

THE SOLUBILITY OF ALUMINIUM IN CRYOLITIC MELTS

R. Ødegård, Å. Sterten and J. Thonstad

Laboratories of Industrial Electrochemistry and the Electrolysis Group of SINTEF*,

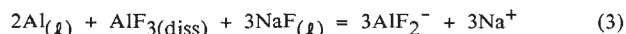
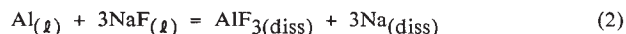
The Norwegian Institute of Technology, N-7034 Trondheim-NTH, Norway.

The solubility of aluminium in NaF-AlF₃-Al₂O₃ melts with various additives was found to increase with increasing NaF/AlF₃ molar ratio (CR) and increasing temperature and to decrease with additions of Al₂O₃, CaF₂, MgF₂ and LiF to the melts. The following empirical equation was derived;

$$\log(c_{Al}) = 1.8251 - 0.5919/CR - 3.429 \cdot 10^3/T - 3.39 \cdot 10^{-3} \cdot c_{Al_2O_3} - 2.49 \cdot 10^{-2} \cdot c_{LiF} - 2.41 \cdot 10^{-2} \cdot c_{MgF_2} - 2.03 \cdot 10^{-2} \cdot c_{CaF_2} \quad (1)$$

where all concentrations are in wt% and T is the temperature (K).

With the use of literature data for the activities of NaF and AlF₃ in cryolitic melts, three dissolution reaction models were found to give a good fit to the experimental solubility data. In the most probable of these models the following sequence of reactions was found to describe the dissolution of aluminium in cryolitic melts;



According to this model the total concentration of dissolved aluminium (aluminium and sodium species) is given by;

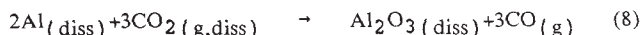
$$c_{Al} = c_{Na(diss)} + c_{AlF_2^-} + c_{Al_2F_3^-} + c_{Al_3F_4^-} + c_{Al_4F_5^-} \quad (7)$$

In NaF rich melts, aluminium will dominantly dissolve as sodium (eq. (2)), while at cryolite ratios commonly used in aluminium electrowinning (CR = 2.25-2.7) the AlF₂⁻-ion is the predominant dissolved metal species (eq. (3)). Other species (Al₂F₃⁻, Al₃F₄⁻, Al₄F₅⁻) were found to be of some significance only in melts with high excess AlF₃ (CR<2).

*: SINTEF = The Foundation for Scientific and Industrial Research at the Norwegian Institute of Technology.

INTRODUCTION

It is known that a fraction of the aluminium which is produced at the cathode is lost due to the so-called "back reaction" (≈5-15%, [3]), generally expressed as:



During the last years many efforts have been made to model the loss in current efficiency in the Hall-Héroult process caused by eq. (8) [4-9]. In these works the need for a reliable equation for the equilibrium concentration of dissolved aluminium as a function of the most common variables has been clearly demonstrated.

As can be seen from the literature data that will be discussed in the following, there have been a relatively large number of papers related to the solubility of aluminium in cryolitic melts. Today there seems to be some agreement about the level of aluminium solubility in alumina saturated cryolite at 1000°C (≈0.1 wt% Al) [3,10]. However, there still is a relative large uncertainty in the functional dependence of dissolved aluminium on the most common variables, as will be discussed below.

The purpose of the present work was to determine the solubility of aluminium more accurately than in previous papers in order to; A: give a reliable equation for the equilibrium concentration of dissolved aluminium in cryolitic melts, B: present a model of dissolved aluminium in terms of the species that are involved in the aluminium dissolution reaction.

EXPERIMENTAL

A vertical tube furnace, of the same type as described by Motzfeldt [11], with argon atmosphere was used for the aluminium solubility measurements. The temperature was measured with a standardized Pt-Pt10%Rh thermocouple and it was kept constant within ± 1°C.

The molten salt (≈140 g, made up of high purity pre-dried components), and aluminium (≈25 g, +99.999% Al) were kept in crucibles of sintered alumina ("Alsint A5", Haldenwanger, i.d. 45 mm, inner height 70 mm) with tight-fitting lids of the same material. In the experiments with varying alumina concentration, Si₃N₄-bonded SiC crucibles (Refrax, Carborundum Co.) with lids of boron nitride (HBN, Union Carbide) were used. The composition of the melt was determined from the weighed-in amounts of the different salts, as analysis showed the composition to change little during a run. In the experiments with sintered alumina crucibles, no alumina was added. Because of dissolution of the alumina crucible, the melt was saturated with alumina after an initial period.

