A REVIEW OF THE PHASE EQUILIBRIUM RELATIONSHIPS,
MELTING TEMPERATURES, AND \( \text{Al}_2\text{O}_3 \) SOLUBILITIES OF HALL CELL
ELECTROLYTE COMPOSITIONS

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ABSTRACT

The electrolyte used in the Hall process for producing aluminum metal consists basically of a fused mixture of alumina \((\text{Al}_2\text{O}_3)\) and cryolite \((\text{Na}_3\text{AlF}_6)\). Other ingredients including \(\text{AlF}_3\), \(\text{LiF}\), and \(\text{CaF}_2\) are added to modify properties such as bath density, electrical conductivity, and freezing temperature. Historically, a variety of experimental techniques has been employed to determine the phase diagrams of systems important to the Hall process. Many of the early experiments were conducted using open containers. This practice resulted in the publication of some inaccurate phase diagrams because of the decomposition of many of the fluoride compounds at high temperatures. In more recent years, it has become standard procedure to encapsulate all samples in sealed platinum containers. Quenching and differential thermal analysis (DTA) experiments using samples sealed in the platinum containers have been used to revise some of the early phase diagrams and to investigate new systems. In this paper, the phase diagrams that are known in the \(\text{Na}_3\text{AlF}_6-\text{CaF}_2-\text{AlF}_3-\text{Al}_2\text{O}_3\) system are reviewed in a systematic manner, with special emphasis on the Hall cell electrolyte composition region.

Aluminum is the most abundant metallic element in the earth's crust and ranks after oxygen and silicon as the third most abundant of all elements. Because of its strong affinity for oxygen, it is not found in nature in the elemental state, but in combined forms such as oxides, silicates, etc. In 1886, Charles Martin Hall and Paul L. T. Heroult discovered almost simultaneously the process in which alumina is dissolved in molten cryolite \((\text{Na}_3\text{AlF}_6)\) and decomposed electrolytically. This reduction process is known as the Hall-Heroult process.

The electrolyte consists basically of a fused mixture of cryolite, aluminum fluoride, calcium fluoride, lithium fluoride, and alumina. Aluminum fluoride is added to the bath to alter the cryolite ratio \((3\text{NaF}/\text{AlF}_3)\) from the stoichiometric value of 1.5 to some lower value. Calcium fluoride is added in amounts between 5 and 6 wt % to
permit lower operating temperatures, with additions of approximately 0.1 wt % LiF used to increase electrical conductivity.

While the basic process for the production of aluminum has not changed significantly since its discovery 90 years ago, the phase equilibrium diagrams involving the components of the electrolyte are in many cases contradictory and in some cases unknown. To some extent this is due to the experimental difficulties encountered in working in these systems (e.g., cryolite decomposes on melting, AlF₃ is volatile, supercooling is often present, and the primary crystallization of Al₂O₃ is difficult to detect by conventional techniques). The inter-relationships between the various fluorides in the bath and their influence on the melting temperature and alumina solubility of the electrolyte can best be understood when reliable phase diagrams for the electrolyte exist.

One Component Systems

Cryolite

Cryolite has been the subject of numerous investigations because of its importance in the industrial production of aluminum. The compound exists in both a low temperature (α) and high temperature (β) polymorphic form. The naturally occurring low temperature polymorph is monoclinic, space group P2₁/n, with cell parameters a = 5.40 Å, b = 5.60 Å, c = 7.78 Å and = 90°11' (1). Between 560 and 572°C, cryolite undergoes a rapid reversible transition to the high temperature cubic form, a = 7.962 Å, with a heat of transition of 2238 cal/mole (2-6). Landon and Ubbelohde (3), on the basis of electrical conductance and thermal arrest data, reported the existence of a third polymorphic variety which they designated γ-cryolite. The β-γ inversion reportedly took place at 881°C with an estimated heat of transition of 200 cal/mole. Attempts by Foster (7) to confirm this transition by electrical conductivity and high temperature X-ray diffraction (XRD) methods were unsuccessful. More recent investigations have also failed to confirm the existence of a gamma form.

The melting point of natural cryolite has received a great deal of attention because of its importance in cryoscopic calculations. Melting points ranging from 977 to 1029°C have been reported (3-6,8-13), with the majority of the more recent investigations yielding values close to 1009°C. Foster (14), working with samples contained in sealed platinum tubes under carefully controlled conditions, used quenching methods to determine a melting temperature of 1009.2°C for natural Greenland cryolite. On the basis of a plot of the liquid fraction as a function of the temperature from which the samples were quenched, the melting point of pure cryolite was determined as 1012 ± 2°C.
The determination of the melting point of cryolite is complicated by the partial dissociation of the compound into several ionic subspecies on melting. Frank and Foster (15) employed calculations based on experimental densities to compare several possible reaction mechanisms. It was concluded that cryolite dissociated into NaAlF$_4$ and NaF on melting according to the reaction:

$$\text{Na}_3\text{AlF}_6 = 2\text{NaF} + \text{NaAlF}_4$$

Foster and Frank (16) recognized that the calorimetric determination of the heat of fusion of cryolite (27.8 kcal/mole) included a heat effect because of partial dissociation. The true cryoscopic heat of fusion was determined to be 19.9 kcal/mole. The refractive indices of the room temperature alpha form of cryolite are $\alpha = 1.3376$, $\beta = 1.3377$, and $\gamma = 1.3387$ (17).

