H_2O$, or as a 28% aqueous solution designated 32°Be′. Polyaluminum chloride, or poly(aluminum hydroxy) chloride [1327-41-9] is a member of the family of basic aluminum chlorides. These are partially neutralized hydrates having the formula $Al_2Cl_{6-x}(OH)_x \cdot 6H_2O$ where $x = 1 - 5$.

5.1. Anhydrous Aluminum Chloride.

Properties. Anhydrous aluminum chloride is a hygroscopic, white solid that reacts with moisture in air. Properties are shown in Table 6. Commercial grades vary in color from light yellow to light gray as a result of impurities. Crystal size is dependent upon method of manufacture. At atmospheric pressure, anhydrous aluminum chloride sublimes at 180°C as the dimer [13845-12-0], Al_2Cl_6, which dissociates to the monomer beginning at approximately 300°C. Dissociation is essentially complete at 1100°C. As can be seen from Figure 6, the liquid form of aluminum chloride exists only at elevated temperatures and pressures.

Aluminum chloride dissolves readily in chlorinated solvents such as chloroform, methylene chloride, and carbon tetrachloride. In polar aprotic solvents, such as acetonitrile, ethyl ether, anisole, nitromethane, and nitrobenzene, it dissolves forming a complex with the solvent. The catalytic activity of aluminum chloride is moderated by these complexes. Anhydrous aluminum chloride reacts vigorously with most protic solvents, such as water and alcohols. The ability to catalyze alkylation reactions is lost by complexing aluminum chloride with these protic solvents. However, small amounts of these “procatalysts” can promote the formation of catalytically active aluminum chloride complexes.

Manufacture. In the United States anhydrous aluminum chloride is manufactured by the exothermic reaction of chlorine [7782-50-5], Cl_2, vapor with molten aluminum [7429-90-5]. The aluminum may be scrap, secondary ingot of varying purity, or prime ingot. Melting of additional metal feed, external cooling of the reactor, and regulation of the chlorine feed rate, control the reactor temperature between 600–750°C. Chlorine is fed into the molten aluminum pool below the pool’s surface. Aluminum chloride sublimes out of the pool and into a condensing vessel where the product solidifies on the condenser walls.

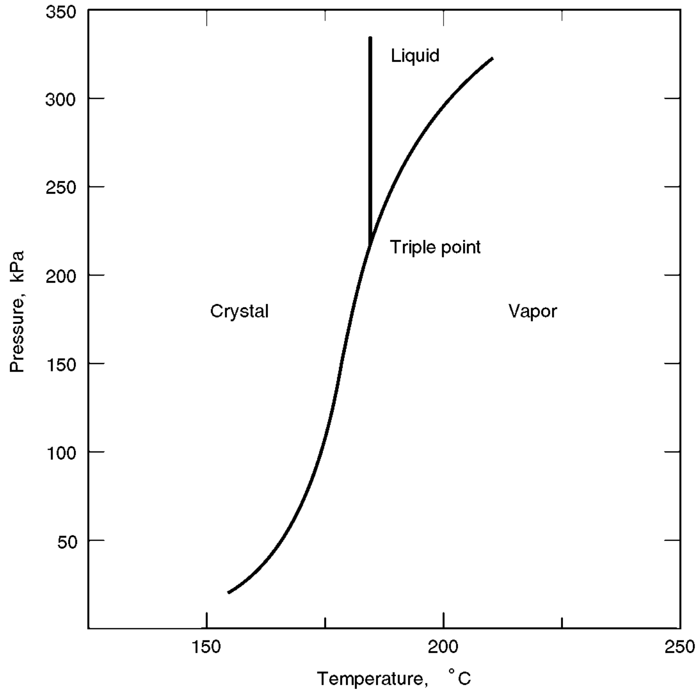

Fig. 6. Aluminum chloride phase diagram. The triple point occurs at 192.5°C at 33 kPa. To convert to psi, multiply by 0.145.