The melt was left for a period of 5-6 hours to ensure saturation with dissolved aluminium. The crucible lid was then removed by means of a molybdenum wire attached to the lid to allow for sampling. Sampling was done by means of a thick-walled steel ladle with a steel lid, kept in the cold part of the furnace. The ladle was lowered quickly into the melt until the ladle top was ≈ 2 cm below the melt surface, and then it was withdrawn to the cold zone. This was done without admitting air to the furnace tube. The quenched melt sample (≈ 5 g) was kept in the cold part of the furnace for 5 minutes and then quickly transferred to a glove box with argon atmosphere (< 5 ppm H_2O). The entire melt sample was ground to -80 mesh in a steel mortar and was immediately transferred to a glass container that was used in the analysis. The container was then sealed with a rubber cork and weighed.

The sample was treated with a 10% HCl solution, and the gas evolved was determined volumetrically. The analysis apparatus was similar to that described by Rogers et al. [12]. The metal phase contained in the solidified melt sample reacted with the acidic solution under hydrogen evolution. Prior to the analysis, the solution was sparged with hydrogen gas to ensure hydrogen saturation at the beginning of the analysis. The hydrogen gas formed as the result of the reaction between the metal phase and the acid was collected in a standardized burette at atmospheric pressure. In the calculations of the amount of dissolved aluminium, corrections were made for temperature, atmospheric pressure (measured with a "Thies" mercury barometer) and the partial pressure of water at the temperature of the analysis.

The accuracy of the analysis apparatus was checked by "analysis" of weighed pieces of super pure aluminium (≈ 10 mg) and zinc (≈ 30 mg). Eight different measurements gave observed gas volumes within an accuracy of $99.5 \pm 1\%$ of the volumes to be expected from the weight of the samples.

In the experiments with Si_3N_4 -bonded SiC crucibles, the evolved gas was analysed by gas chromatography. The analysis showed within the detection limit ($\approx 1\%$) the existence of hydrogen gas only.

RESULTS AND DISCUSSION

Aluminium Solubility in Alumina-Saturated Melts.

The concentration of dissolved aluminium as a function of the NaF/AlF₃ molar ratio (CR) at $1000 \pm 2^\circ C$ is given in Fig. 1. Some literature data are also given in the figure.

The metal-containing reactants resulting in H₂ formation (Al+Na) were in the present work formally treated as being metallic Al. The results are therefore given as wt% Al and designated dissolved aluminium. The experiments were performed with alumina crucibles, and consequently the melts were saturated with alumina.

The concentration of dissolved aluminium in alumina-saturated cryolite (CR=3.00) at $1000^\circ C$ was found to be 0.082 wt% Al. This is about 1.6 times that reported by Yoshida and Dewing [13], but only $\approx 10\%$ more than that reported by Arthur [14] and $\approx 20\%$ less than that reported by Thonstad [15] and by Vetyukov and Vinokurov [16,17,18]. This saturation level and the variation with the cryolite ratio will be discussed in the following.

The quenching of the melt samples was very rapid in this investigation. Cooling from 1000 to $750^\circ C$ was by experiments proved to be accomplished in less than three

seconds. The loss of metal during quenching is therefore believed to be small. The cooling rate was somewhat lower in the work of Arthur [14], and this could be the reason why that solubility value is a little lower than that of this investigation.

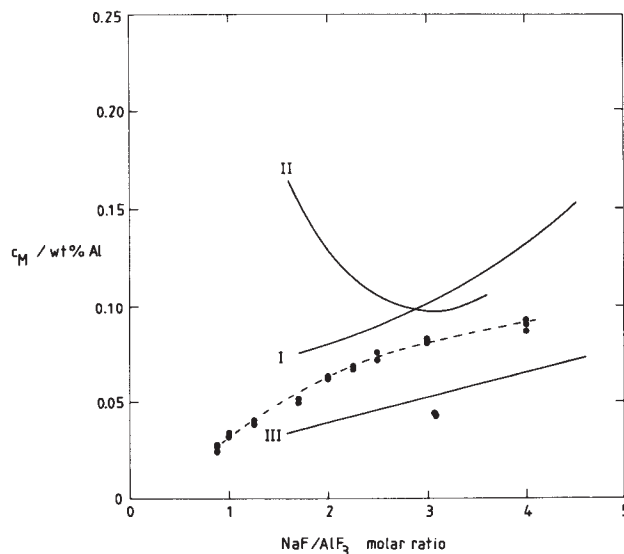


Fig. 1. Concentration of dissolved aluminium (wt% Al) as a function of the NaF/AlF₃ molar ratio at $1000 \pm 2^\circ C$. The melts were saturated with alumina. ●: Present investigation. Solid lines: I: Thonstad [15], II: Vetyukov and Vinokurov [17], III: Yoshida and Dewing [13].