**Aluminum Fluoride**

Aluminum fluoride is rhombohedral, space group $R3$, with cell parameters $a_{\text{rh}} = 5.016$ Å and $\alpha = 58^\circ32'$ (18). The compound is uniaxial positive with indices of refraction of 1.3765 and 1.3767 (19).

During an investigation of the heat contents of Na$_3$AlF$_6$, AlF$_3$, and NaF, O'Brien and Kelley noted the existence of a new polymorph of AlF$_3$. The transition to the high temperature form took place at 454°C and was accompanied by a weak heat effect of approximately 150 cal/mole. Holm and Holm (20) used differential thermal analysis (DTA) to confirm the existence of the polymorph, which they designated $\beta$-AlF$_3$, and set the transition temperature at 453°C. The new polymorph, also noted by Schultz et al. (21), could not be quenched to room temperature and no optical or XRD data were reported. Shinn, Crocket, and Haendler (22) reported the existence of a third (gamma) polymorph of AlF$_3$, which could be obtained either by heating ammonium hexafluoroaluminate to 400°C or decomposing ammonium tetrafluoroaluminate. The transition to the new tetragonal form ($a = 3.54$ Å and $c = 6.00$ Å) takes place at 300°C. No confirmation of the existence of this polymorph is found in the literature.

Mesrobian, Rolin, and Pham (23) studied mixtures of NaF and AlF$_3$ under pressure using thermal arrest methods. A peak at 1300°C for samples containing more than 50 wt % AlF$_3$ was interpreted as resulting from a previously unknown inversion of AlF$_3$. In addition, the triple point of pure AlF$_3$ was placed above 200 bars pressure and 1700°C. Aluminum fluoride is normally reported to sublime at 1291°C at one atmosphere pressure.

**Calcium Fluoride**

Calcium fluoride (fluorite) exists in only one form which
has a face centered cubic structure, space group Fm3m, and a cell parameter $a = 5.4626\text{Å}$ (24). Kojima et al. (25) suggested that the variations in the melting point found in the literature (26) are caused by slight hydrolysis during heating ($\text{CaF}_2 + \text{H}_2\text{O} \rightarrow \text{CaO} + 2\text{HF}$). Using anhydrous HF as a deoxidizing and purifying agent, the melting point of high purity CaF$_2$ was determined as 1423°C. The refractive index of the compound is 1.434 (27).

Aluminum Oxide

Aluminum oxide exists in at least seven crystalline modifications which are arbitrarily designated as alpha, gamma, delta, eta, theta, kappa, and chi. The most common form, $\alpha$-Al$_2$O$_3$, or corundum, belongs structurally to space group $R\bar{3}c$ with cell parameters $a_{\text{hex}} = 4.758 \text{Å}$ and $c_{\text{hex}} = 12.991 \text{Å}$ (28). Corundum is a uniaxial positive mineral with indices of refraction 1.768 and 1.760 (27).

Eta-aluminum oxide, like corundum, has been reported as the crystalline modification of Al$_2$O$_3$ present in certain areas of phase diagrams dealing with the electrolyte used in the smelting of aluminum (29). The eta form is cubic with a spinel type structure and cell parameter $a_0 = 7.94 \text{Å}$ (30). The index of refraction is 1.670.

A metastable alumina phase designated as $\gamma$-alumina by Foster (31) and later as tau-alumina by Wefers and Bell (32) has also been reported. Tau-alumina converts first to eta- and finally to alpha-alumina on heating. The XRD pattern is similar to that of mullite.

Two Component Systems

System CaF$_2$–AlF$_3$

The earliest investigation of the system was conducted by Fedotieff and Iljinsky (8). On the basis of DTA data collected from samples heated in air, a eutectic system was identified. The invariant point was placed at 37.5 mole % AlF$_3$ and 820°C. Ravez and Hagenmuller (33) and Ravez et al. (34) reinvestigated the system using powder XRD. Samples were encapsulated in copper and reacted at 600, 700, 800, and 840°C. One compound, CaAlF$_5$, was identified and found to exist in both a low (alpha) and high (beta) temperature polymorph. Debye Sherrer patterns of $\alpha$-CaAlF$_5$ were used to index the compound in the orthorhombic system with cell parameters $a = 11.81 \pm 0.03 \text{Å}$, $b = 9.16 \pm 0.02 \text{Å}$, and $c = 6.35 \pm 0.01 \text{Å}$. The high temperature polymorph was found to be isotypic with CaFeF$_5$ and was also indexed in the orthorhombic system ($a_0 = 20.04 \pm 0.03 \text{Å}$, $b_0 = 9.81 \pm 0.01 \text{Å}$, and $c_0 = 7.31 \pm 0.01 \text{Å}$).

DTA results established the transition and melting temperatures of the compound at 820°C and 850°C, respectively.

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Pycnometric methods were used to determine the densities of α- and β-CaAlF₅ as 3.09 and 2.96 g/cm³, respectively.