Condensers are normally air-cooled, thin-walled steel vertical cylinders having cone-shaped bottoms. The aluminum chloride grows into teardrop-shaped crystals which are periodically removed, crushed, screened, and packaged under a dry air or nitrogen atmosphere. The product may be colored yellow because of the presence of excess chlorine or ferric chloride [7705-08-0]. A gray or greenish coloration indicates the presence of condensed aluminum vapor in the product.

The chlorination of aluminous materials in the production of aluminum chloride has been thoroughly investigated (93). The Gulf Oil Company produced aluminum chloride from calcined bauxite [1318-16-7] and coke from 1920 to 1960 (94).

In 1948 BASF commercialized the process of catalytic chlorination of gamma-alumina in a fluidized bed (95). This process is still used in Germany. A mixture of chlorine and carbon monoxide passes over a beechwood charcoal catalyst in a preliminary step which partially converts the gases to phosgene. The hot gas mixture enters the bottom of a lined reactor and as the gas flows upward through a bed of finely divided particles of gamma-alumina, aluminum chloride gas forms. Catalytic amounts of sodium chloride are added to maintain a liquid phase within the fluidized bed of alumina and promote the conversion of the solid gamma-alumina to aluminum chloride vapor. Finely divided droplets of molten sodium aluminum chloride develop under these reaction conditions. The hot gas which exits the top of the reactor is filtered to remove entrained liquids and solids. The anhydrous aluminum chloride solidifies in a condenser, is collected, and packaged. Off-gases are purified before recycling.

The hot (400–500°C) inlet gases warm the alumina particles and the mildly exothermic reaction serves to maintain the heat of the furnace between 500 and 600°C. The alumina particle size is critical for maintaining a good reaction rate and a fluidized bed.

The main impurities of the reaction product are iron (0.02 to 0.03%) and small quantities of sodium (<0.01%) as chlorides. No chlorine-consuming side reactions occur and the product requires only one step to obtain a product free of significant impurities. The lower process temperatures also reduce demands on the materials of plant construction and maintenance.

Both the Toth and Alcoa processes provide aluminum chloride for subsequent reduction to aluminum. Pilot-plant tests of these processes have shown difficulties exist in producing aluminum chloride of the purity needed. In the Toth process for the production of aluminum chloride, kaolin [1332-58-7] clay is used as the source of alumina (96). The clay is mixed with sulfur and carbon, and the mixture is ground together, pelletized, and calcined at 700°C. The calcined mixture is chlorinated at 800°C and gaseous aluminum chloride is evolved. The clay used contains considerable amounts of silica, titania, and iron oxides, which chlorinate and must be separated. Silicon tetrachloride and titanium tetrachloride are separated by distillation. Resublimation of aluminum chloride is required to reduce contamination from iron chloride.

In the Alcoa process, high purity aluminum chloride is prepared for electrolytic reduction to aluminum (97). The starting material is Bayer process alumina. A small amount of sodium compounds (2.0–0.5% as Na_2O) is added to facilitate alumina chlorination. This alumina is coked or impregnated with carbon to yield a product containing 15–24 wt % carbon and the coked alumina, contaminated with sodium but otherwise substantially free of elements yielding volatile chlorides, reacts with chlorine in a fluidized-bed reactor. Reaction temperature is controlled preferably at about 600°C. Effluent gases from the reactor are cooled below the reaction temperature, but above the condensation temperature of aluminum chloride, and filtered. Solids consisting of aluminum oxide, carbon dust, aluminum oxychloride [13596-11-7], AlOCl, and a liquid composed of equimolar quantities of sodium and aluminum chlorides are removed from the gas stream. Material retained on the filter is returned in controlled amounts to the reactor to improve the efficiency of operation. After filtration, the gas stream containing essentially pure aluminum chloride and oxides of carbon is conducted to a desublimer (98). The aluminum chloride vapor can be condensed on solid particles of aluminum chloride maintained in a temperature-controlled fluidized bed (99). Product condensed in this manner is a lobular, free-flowing powder suitable for electrolytic reduction to aluminum. Traces of chlorinated biphenyls and phosgene contaminate aluminum chloride produced in this manner, making this product unsuitable for most commercial aluminum chloride applications. An electrolytic method for the production of sodium and aluminum chloride has been reported (100).