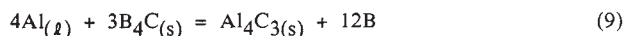
The major problem in these experiments was to ensure saturation of dissolved aluminium. The results showed that the analysed concentration was far too low if the lid did not close the crucible tightly. This could in most cases be detected by inspecting the lid after the experiments. The results from such experiments are not reported. When no lid was used, the analysed concentration of dissolved aluminium at CR=3.00 and $1000^\circ C$ was roughly 60% of the concentration found with a tight-fitting lid under otherwise identical conditions. Under these conditions the observed concentrations of dissolved aluminium are very close to those reported by Yoshida and Dewing [13], who did not have a lid on the compartment where the melt was "titrated" with oxygen. This is probably the reason why their results were low in dissolved aluminium.

When several samples were taken in succession from the same melt at CR=3.00, the concentration of dissolved aluminium was found to decrease as a function of time after removal of the lid. This is probably due to evaporation of sodium, since $P_{Na} \approx 60$ torr at CR=3.00 and $1000^\circ C$ [19].

Similar to observations reported by Rolseth [20] and Bjørgum et al. [21], some sort of passivation of the aluminium surface occurring in alumina-saturated melts was also encountered in the present work. This passivation problem was more or less overcome by stirring the melt and the aluminium after one hour at the experimental temperature, and by not adding any alumina when mixing the components. When the lid was tightly fitted and when precautions were taken to avoid passivation, the solubility experiments were fairly reproducible, as can be seen from Fig. 1.

The variation of the concentration of dissolved aluminium as a function of the NaF/AlF₃ molar ratio shows the same trend as reported by Haupin [22], Thonstad [15] and Yoshida and Dewing [13], but it is opposite to that reported by Zhurin [23] and Vetyukov and Vinokurov [16,17,18]. Zhurin and Haupin used graphite crucibles, which probably resulted in aluminium carbide formation. The concentration of dissolved aluminium carbide increases with decreasing cryolite ratio in the CR range in question [24], [25].

Aluminium carbide gives methane upon reaction with HCl. Zhurin did not separate hydrogen and methane and a part of the reported value for dissolved aluminium in his work must therefore in fact be due to dissolved aluminium carbide. Haupin [22] tried to separate the hydrogen and methane resulting from the reaction between HCl and the melt samples. However, the reported concentrations of dissolved aluminium carbide, based on the volume of methane, are low, and the concentration was reported not to vary with the cryolite ratio. Therefore, it is possible that the gas separation had not been complete and that a fraction of the dissolved metal in fact was due to dissolved aluminium carbide. Vetyukov and Vinokurov [16,17,18] used crucibles of Russian-made boron carbonitride (BNC), for which the exact composition and stability is not known. However, in the presence of B₄C, formation of Al₄C₃ is thermodynamically feasible according to the following reaction:



$$\Delta G_{1200}^{\circ} = -7.72 \text{ kJ/mol and } \Delta G_{1300}^{\circ} = -0.51 \text{ kJ/mol [26].}$$

The discrepancy in the solubility data as a function of the NaF/AlF₃ ratio reported by Vetyukov and coworkers [16,17,18,46], relative to all other reported data including the present, could in light of the Gibbs energy calculations of eq. (9), be due to the presence of some aluminium carbide, leading to formation of methane in the analysis. Aluminium carbide formation could also be part of the reason for the relatively high level of dissolved aluminium reported in those works.

Possible reasons for the deviation between the present data and those given by Thonstad [15] are not easy to know, since almost identical crucibles and sampling procedures were used in the two works. However, Thonstad used open sampling ladles. That could probably cause condensation of small amounts of metallic sodium in the ladle during the holding time. This could give high solubility results, especially for basic NaF-AlF₃ melts, where the deviation between the present solubility data and those given in Thonstad's work is most pronounced.

The differences between two corresponding runs were less than 7% at all NaF/AlF₃ ratios, except for the experiments with AlF₃ saturated melt, where the difference between the highest and lowest concentration of dissolved aluminium was 12% (0.0034 wt% Al). Test runs showed the analysis apparatus to be accurate within ±0.5%. The main reason for the differences between corresponding experiments on dissolved aluminium is therefore due to differences in the actual concentration in the melt when sampling or to losses during sampling. The reproducibility of the results under the same conditions and the consistency of the results as a function of the variables under different conditions, lead to the conclusion that this investigation represents the equilibrium concentration of dissolved aluminium in the NaF-AlF₃-Al₂O₃(sat) system well.

The concentration of dissolved aluminium as a function of temperature at NaF/AlF₃ molar ratio 2.25 in alumina-saturated melts is given in Fig. 2. Some literature data are also shown in the figure.