Holm (35) confirmed the existence of the 1:1 compound and, on the basis of DTA data, showed the α-β transition to take place at 740°C. The compound formed highly twinned crystals with a mean refractive index of 1.375 and a density of 2.947 g/cm³. Incongruent melting to AlF₃ and a liquid containing 44 mole % took place at 881°C. The eutectic for the system was located at 37 mole % AlF₃ and 828°C. Pronounced supercooling was noted in the area of the diagram containing 60% or more CaFₑ and DTA heating curves were therefore used to gather data in this region. No liquidus data were presented for the portion of the system richer in AlF₃ than the peritectic composition. Malinovsky, Vrbenska, and Cakajova (36) and Millet, Pham, and Rolin (37) reinvestigated the system using thermal arrest methods and presented diagrams very similar to those of Holm. Both studies confirmed the existence of CaAlF₅ in both a low and high temperature polymorphic form. Malinovsky et al. located the invariant points at 37.5 mole % AlF₃ and 829°C and 47.5 mole % AlF₃ and 893°C. Millet et al. reported slightly different compositions and temperatures (36 mole % AlF₃ and 820°C and 44 mole % AlF₃ and 880°C). The latter authors also noted that the extrapolation of the liquidus curve in the high AlF₃ end of the diagram locates the triple point of AlF₃ in the neighborhood of 2250°C.

Using a combination of optical microscopy, powder XRD, quench techniques, and DTA, Craig and Brown (38) also reexamined the CaF₂-AlF₃ system. To prevent volatilization of AlF₃, all heat treatments and DTA experiments were performed on samples encapsulated in sealed platinum tubes. Because pronounced supercooling existed in the system, DTA heating curves at 3°C/min (as opposed to cooling curves) were used to obtain reaction temperatures. Quenching experiments were then performed to verify that these temperatures represented equilibrium data.

Two compounds were found to exist in the system. The 1:1 compound, noted by previous authors, melted incongruently at 873 ± 3°C to AlF₃ and a liquid containing 44 mole % AlF₃. The α-β inversion remained constant at 743 ± 3°C. A previously unreported 2:1 compound, Ca₂AlF₇, was found to melt incongruently at 845 ± 3°C to CaF₂ and a liquid containing 35 mole % AlF₃. The eutectic for the system was placed at 37.5 mole % AlF₃ and 836 ± 3°C.

The authors noted that while Ca₂AlF₇ had not been previously reported, a hydrated form Ca₂AlF₇·2H₂O and a hydrated hydroxide Ca₄Al₂(OH)₅·5H₂O (39) are known to exist. The anhydrous compound was successfully formed using either AlF₃, AlF₃·3H₂O, or CaAlF₅ as a starting material. The absence of any previous reports on the existence of the compound was attributed to its sluggish formation and to non-equilibrium cooling. Only the peritectic reaction was
consistently observed during DTA heating experiments; but on cooling, three peaks were observed. The lowest corresponded to the \( \alpha \rightarrow \beta \) CaAlF\(_5\) inversion. Powder XRD data of samples after DTA experiments showed a mixture of \( \alpha \)-CaAlF\(_5\) and AlF\(_5\) which converted back to Ca\(_2\)AlF\(_7\) on reheating.

The 2:1 compound was tentatively indexed on the basis of powder XRD data \((1/4\theta \ 2\theta/\text{min-CuK} \alpha)\) as orthorhombic with lattice parameters \(a = 18.22 \ \text{Å}, b = 9.06 \ \text{Å},\) and \(c = 7.11 \ \text{Å} \). A least squares cell refinement program developed by Evans, Appleman, and Handwerker \((40)\) was used to obtain the final cell parameters.

The structural relationships between \( \beta \)-CaAlF\(_5\) and SrAlF\(_5\) noted by Ravez et al. \((34)\) were also found to exist between Ca\(_2\)AlF\(_7\) and Sr\(_2\)AlF\(_7\). These suggest that the \(a\) and \(b\) parameters of the orthorhombic cell of Ca\(_2\)AlF\(_7\) roughly coincide with the face diagonal and 1/2 the face diagonal of the \((001)\) plane of the tetragonal cell of Sr\(_2\)AlF\(_7\), with \(c\) being common to both cells.

System Na\(_3\)AlF\(_6\)–CaF\(_2\)

The first study of the Na\(_3\)AlF\(_6\)–CaF\(_2\) binary system was conducted by Pascal \((13)\) in 1913. He was primarily concerned with the liquidus curves, reporting a eutectic at 47.8 mole \% CaF\(_2\) and 905°C. Minor modifications of the temperature and composition of the eutectic were made by Fedotieff and Iljinsky \((8)\) \((48.1 \ \text{mole} \% \ CaF_{2} \text{ and } 930^\circ \text{C})\), Matiasovsky and Malinovsky \((41)\) \((50.5 \ \text{mole} \% \ CaF_{2} \text{ and } 940^\circ \text{C})\), and Fenerty and Hollingshead \((42)\) \((48.6 \ \text{mole} \% \ CaF_{2} \text{ and } 946^\circ \text{C})\).