Economic Aspects. The U.S. exported 15,700 t of aluminum chloride and imported 1,160 t of aluminum chloride in 2001 (101). Current price of aluminum chloride anhydrous is in the range of $ 0.85–90/lb (102).

Table 7. **Properties of Commercial Anhydrous Aluminum Chloride**[a]

Property	Value
mesh size, U.S. sieve series	-20^b
nonvolatile material, %	0.15
aluminum chloride, %	99.6
water insolubles, ppm	150
free aluminum, ppm	30
iron, ppm	30
magnesium, ppm	5

[a] Ref. 11.

[b] Corresponds to pore size of 840 μm.

Specifications and Packaging. Aluminum chloride's catalytic activity depends on its purity and particle size. Moisture contamination is an important concern and exposure to humid air must be prevented to preserve product integrity. Moisture contamination can be determined by a sample's nonvolatile material content. After subliming, the material remaining is principally nonvolatile aluminum oxide. Water contamination leads to a higher content of nonvolatile material.

In many chemical processes the catalyst particle size is important. The smaller the aluminum chloride particles, the faster it dissolves in reaction solvents. Particle-size distribution is controlled in the manufacturer's screening process. Typical properties of a commercial powder are shown in Table 7.

Aluminum chloride is available in a wide variety of moisture-free packages. Pails and drums are often used when fixed amounts of aluminum chloride are required for batch operations. For small operations, bags having a specially designed liner to maintain moisture-free product are available. For shipments from 200 to 1200 kilograms net, suppliers offer 37.8, 75.7, 113.6, and 208-L drums. Semibulk bins hold up to 11,000 kilograms net. These returnable containers are constructed of fiberglass to make shipping, storage, and handling of aluminum chloride more convenient. Aluminum chloride can also be purchased in bulk truck trailers in quantity up to 90,000 kg net (103).

Safety and Handling. Anhydrous aluminum chloride reacts with water or moisture, generating heat, steam, and hydrochloric acid vapors. Product containers should be stored inside a cool, dry, well-ventilated area and bulk handling systems must be waterproofed; the product transferred only in a nitrogen or dry air system. Although aluminum chloride is nonflammable, it should also be stored away from combustible materials. In storage, some reaction with moisture may occur and over time can lead to a pressure build-up from HCl in the container. Containers should be carefully vented before being opened (103). Safety goggles or face shields, rubber gloves, rubber shoes, and coveralls made of acid-resistant material should be used in handling. A NIOSH/OSHA-certified respirator is also required to prevent breathing fumes and dust (103). Aluminum chloride reacts with moisture in the skin, in the eyes, ears, nose, and throat (103).

The ACGIH TLV TWA is 2.0 mg/m^3 soluble salts, as aluminum. The TLV is based on the amount of hydrolyzed acid and the corresponding TLV (104).

Environmental Protection. Fumes resulting from exposure of anhydrous aluminum chloride to moisture are corrosive and acidic. Collection systems should be provided to conduct aluminum chloride dusts or gases to a scrubbing device. The choice of equipment, usually one of economics, ranges from simple packed-tower scrubbers to sophisticated high energy devices such as those of a Venturi design (103).

Spills should be picked up before flushing thoroughly with water and neutralizing with soda ash or lime. The introduction of aluminum chloride into any drainage system results in the reduction of effluent pH, which can be adjusted using caustic soda or lime (103).

Uses. Aluminum chloride is used as a catalyst in a wide variety of manufacturing processes, such as the polymerization of light molecular weight hydrocarbons in the manufacture of hydrocarbon resins. Friedel-Crafts reactions (qv) which employ this catalyst are used extensively in the synthesis of agricultural chemicals, pharmaceuticals (qv), detergents, and dyes (105).