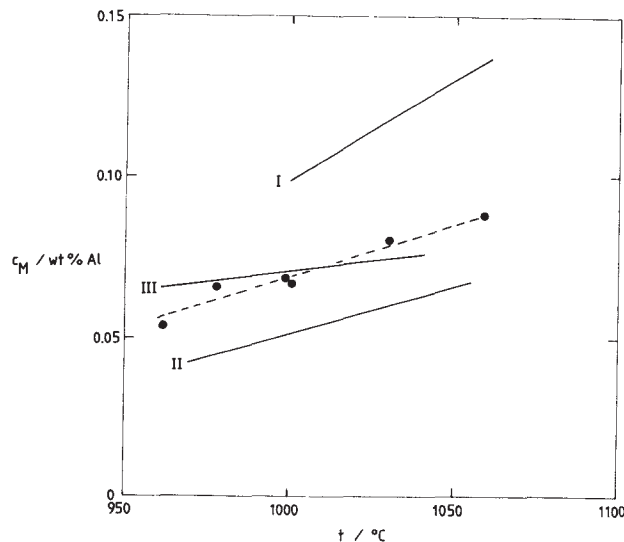


Fig. 2. Concentration of dissolved aluminium (wt% Al) as a function of temperature at NaF/AlF₃ molar ratio 2.25 ●: Present work. Solid lines: I: Thonstad [15], II: Yoshida and Dewing [13], III: Arthur [14]. I,II and III are for CR=3.00. The melts were saturated with alumina in all four investigations.

With the assumptions of ideal solution, no solid solution of aluminium, and constant heat of solution of aluminium in NaF-AlF₃ melts as a function of temperature, the apparent heat of solution of aluminium in NaF-AlF₃ melts at CR=2.25 ($\Delta \bar{H}$) can be calculated from equation (10), [27].

$$\frac{d \ln x}{dT} = \frac{\Delta \bar{H}}{RT^2} \quad (10)$$

where x is the molar fraction at saturation, T is the temperature (K) and R is the gas constant. In the dilute range:

$$x = k \cdot c \quad (11)$$

$$d \ln x = d \ln c \quad (12)$$

where c is the concentration (wt%).

Using the data in in Fig. 2, eq. (10) gives $\Delta \bar{H}_{Al} = 60 \pm 6$ kJ/mol for the present work. It should be emphasized that the solution of aluminium probably involves at least two species (Al-containing, Na-containing), and this calculation therefore gives only an apparent heat of solution for aluminium in the melt. Furthermore, the NaF-AlF₃ solution cannot be ideal, since that would imply a zero heat of solution of one liquid in another liquid (Al(l) in NaF-AlF₃(l)) in the present case). The calculated apparent heat of solution must therefore only be taken as an indication of the heat involved when dissolving aluminium in NaF-AlF₃ melts at CR=2.25.

The calorimetrically measured heat of solution of Al in cryolite at 1017°C is reported by Phan-Xuan et al. [28] to be -250 kJ/mol. If that was correct, it would give a decreasing concentration of dissolved aluminium with

increasing temperature. However, the crucible materials used in that work (graphite and inconel) will interact with aluminium, forming carbide or alloys. Calorimetric data for the dissolution of aluminium in cryolite conducted in inert crucibles are thus needed to confirm or invalidate the result of Phan-Xuan et al.

The calculated heat of solution from equation (10) can be used as an apparent heat of activation for the dissolution of aluminium in NaF-AlF₃ melts at CR=2.25. The apparent heat of activation is, according to the above data, of the same order of magnitude in this investigation as in the investigation of Thonstad [15] and Yoshida and Dewing [13]. The results of Arthur [14] indicate an apparent heat of activation which is only 1/2 of that found in the present work.

The concentration of dissolved aluminium in alumina-saturated cryolitic melts with CR=2.25 as a function of the concentration of some additives at 1000°C is shown in Fig. 3. The concentration of dissolved aluminium decreased with increasing concentration of CaF₂ up to 20 wt%. An addition of 5 wt% MgF₂ and LiF also lowered the concentration of dissolved metal. This is in accordance with previously reported data on aluminium solubility [13],[18], and with data on the solubility of metal in other systems [29].

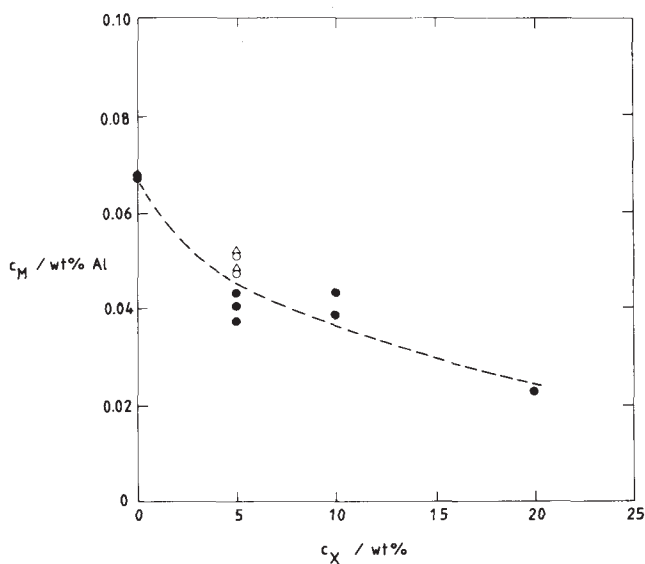


Fig. 3. Concentration of dissolved aluminium as a function of the concentration of some additives. AlF₃/NaF molar ratio 2.25, temperature=1000 ± 1°C. The melts were saturated with alumina. ●: CaF₂ addition, ○: LiF addition, △: MgF₂ addition.