In 1961, Rolin \((43)\) reported solidus data for the system. Using thermal arrest cooling curves of closely spaced compositions containing up to 53.5 mole \% CaF\(_2\), the eutectic was placed at 47.3 mole \% CaF\(_2\) and 946°C. Samples higher in Na\(_3\)AlF\(_6\) than the eutectic composition showed a marked decrease in the eutectic temperature with increasing cryolite content. Rolin concluded that a large solid solution of CaF\(_2\) in cryolite must exist, extending almost to the eutectic composition at 946°C. Following Rolin’s suggestion that the system should be re-examined by other methods before the phase relations could be definitely established, Holm \((44)\) studied the system using a combination of thermal analysis, DTA, XRD, quenching techniques, optical microscopy, and density determinations. Again, the eutectic halt on the high cryolite side of the diagram was not observed during DTA; however, a small exothermic peak at 785°C was noted. Because this temperature is close to the reported eutectic temperature for the system NaF–Na\(_3\)AlF\(_6\)–CaF\(_2\) \((8)\), Holm postulated that the depression of the eutectic temperature seen by Rolin could be caused by volatilization of small amounts of AlF\(_3\) or NaAlF\(_4\) rather than by solid solution. As further proof that solid solution of CaF\(_2\) in Na\(_3\)AlF\(_6\) does not exist, Holm noted that samples containing 5 to 90 mole \% CaF\(_2\) quenched from 950°C showed Na\(_3\)AlF\(_6\) or CaF\(_2\) in equilibrium.
with liquid. In addition, the densities of samples containing up to 60 mole % CaF$_2$ quenched from 970°C compared closely with calculated densities of mechanical mixtures of CaF$_2$ and Na$_3$AlF$_6$. Holm's simple eutectic system showed no solid solution and a eutectic at 50 mole % CaF$_2$ and 945.5°C.

Verdan and Monnier (45), using DTA experiments on samples contained in sealed crucibles, studied the system to resolve the controversy between Holm and Rolin over the existence of solid solution. They noted that the presence of a Na$_3$AlF$_6$ solid solution would explain the difficulty in purifying cryolite when CaF$_2$ is present. Liquidus and solidus data were obtained which indicated a solid solution of CaF$_2$ in Na$_3$AlF$_6$ approaching a maximum of 20 mole % CaF$_2$ at the eutectic temperature. A decrease in the α→β Na$_3$AlF$_6$ transition from 563°C for pure cryolite to 530°C for a sample containing between 5 and 6 mole % CaF$_2$ was also noted. A eutectoid reaction was therefore located at 5.5 mole % CaF$_2$ and 530°C.

Craig and Brown (46) studied samples containing 0 to 30 mole % CaF$_2$ using DTA of samples encapsulated in sealed platinum tubes. The α→β Na$_3$AlF$_6$ inversion remained constant at 567°C. Peaks corresponding to a solidus line were not observed and all data agreed well with the simple eutectic diagram of the system presented by Holm.

System Na$_3$AlF$_6$–AlF$_3$

The system Na$_3$AlF$_6$–AlF$_3$ has been investigated periodically since the first published version by Fedotieff and Iljinsky (8) in 1923. Foster (47) gives an excellent review of the more recent publications. The majority of the diagrams agree well with respect to the liquidus curve up to 30 wt % AlF$_3$; however, disagreement exists above this value as to the location and composition of the invariant point(s), shape of the chiolite (Na$_3$AlF$_6$) liquidus curve, and identity of the primary phase in equilibrium with liquid in the high AlF$_3$ end of the diagram.

A major point of contention is whether NaAlF$_4$ exists as a stable phase. Grjotheim (5) reported NaAlF$_4$ to melt congruently at 731°C. Ginsberg and Wefers (48) agreed with Grjotheim that NaAlF$_4$ is a stable phase in the system, but found it to melt incongruently at 710°C. In addition, a eutectoid reaction was found at 680°C with Na$_5$Al$_3$F$_{14}$ and AlF$_3$ forming at the expense of NaAlF$_4$.

Several other authors (10,42,49,50) have disagreed with the equilibrium existence of NaAlF$_4$ and presented diagrams showing AlF$_3$ as opposed to NaAlF$_4$ as an equilibrium solid at the eutectic. Holm (50) suggested that NaAlF$_4$ was not a stable phase because solid NaAlF$_4$ collected from the vapor above a melt of the same composition decomposed during DTA at 500°C to Na$_5$Al$_3$F$_{14}$ and AlF$_3$. 

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Foster (47) working with samples in sealed platinum tubes, used a combination of optical microscopy, DTA, XRD, and quench techniques to establish the diagram. It was concluded that NaAlF₃ is not a stable phase because (1) it was only found when liquid was present before quenching; (2) samples quenched from the region reported to contain NaAlF₃ and chiolite in equilibrium showed only chiolite and AlF₃; (3) samples quenched from the region of the diagram reported to have NaAlF₃ and liquid in equilibrium showed AlF₃ to be the primary crystalline phase; and (4) DTA (in sealed tubes) of melts that precipitated Na₃Al₂F₁₄ as the primary phase did not show any peaks that would indicate a phase field containing solid NaAlF₃.

Mesrobian et al. (23) studied mixtures of AlF₃ and NaF and, in addition to locating the triple point of AlF₃ above 200 bars pressure and 1700°C, reported two new invariant lines in the system. The first was located by constant temperature peaks of thermal arrest cooling curves for compositions ranging from 45 to 95 wt % AlF₃ at approximately 1300°C. It was postulated that the peaks were caused by an allotropic transformation of AlF₃. A second set of peaks, measurable from 45 to 68 wt % AlF₃ at 1250°C, was considered to represent a peritectic line extending from an incongruently melting compound of possible composition NaAl₂F₇. It was felt that, like NaAlF₃, this new compound was unstable and decomposed on cooling and, therefore, is not seen in the subsolidus region.