Aluminum chloride is a nucleating agent in the production of titanium dioxide [13463-67-7] (rutile) used as a white pigment in a variety of paints, paper, and plastics. In the manufacture of titanium dioxide (106), aluminum chloride is mixed with titanium tetrachloride to ensure the formation of the rutile crystalline structure during the reaction with oxygen at 1300−1450°C (see TITANIUM COMPOUNDS). Sufficient aluminum chloride is used to produce TiO_2 containing 1% Al_2O_3. The pigment is wet treated, filtered, washed, dried, and fluid-energy-milled to form a dry TiO_2 for plastic pigmentation and for paints. Environmental and cost problems have favored use of this chloride process. Aluminum chloride is also used in water treatment (107).

5.2. Aluminum Chloride Hexahydrate. The hexahydrate of aluminum chloride is a deliquescent, crystalline solid soluble in water and alcohol and usually made by dissolving aluminum hydroxide [21645-51-2], $Al(OH)_3$, in concentrated hydrochloric acid. When the acid is depleted, the solution is cooled to 0°C and gaseous hydrogen chloride is introduced. Crystalline aluminum chloride hexahydrate, $AlCl_3{\cdot}6H_2O$, is precipitated, filtered from the liquor, washed with ethyl ether, and dried. Alternatively, anhydrous aluminum chloride may be hydrolyzed in chilled dilute hydrochloric acid. Briquetting of the anhydrous material slows the reaction and the hydrogen chloride evolved may be recycled to aid precipitation of the hexahydrate.

Aluminum chloride hexahydrate is available in a 28% by weight (32° Be′) aqueous solution shipped in glass carboys, tank cars, or trucks. Crystalline hexahydrate is shipped in glass containers or plastic-lined drums. In 1980, 5200 metric tons of aluminum chloride hexahydrate on a 100% $AlCl_3$ basis was produced in the United States (106).

Roofing granules and mineral aggregate for bituminous products are treated with aluminum chloride solution to improve adhesion of the asphalt (108) (see BUILDING MATERIALS, SURVEY). Pigmented coatings (qv), containing sodium silicate, Na_2SiO_3, and used to color roofing granules, are insolubilized by spraying with aluminum chloride solution and then heating. Aluminum chloride hydrates are the alumina sources used in the manufacture of special forms of alumina and alumina-silica refractories (qv) such as alumina fibers (109), finely dispersed alumina for pesticide carriers (110), and catalyst substrates. Certain casting molds are hardened by spraying with a solution of aluminum chloride before firing.

Aluminum chloride hydrate is used in textile finishing to impart crease recovery and nonyellowing properties to cotton (qv) fabrics, antistatic characteristics to polyester, polymide, and acrylic fabrics, and to improve the flammability rating of nylon (see TEXTILES). Dye-bleeding of printed textile may be blocked (111) by treatment with aluminum chloride and zinc acetate, $Zn(O_2CCH_3)_2$, followed by solubilizing with ethylenediamine tetraacetic acid, and washing from the fabric. Aluminum chloride hexahydrate is used in cosmetics (antiperspirants) and the pharmaceutical industry.

5.3. Basic Aluminum Chlorides.

The class of compounds identified as basic aluminum chlorides [1327-41-9] is used primarily in deoderant, antiperspirant, and fungicidal preparations. They have the formula $Al_2(OH)_{6-x}Cl_x$, where $x = 1$–5, and are prepared by the reaction of an excess of aluminum with 5–15% hydrochloric acid at a temperature of 67–97°C (112). The same compounds are obtained by hydrolyzing aluminum alkoxides with hydrochloric acid (113,114) (see ALKOXIDES, METAL). Basic aluminum chloride has also been prepared by the reaction of an equivalent or less of hydrochloric acid with aluminum hydroxide at 117–980 kPa (17–143 psi) (114).