Model Fitting in Alumina-Saturated Melts.

In the attempts to fit models for the solubility of aluminium to the experimental data, no single species has been found that entirely explains the variation in the concentration of dissolved aluminium in the NaF-AlF₃ system. Thus, only models involving two or more species will be considered.

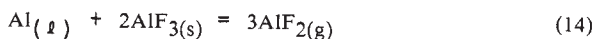
Sodium is soluble in pure NaF (≈2 mol% Na at 1000°C [30]. Sodium metal has also been found in quenched NaF-AlF₃ melts equilibrated with aluminium [22], [15]. The vapour pressure of sodium is rather high over such melts. This pressure increases with increasing NaF/AlF₃ molar ratio from ≈ 64 torr over cryolite [19] to 1 atm at CR = 10 [1] and to 2.63 atm over pure NaF(l) in equilibrium with pure liquid sodium [31], all at 1000°C. These results strongly indicate that at least a part of the dissolved metal in cryolitic melts in fact consists of sodium. The fraction of the dissolved metal which is due to sodium is expected to increase with increasing NaF/AlF₃ molar ratio. The model calculation showed that among the possible sodium species only Na_(diss) (Na, Na⁺ + e, or Na₂⁺) gave a detectable concentration of dissolved sodium at CR<=2.5, when extrapolated from pure NaF. All other tested sodium-containing species gave a very low concentration, even in cryolite. In all the models that will be presented, Na_(diss) is therefore one of the components. Another reason to include Na_(diss) as one of the species in the models is the fact that a better fit between model predictions and experimental results was found in the calculation when including Na as one of the dissolved "aluminium" species.

For the reaction



calculations give p_{AlF} = 39.3 torr at 1000°C. (Thermodynamic data from JANAF [26,32]). This agrees well with vapour pressure data of Kvande [19]. Electrochemical measurements also indicate that monovalent aluminium species are present in cryolitic melts [33], [34]. The experimental indications of the presence of monovalent aluminium in the vapour and in the melt require that such species should be included in the models. AlF_x^(+1-x) with x>2 is not used in the models, because such ions are not very probable, and the fit between the model and the experimental results gets poorer when they are included.

According to JANAF [26,32], the vapour pressure of AlF₂(g) according to the reaction:



is ≈2.1 torr at 1000°C. This pressure is rather uncertain since the thermodynamic data for AlF₂ are determined only within rather wide margins of error, as can be seen from the most recent JANAF edition (ΔH_f^o_{AlF₂} = 695 ± 42

kJ/mol, [32]). This means that eq. (14) gives 0.57 < p_{AlF} < 7.9 torr at 1000°C.

An AlF₂ pressure on the lower side of this range is probable according to the vapour pressure data of Kvande [19]. Solubility of aluminium partly in the form of divalent aluminium species can therefore not be excluded without more careful consideration, especially not in acidic NaF-AlF₃ melts, since uncommon oxidation states have been established on the acidic side of the corresponding NaCl-AlCl₃ system [35]. Models involving divalent aluminium species will therefore be presented in the discussion of possible dissolution reactions.

Because of the complexity of the solution of aluminium in cryolitic melts, it is crucial in the fitting of a model to have solubility data for a wide range of NaF/AlF₃ ratios. In the present work solubility data have been determined over a wider CR range than had been done previously (0.878 ≤ CR ≤ 4), and the solubility of sodium in pure sodium fluoride (CR = ∞) has also been taken into account in the modelling. The present solubility data and the new activity data of Sterten and coworkers [1,2], for the first time

allow for a good modelling of the solubility of aluminium in the NaF-AlF₃ system.

In light of the above discussion, the total aluminium solubility can be defined in the following six ways by taking the various possible dissolved species into consideration. The reason for the selection of these models is that they either have been proposed before (I) or that they more or less fit the experimental data.