System Na₃AlF₆-Al₂O₃

A number of phase diagrams exist in the literature for the system Na₃AlF₆-Al₂O₃. Roush and Miyake (51) reviewed the diagrams published up to 1925; Phillips, Singleton, and Hollingshead (10) summarized the more recent works. There were significant differences between the various diagrams with the eutectic for the system ranging from 10 to 18.5 wt % Al₂O₃ and 930 to 962°C. Several diagrams showed appreciable solid solubility. The possibility of solid solubility of Al₂O₃ in cryolite creates particular interest in the system because of its significance in the interpretation of the solution mechanism of Al₂O₃ in the Hall electrolyte and in the determination by cryoscopic methods of the number and structure of entities present in the molten binary mixtures.

Foster (7,31) studied the cryolite-alumina binary using a combination of quench methods, optical microscopy, and XRD. The simple eutectic system shows no solid solution and an invariant point at 10.5 wt % Al₂O₃ and 961°C. The primary phase on the low alumina side of the eutectic was identified by XRD and refractive index measurements as cryolite. On the high alumina side of the eutectic, the primary phase was found to be corundum. While the cryolite examined in the low-alumina end of the diagram was α-Na₃AlF₆, the existence of a solid solution in the high temperature form was ruled out because the alpha form did not contain polycrystalline fractures.
with alumina segregating at the boundaries. It was also noted that extremely rapid quenching from the liquid resulted in a new alumina phase (m- or tau-alumina) with a diffraction pattern similar to mullite. On heating, this phase transformed first to eta-alumina and then to corundum.

Rolin (52) reinvestigated the system using thermal arrest methods. He arrived at the conclusion that if solid solution could not be totally disproved, this new alumina phase was less than 1 wt % Al$_2$O$_3$. He presented a simple eutectic diagram with the invariant point at 11.5 wt % Al$_2$O$_3$ and 960°C. However, the reported eutectic arrest for a sample containing 1 wt % Al$_2$O$_3$ occurred 18°C below the established eutectic temperature. The decrease was attributed to the inability to obtain thermal equilibrium because of a large mass of solid pre-existing at the moment of eutectic crystallization. Duruz and Monnier (53) attempted to verify this assumption by investigating the system using DTA techniques. To avoid the problem of volatility, samples were sealed in a nickel container. Compositions containing amounts as small as 0.5 wt % Al$_2$O$_3$ showed a eutectic peak at the same temperature as samples containing 10 wt % or more Al$_2$O$_3$. Below 0.5 wt % Al$_2$O$_3$, the sensitivity of the equipment was not sufficient to pick up the small thermal effect. A plot of the surface area of the eutectic peak versus the concentration of Al$_2$O$_3$ extrapolated through the origin indicated that no solid solution existed between 0 and 0.5 wt % Al$_2$O$_3$.

A substantial amount of literature is also available on the reaction mechanism for the solution of alumina in cryolite-alumina melts. Foster and Frank (16) reviewed the proposed reaction mechanisms and used Temkin’s ionic model to calculate activities. A graph of $-\log \alpha$ versus $1/T$ was then constructed to demonstrate that the most probable scheme was $3F + Al_2O_3 = 3/2 AlF_3 + 1/2 AlF_6^-$. However, considerable controversy still exists over the true reaction mechanism (54).

System CaF$_2$-Al$_2$O$_3$

The binary system CaF$_2$-Al$_2$O$_3$ was first studied in 1913 by Pascal (13). Extensive solid solution at both ends of the system was noted. At the eutectic temperature, 20 wt % Al$_2$O$_3$ was soluble in CaF$_2$ and 71.5 wt % CaF$_2$ was soluble in Al$_2$O$_3$. The eutectic was placed at 26.5 wt % Al$_2$O$_3$ and 1270°C.

Gunther et al. (55), during a study of the luminescence of phosphors of the aluminum oxide-calcium fluoride type, reported the existence of a 1:5 compound CaAl$_{10}$O$_{15}$F$_2$. The compound was obtained by heat treating CaF$_2$ and NH$_4$(SO$_4$)$_2$·12H$_2$O with small amounts of MnSO$_4$·4H$_2$O (added as an activator) in air at 1200 to 1450°C.
Using quench methods, Kuo and Yen (56) reported a simple eutectic diagram for the system with the invariant point at 7 mole % $\text{Al}_2\text{O}_3$ and 1290°C. Neither the extensive solid solution nor the compound formation reported earlier could be verified. The authors noted that while in a closed system, $\text{CaF}_2$ and $\text{Al}_2\text{O}_3$ were the stable coexisting phases; in open air under ordinary atmospheric conditions, $\text{CaAl}_4\text{O}_7$ formed as the unique product according to one of the two reaction schemes shown below.

\begin{equation}
\text{1. } \text{CaF}_2 + 2 \text{Al}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow \text{CaAl}_4\text{O}_7 + 2 \text{ HF}
\end{equation}

\begin{equation}
\begin{align}
\text{2. (a) } & 3 \text{CaF}_2 + 7 \text{Al}_2\text{O}_3 = 3 \text{CaAl}_4\text{O}_7 + 2 \text{AlF} \\
& \quad (b) 2 \text{AlF}_3 + 3 \text{H}_2\text{O} = \text{Al}_2\text{O}_4 + 6 \text{HF}
\end{align}
\end{equation}

Chatterjee and Zhmoilin (57) reinvestigated the system by sintering samples in hermetically sealed capsules. Quenching, DTA, and optical microscopy were used to obtain data which suggested a eutectic system. The invariant point was placed at approximately 2 wt % $\text{Al}_2\text{O}_3$ and 1395°C. The liquidus curve had a pronounced "S" shape suggestive of metastable liquid phase separation.