Aluminum chloride solutions used in antiperspirants and deoderant preparations must be buffered for the protection of skin and clothing (see COSMETICS). Lactic acid [598-82-3] is usually employed for neutralizing these formulations. Hydrates of aluminum chloride and basic aluminum chlorides are also effective in a number of difficult water treatment problems (see FLOCCULATING AGENTS). A polymeric form, called polyaluminum chloride, is added in amounts of 50–500 ppm and the pH adjusted to about 6.5 in the presence of treatment aids such as emulsion breakers, anionic surfactants, diatomaceous earth, or a high molecular weight flocculant. The resulting floc may be separated by aeration and flotation, settling and decantation, electrophoresis, or filtration. Latex, acrylic paint and oil emulsions, dyes, clay suspensions, and effluent from sanitary waste digestion respond to this treatment (see ALUMINUM COMPOUNDS, POLYALUMINUMS).

6. Aluminum Bromide

Anhydrous aluminum bromide, $AlBr_3$, forms colorless trigonal crystals and exists in dimeric form, Al_2Br_6, in the crystal and liquid phases (1). Dissociation of the dimer to the monomer occurs in the gas phase. The bromide is produced commercially only in small quantities. This product melts at 97.45°C, boils at 256°C, and has a specific gravity at 25°C of 3.01.

Aluminum halides change from ionic to covalent character as the electronegativity of the halogen decreases ($F > Cl > Br > I$). Aluminum bromide, because of its covalent nature, is more soluble in many organic solvents than anhydrous aluminum chloride. Although its catalytic activity is moderate, it can be used in Friedel-Crafts reactions (qv) where selectivity is important (105). Anhydrous aluminum bromide, prepared from bromine [7726-95-6] and metallic aluminum, decomposes upon heating in air to bromine and alumina. Caution should be exercised in handling this hazardous compound because of its reactivity with water. Aluminum bromide may cause tissue burns, and both the anhydrous and the hydrate forms may be toxic upon ingestion.

Aluminum bromide hexahydrate [7784-11-4], $AlBr_3 \cdot 6H_2O$, may be made by dissolving aluminum or aluminum hydroxide in hydrobromic acid [10035-10-6], HBr. This white, crystalline solid is precipitated from aqueous solution.

7. Aluminum Iodide

Aluminum iodide [7884-23-8], AlI_3, is a crystalline solid with a melting point of 191°C. The presence of free iodine in the anhydrous form causes the platelets to be yellow or brown. The specific gravity of this solid is 3.98 at 25°C. Aluminum iodide hexahydrate [10090-53-6], $AlI_3 \cdot 6H_2O$, and aluminum iodide pentadecahydrate [65016-30-0], $AlI_3 \cdot 15H_2O$, are precipitated from aqueous solution. They may be prepared by the reaction of hydroiodic acid [10034-85-2], HI, with aluminum or aluminum hydroxide.

8. Aluminum Nitrate

Aluminum nitrate is available commercially as aluminum nitrate nonahydrate [7784-27-2], $Al(NO_3)_3 \cdot 9H_2O$. It is a white, crystalline material with a melting point of 73.5°C, that is soluble in cold water, alcohols, and acetone. Decomposition to nitric acid [7699-37-2], HNO_3, and basic aluminum nitrates [13473-90-0], $Al(OH)_x(NO_3)_y$ where $x + y = 3$, begins at 130°C, and dissociation to aluminum oxide and oxides of nitrogen occurs above 500°C. Aluminum nitrate nonahydrate is prepared by dissolving aluminum or aluminum hydroxide in dilute nitric acid, and crystallizing the product from the resulting aqueous solution. It is made commercially from aluminous materials such as bauxite. Iron compounds may be extracted from the solution with naphthenic acids (115) before hydrate precipitation. In the laboratory it is prepared from aluminum sulfate and barium nitrate.

Anhydrous aluminum nitrate [13473-90-0] is covalent in character, easily volatilized, and decomposes on heating (116). Hydrated aluminum nitrate is used in the preparation of insulating papers, on transformer core laminates, and in cathode-ray tube heating elements. Solution of aluminum hydroxide through digestion of core materials in nitric acid has been proposed in aluminum extractive metallurgy. The resulting solution of aluminum nitrate is separated from other metal ions, and the aluminum oxide is recovered by thermal decomposition of the aluminum nitrate solution (117,118). A process for producing the nitrate from gibbsite has been reported (119).

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