$$\text{I: } c_{\text{Al}} = c_{\text{Na(diss)}} + c_{\text{AlF(diss)}} \quad (15)$$

$$\text{II: } c_{\text{Al}} = c_{\text{Na(diss)}} + c_{\text{AlF}_2^-} + c_{\text{AlF(diss)}} \quad (16)$$

$$\text{III: } c_{\text{Al}} = c_{\text{Na(diss)}} + c_{\text{AlF}_2^-} \quad (17)$$

$$\text{IV: } c_{\text{Al}} = c_{\text{Na(diss)}} + c_{\text{AlF}_2^-} + c_{\text{AlF}_3^-} + c_{\text{AlF(diss)}} \quad (18)$$

$$\text{V: } c_{\text{Al}} = c_{\text{Na(diss)}} + c_{\text{Al}_2\text{F}_4^{2-}} + c_{\text{AlF}_3^-} + c_{\text{AlF(diss)}} \quad (19)$$

$$\text{VI: } c_{\text{Al}} = c_{\text{Na(diss)}} + c_{\text{AlF}_2^-} + c_{\text{Al}_2\text{F}_3^-} + c_{\text{Al}_3\text{F}_4^-} + c_{\text{Al}_4\text{F}_5^-} \quad (20)$$

The best fits for the various models to the experimental results are presented in Figs. 4-9.

In the model calculation the activity coefficients of the various species were assumed to be independent of the cryolite ratio, and according to the ideal Temkin model, the activity of Na⁺ was set equal to unity. As standard states for the dissolved aluminium species were chosen; 1 wt% dissolved aluminium, and NaF(l) and AlF₃(s) were used as standard states for NaF and AlF₃ respectively. The modelling is discussed extensively in [34].

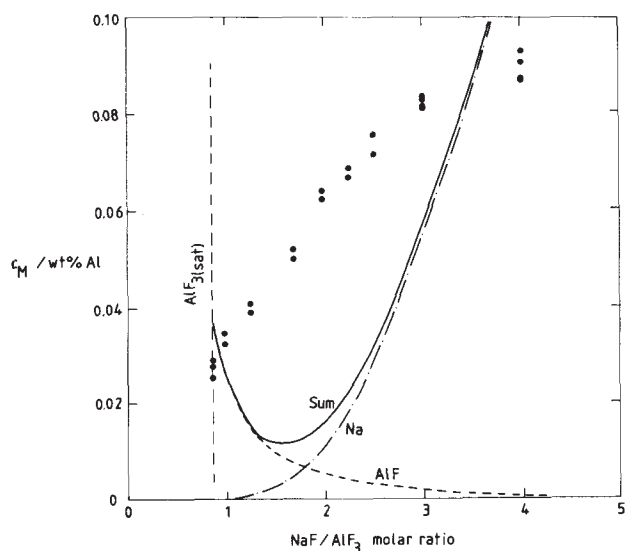


Fig. 4. The concentration of dissolved aluminium in alumina-saturated NaF-AlF₃ melts as predicted by Model I (eq. (15)) (solid line) compared with the experimental results (●) as a function of the NaF/AlF₃ molar ratio at 1000°C. The partial solubilities of Na_(diss) and AlF_(diss) are also presented.

The model fitting for Model I was performed by varying the equilibrium constants in the equations giving aluminium dissolved as AlF_(diss) and Na_(diss) in order to minimize the relative least square difference between the measured

concentrations of dissolved aluminium and the concentrations predicted by the model. This was done by a MODFIT computer program [36]. In the calculation activities for NaF and AlF₃ for alumina-saturated melts at 1000°C [1] were used. A similar procedure was used for the other models.

As Fig. 4 shows, the fit between Model I and the experimental data is poor. Therefore, the two species AlF_(diss) and Na_(diss) cannot explain the variation of concentration of dissolved aluminium in the NaF-AlF₃ system. AlF_(diss) cannot be the only aluminium-containing species formed in the Al dissolution reaction.

The fitting of Model II (equation (16)) to the experimental solubility data is shown in Fig. 5. The partial concentrations of AlF_(diss), AlF₂⁻ and Na_(diss) are also given in the figure.

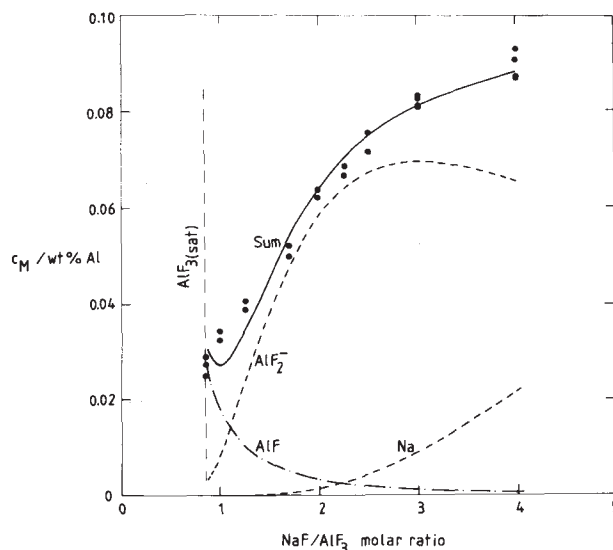


Fig. 5. The concentration of dissolved aluminium in alumina-saturated NaF-AlF₃ melts predicted by Model II (eq. (16)) (solid line) compared with the experimental data (●) as a function of the NaF/AlF₃ molar ratio at 1000°C. The partial concentrations of AlF_(diss), AlF₂⁻ and Na_(diss) are also presented.