System $\text{AlF}_3-\text{Al}_2\text{O}_3$

While numerous authors (29,58-61) have reported results in ternary and quaternary systems involving the binary system $\text{AlF}_3-\text{Al}_2\text{O}_3$, their investigations have been confined to portions of the diagrams far removed from the binary system. At the present time no phase equilibrium data are available on the system.

Three Component Systems

System $\text{CaF}_2-\text{AlF}_3-\text{Na}_3\text{AlF}_6$

Fedotieff and Illjinsky (8) presented a liquidus surface diagram of the $\text{CaF}_2-\text{AlF}_3-\text{NaF}$ ternary system based on the results of DTA experiments performed in air on over 100 compositions. At the time of the work, no ternary compounds were known to exist and only chiolite and cryolite were identified in any of the binary systems. Two ternary eutectics were reported. The first was located at 50.2 mole % NaF, 5.0 % $\text{CaF}_2$, and 44.8% $\text{AlF}_3$ and 675°C with $\text{AlF}_3$ in equilibrium with $\text{Na}_3\text{AlF}_6$ and $\text{CaF}_2$. The second eutectic was placed at approximately 73 mole % NaF, 20% $\text{CaF}_2$, and 7% $\text{AlF}_3$ and 780°C with NaF in equilibrium with $\text{Na}_3\text{AlF}_6$ and $\text{CaF}_2$. A ternary peritectic was found at approximately 49 mole % NaF, 10% $\text{CaF}_2$, and 41% $\text{AlF}_3$ and 705°C with chiolite, cryolite, and $\text{CaF}_2$ in equilibrium.

Rolin (62), using thermal arrest methods, investigated the portion of the $\text{CaF}_2-\text{AlF}_3-\text{Na}_3\text{AlF}_6$ system containing 24 and 62.5 mole % or less $\text{CaF}_2$ and $\text{AlF}_3$, respectively. Phases precipitating from the
melt were identified by the shape and sharpness of the thermal arrest peaks. A ternary eutectic was located at 35.9 mole % cryolite, 56.7% AlF₃, and 7.4% CaF₂ and 682°C, with chiolite in equilibrium with CaF₂ and AlF₃. Two points on the chiolite-CaF₂ boundary curve were also located: the first at 32.7 mole % cryolite, 50.5% AlF₃, and 16.8% CaF₂ and 689°C and the second at 34.3 mole % Na₃AlF₆, 52.7% AlF₃, and 13.0% CaF₂ and 688°C. A point on the CaF₂-AlF₃ boundary was located at 28.7 mole % Na₃AlF₆, 55.3% AlF₃, and 16.7% CaF₂ and 708°C. On the basis of these points, a partial ternary diagram was presented. Supercooling in the region of the diagram containing CaF₂ as the primary phase was noted. At the time of the work, no compounds were known to exist in either the CaF₂-AlF₃ binary or the ternary system.

Pfundt and Zimmermann (63) investigated both the ternary system and the quasi-binary system NaF-CaAlF₅ using DTA of samples contained in pressure-tight nickel crucibles. They agreed with the earlier investigations that the ternary system could be divided into two subsystems, NaF-Na₃AlF₆-CaF₂ and CaF₂-AlF₃-Na₃AlF₆. The invariant temperature for the NaF containing system was placed at 780°C.

The diagram of the quasi-binary system contains one compound, NaCaAlF₆, which was found to melt incongruently at 740°C. The compound existed in both a low temperature (beta) and high temperature (alpha) form with the transition taking place at 653°C on heating. The beta form exhibited tetragonal symmetry with lattice parameters a₀ = 7.32 Å and c₀ = 10.18 Å. The existence of the high temperature polymorph at room temperature was noted in both air cooled and water quenched samples, but diffraction data were not reported.

Working with samples encapsulated in sealed platinum tubes and using DTA heating curves taken at 3°C/min, supplemented by optical microscopy, powder XRD, and quench experiments, Craig and Brown (56) investigated the CaF₂-AlF₃-Na₃AlF₆ ternary system. The compound NaCaAlF₆, first noted by Pfundt and Zimmermann (63), was found to exist in a previously unreported γ form in addition to the α and β polymorphs. DTA showed the inversion to the new form, characterized by a sharp but small exothermic peak, to take place at 720°C. Gamma-NaCaAlF₆ was not quenchable and no diffraction data were reported. The compound melted incongruently at 737°C to CaF₂ and a liquid. In addition to NaCaAlF₆, a previously unreported compound NaCaAl₂F₇ was identified. Based on powder XRD data taken at scanning speeds of 1/4° 2θ/min using CuKα radiation, the compound was indexed as body centered cubic (h + k + l = 2n) with a₀ = 10.76 Å. The compound melted incongruently to AlF₃ and a liquid at 715°C; however, metastable congruent melting at 723°C was often observed.

On the basis of samples reacted for 394 h in the solid state, the subsolidus compatibility relationships were established. In the compatibility triangles containing cryolite, a decrease in the α-β inversion temperature was noted. Investigation of the
NaCaAlF₆ - Na₃AlF₆ ternary join revealed that this decrease from 567 to 525°C was caused by a solubility of approximately 7 mole % NaCaAlF₆ in α-Na₃AlF₆.

The authors noted, in support of Holm's (44) simple eutectic diagram for the CaF₂-Na₃AlF₆ system, that slight compositional errors introducing excess AlF₃ to the binary system would result in the solid solution diagrams for the system reported by Rolin (43) and Verdan and Monnier (45). Craig and Brown (46) cited as additional evidence the work of Dewing (64) who postulated that a 50-fold increase in the conductivity of a sample in the CaF₂-AlF₃-Na₃AlF₆ system (as compared to pure Na₃AlF₆) could be explained by a solid solution of CaF₂ in Na₃AlF₆ and that such a solid solution was only reasonable when AlF₃ was present. It was noted that while Dewing was unaware of the existence of NaCaAlF₆, the sample studied actually lay on the NaCaAlF₆-Na₃AlF₆ ternary join. The conductivity increase, therefore, should be attributed to a solid solution of NaCaAlF₆ in Na₃AlF₆ and not to CaF₂ in cryolite. While firm evidence of the solubility of NaCaAlF₆ in the low temperature form of cryolite exists, the use of DTA to investigate solubility in the high form of cryolite was complicated by the dissociation of Na₃AlF₆ near its melting point. While a peak corresponding to a solidus line was often observed on cooling, the dissociation of cryolite masked its existence (if indeed it was present) on heating. The solubility of NaCaAlF₆ is, therefore, difficult to conclusively confirm.

The full phase diagram for the CaF₂-AlF₃-Na₃AlF₆ presented by Craig and Brown is shown in Figure 1 and the compositions, temperatures, and phase assemblages of the invariant points are given in Table I.

Lee, et al. (67) more recently reexamined the liquidus surface in a portion of this system. Twenty compositions were selected systematically throughout the electrolyte composition range. The liquidus temperatures for these compositions were measured to ± 2°C. The liquidus surface over the Hall cell electrolyte composition range is not smooth, but instead contains a deep inflection or swale (Figure 2). The liquidus temperatures over this range (CaF₂ from 3.8 to 11.3 wt % and AlF₃ from 5 to 20 wt %) can be calculated using the empirical expression:

\[
\text{Liquidus} \ (°C) = 1009.4 + 4.059 \ (\text{CaF}_2) - 1.167 \ (\text{CaF}_2)^2 + 0.968 \ (\text{CaF}_2) (\text{AlF}_3) - 0.105 \ (\text{CaF}_2) (\text{AlF}_3)^2 + 0.073 \ (\text{CaF}_2)^2(\text{AlF}_3) + 0.002 \ (\text{CaF}_2)^2(\text{AlF}_3)^2 - 4.165 \ (\text{AlF}_3) - 0.054 \ (\text{AlF}_3)^2 - 5.33 \ (\text{Al}_2\text{O}_3).
\]
Fenerty and Hollingshead (42) investigated the liquidus curves in the cryolite-rich portion of the system using cooling curve methods supplemented by visual observation of crystallization. The Na$_3$AlF$_6$-Al$_2$O$_3$ phase boundary showed a gradual decrease in Al$_2$O$_3$ up to 25 wt % AlF$_3$. Above this value the boundary curved sharply with a rapid decrease in Al$_2$O$_3$ content. The ternary peritectic and eutectic were both located at alumina contents less than 1 wt %. Rolin’s (58) investigation of the system agreed well with the previous authors up to 25 wt % AlF$_3$. Above this value, however, the boundary curve continued a smooth approach to the ternary peritectic located at 5 wt % Al$_2$O$_3$, 28.5% AlF$_3$, and 66.5% Na$_3$AlF$_6$ and 710°C. A ternary eutectic was located at 60 wt % Na$_3$AlF$_6$, 37% AlF$_3$, and 3% Al$_2$O$_3$ and 670°C. Possible sources of error which could account for the previous results were noted, such as the slow dissolution of Al$_2$O$_3$, the lack of a thermal arrest corresponding to the primary crystallization of Al$_2$O$_3$, and the purity of starting materials.

Using samples sealed in platinum tubes, Foster (65) employed quench methods, optical microscopy, and XRD to reinvestigate the cryolite-rich portion of the diagram. In support of Rolin’s diagram, the Na$_3$AlF$_6$-Al$_2$O$_3$ boundary fell regularly to the peritectic composition at 28.3 wt % AlF$_3$, 4.4% Al$_2$O$_3$, and 67.3% Na$_3$AlF$_6$ and 723°C. The ternary eutectic was located at 37.3 wt % Na$_3$AlF$_6$, 3.2% Al$_2$O$_3$, and 59.5% Na$_3$AlF$_6$ and 684°C. Compositions containing 20 wt % or less AlF$_3$ precipitated α-Al$_2$O$_3$ in the primary phase field of Al$_2$O$_3$, while those containing 25 wt % or more precipitated n-Al$_2$O$_3$.