As Fig. 5 shows, the introduction of the AlF₂⁻ species in Model II results in a far better agreement with the experimentally measured solubilities than Model I does with only AlF_(diss) and Na_(diss). The AlF₂⁻ ion has been proposed previously [33,38], but not as a part of a model involving more than one species. However, the discrepancy between the solubilities predicted by Model II and the experimental data is considerable at low NaF/AlF₃ ratios (CR < 1.70), and it is definitely larger than the standard deviation of the experimental results.

As shown by Fig. 6, Model III (AlF₂⁻ and Na_(diss)) cannot explain the variation of the concentration of dissolved aluminium in strongly acidic NaF-AlF₃ melts (CR < 1.5). Species with a high concentration at these low CR's must therefore be included in the modelling.

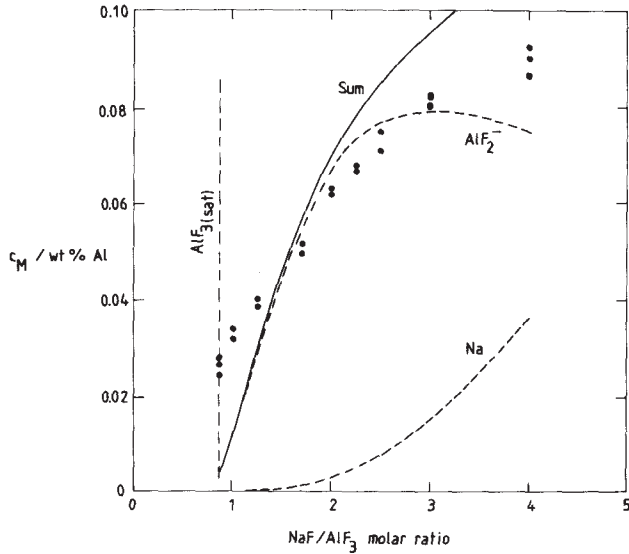


Fig. 6. The concentration of dissolved aluminium in alumina-saturated NaF-AlF₃ melts predicted by Model III (eq. (17)) (solid line) compared with the experimental data (●) as a function of the NaF/AlF₃ molar ratio at 1000°C. The partial concentrations of AlF₂⁻ and Na_(diss) are also presented.

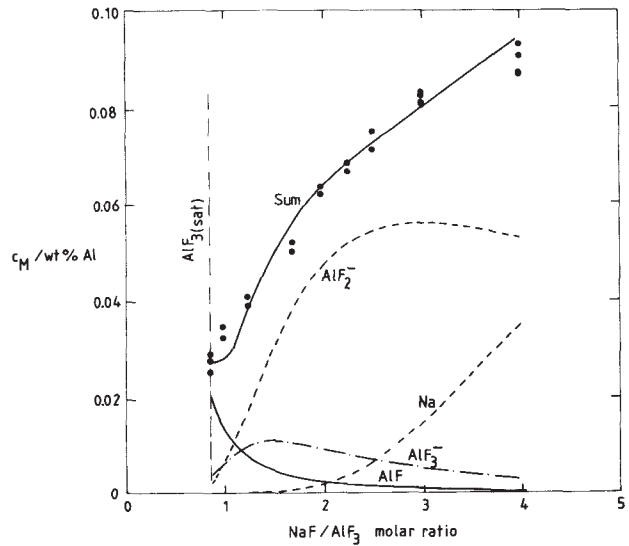


Fig. 7. The concentration of dissolved aluminium predicted by Model IV (eq. (18)) (solid line) compared to the experimental data (●) in alumina-saturated melts as a function of the NaF/AlF₃ molar ratio at 1000°C. The partial solubilities of AlF_(diss), AlF₃⁻, AlF₂⁻ and Na_(diss) predicted by the model are also given.

In Model IV (eq. (18)) the divalent aluminium species AlF₃⁻ is introduced in addition to the species in Model III. As Fig. 7 shows, the solubilities predicted by Model IV and the experimental results are in fair agreement over the entire NaF/AlF₃ range studied. The partial concentrations of AlF₂⁻ and AlF₃⁻ are equal at CR = 1.00 (see Fig. 7). This may appear to be an unexpectedly high AlF₃⁻ concentration since the ratio of P_{AlF}/P_{AlF₂} is roughly 25

over the melt in equilibrium with aluminium at 1000°C (Data from [1,26,32]). The ratio of monovalent to divalent aluminium in the melt is not necessarily the same as in the vapour phase, but it is somewhat surprising if the concentration of AlF₃⁻ is much higher than that of AlF₂⁻.