System Na$_3$AlF$_6$-CaF$_2$-Al$_2$O$_3$

Fenerty and Hollingshead (42) investigated the ternary diagram by the same procedure used in their investigation of the Na$_3$AlF$_6$-CaF$_2$ and Na$_3$AlF$_6$-AlF$_3$-Al$_2$O$_3$ systems. On the basis of results obtained for cuts taken at 5, 10, 15, 20, 22, 24, 25, and 26 wt % CaF$_2$, a simple eutectic diagram with the ternary invariant point at 76.1 wt % cryolite, 21% CaF$_2$, and 2.9% Al$_2$O$_3$ and 933°C was presented. A later investigation by Rolin (43), using the method of thermal arrest, placed the eutectic at 78 wt % Na$_3$AlF$_6$, 17% CaF$_2$, and 5% Al$_2$O$_3$ and 927°C. The major difference between the results of the two investigations was in the Al$_2$O$_3$ content of the cryolite-alumina phase boundary. Rolin’s diagram shows the boundary curve to be higher in Al$_2$O$_3$ than that of Fenerty and Hollingshead.

System CaF$_2$-AlF$_3$-Al$_2$O$_3$

In the CaF$_2$-AlF$_3$-Al$_2$O$_3$ ternary system, only the CaF$_2$-AlF$_3$ and CaF$_2$-Al$_2$O$_3$ binary systems are known. Several authors have investigated quaternary systems involving the ternary (42,60,61,66); however, their work has been confined to areas far removed from the
ternary. At the present time, no phase equilibrium data are available on the system.

Four Component Systems

System Na₃AlF₆-AlF₃-CaF₂-Al₂O₃

The quaternary system Na₃AlF₆-AlF₃-CaF₂-Al₂O₃ has been investigated several times. The studies were performed prior to the reported existence of any ternary compounds and were concerned only with very limited portions of the liquidus surface of the system.

Abramov et al. (60) studied the Na₃AlF₆-CaF₂-Al₂O₃ cross section of the quaternary system. The liquidus surface of the section contained phase fields for cryolite, Al₂O₃, and CaF₂. A quaternary peritectic at 34.5 mole % Na₃AlF₆, 45.9% AlF₃, 13.9% CaF₂, and 5.7% Al₂O₃ and 685°C in addition to a quaternary eutectic temperature of 665°C were reported.

Fenerty and Hollingshead (42) studied the system by noting the change in the Na₃AlF₆-Al₂O₃ and Na₃AlF₆-CaF₂ boundary curves as mixed additions of up to 15 wt % AlF₃ and 20 wt % CaF₂ were added to the system Na₃AlF₆-Al₂O₃. An addition of 10 wt % AlF₃ moved the ternary eutectic for the system Na₃AlF₆-CaF₂-Al₂O₃ from 21 wt % CaF₂ and 933°C to 13 wt % CaF₂ and 927°C.

Rolin (61) investigated the portion of the system bounded by 10 wt % CaF₂ and 20% AlF₃. On the basis of thermal arrest data, a partial diagram of the cryolite-rich end of the quaternary system showing the boundary surface between cryolite and Al₂O₃ was proposed. Foster (66) also presented a few selected liquidus curves in the NaF-AlF₃-CaF₂-Al₂O₃ system for compositions with constant NaF/AlF₃ ratios.

Craig and Brown (46), working with samples encapsulated in sealed platinum tubes (reacted in the solid state and in the presence of liquid), established the eight compatibility tetrahedra for the system CaF₂-AlF₃-Na₂AlF₆-Al₂O₃ shown in Figure 3. No quaternary compounds were found to exist, and in all cases where Al₂O₃ was present it was identified by XRD as α-Al₂O₃.

Lee et al. (67) determined the Al₂O₃ solubility in 20 compositions covering typical Hall cell electrolyte compositions. The liquidus temperatures for these compositions containing up to 8 wt % Al₂O₃ were measured to ± 2°C. In all cases the double solubility limit of Al₂O₃ was found to exist below the 8 wt % Al₂O₃ level, and was found to vary from 2.0 to 6.5 wt % Al₂O₃ over a temperature range of 860 to 960°C.
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Figure 1. System CaF$_2$-AlF$_3$-Na$_3$AlF$_6$. MOLE % vs. Temperature (°C).
Figure 2. Isotherms for cryolite-rich portion of the ternary system Na₃AlF₆ – CaF₂ – AlF₃.⁶/
Figure 3. Subsolidus compatibility relationships in the system Na$_3$AlF$_6$-AlF$_3$-CaF$_2$-Al$_2$O$_3$.

Table I. Compositions and Locations of Peritectics, Eutectics, and Saddle Points in the System CaF$_2$-AlF$_3$-$\text{Na}_3\text{AlF}_6$

| Composition (mol%) | Equilibrium phase assemblage |
|--------------------|------------------------------|
| CaF$_2$ | AlF$_3$ | Na$_3$AlF$_6$ | Type | $T$ (°C) |
| 49.0 | 33.5 | 17.5 | Peritectic | 731 |
| 49.5 | 35.0 | 15.5 | Peritectic | 718 |
| 48.5 | 37.5 | 14.0 | Peritectic | 713 |
| 43.0 | 46.0 | 11.0 | Peritectic | 710 |
| 38.0 | 44.0 | 18.0 | Peritectic | 709 |
| 25.0 | 45.0 | 30.0 | Peritectic | 688 |
| 18.0 | 52.0 | 30.0 | Peritectic | 683 |
| 15.0 | 55.0 | 30.0 | Eutectic | 680 |
| 49.0 | 34.0 | 17.0 | Saddle point | 735 |
| 39.5 | 47.5 | 13.0 | Saddle point | 712 |