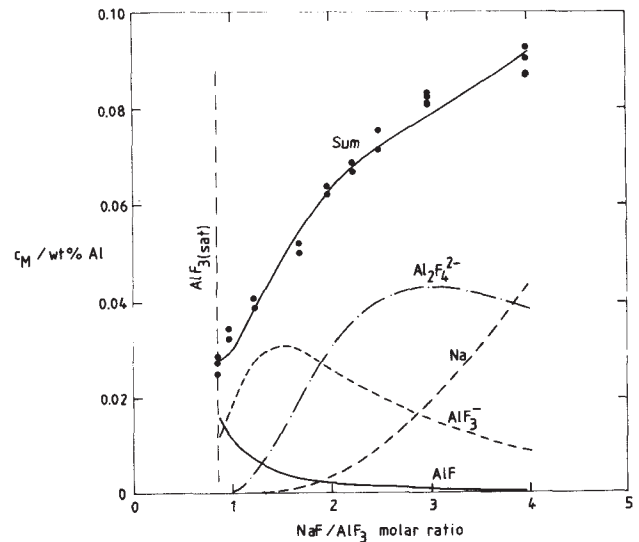


Fig. 8 shows the fit between Model V (eq. (19)) and the experimental results. This model gives an even better fit between the predicted solubilities and the experimental results than Model III does. However, this model includes the dimer of AlF₂⁻, the existence of which can be questioned. Another and perhaps more serious objection to this model is that the AlF₃⁻ to Al₂F₄²⁻ concentration ratio is questionably high at low CR's (≈30 at CR = 1.00, see Fig. 8).

Fig. 8. The concentration of dissolved aluminium predicted by Model V (eq. (19)) (solid line) compared to the experimental data (●) in alumina-saturated melts as a function of the NaF/AlF₃ molar ratio at 1000°C. The partial solubilities of AlF_(diss), Al₂F₄²⁻, AlF₃⁻ and Na_(diss) predicted by the model are also given.

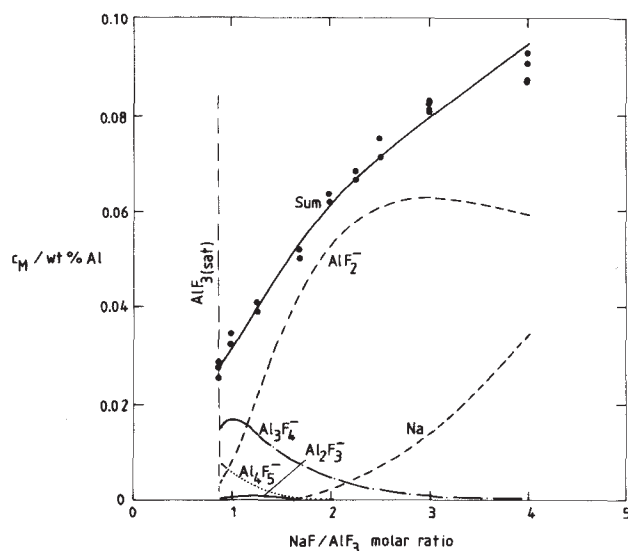


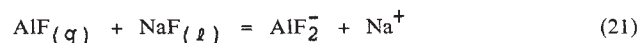
Fig. 9. The concentration of dissolved aluminium predicted by Model VI (eq. (20)) (solid line) compared to the experimental data (●) in alumina-saturated melts as a function of the NaF/AlF₃ molar ratio at 1000°C. The partial solubilities of Na_(diss), AlF₂⁻, Al₂F₃⁻, Al₃F₄⁻ and Al₄F₅⁻ are also given.

In Fig. 9 the fit of Model VI (eq. (20)) to the experimental results is shown. This model gives an excellent prediction of the concentration of dissolved aluminium over the entire examined NaF/AlF₃ range. However, one should keep in mind that an increase in the number of probable components in model calculations (five species in Model VI compared to four in models IV and V) often results in better fit to the experimental data, because the number of free variables increases.

Bridging fluorine between two aluminium atoms has been proposed by Sterten [39] for the postulated Al₂F₇⁻ complex ion in acidic NaF-AlF₃ melts. Fluorine is also known to form bridging bonds in other systems, for instance Be-F-Be in BeF₂ and mixtures of BeF₂ and alkali fluorides, [40]. Chains with oxygen bonds are known for several systems (Na₂O-SiO₂, [41], NaF-B₂O₃ and NaF-NaPO₃, [42]). In these systems the chain length increases with increasing acidity of the melts. Fluorine is a weaker acid than oxygen, therefore the formation of chains with fluorine bonds would probably be weaker than the corresponding oxygen bridges. In acidic NaF-AlF₃ melts where the sodium fluoride activity decreases strongly, formation of fluorine-bridged chains with dissolved aluminium would be an analogue to the chains linked with oxygen in other systems.

As can be seen from Figs. 7-9, models IV, V and VI fit the experimental data reasonably well. Models IV and V include the AlF_(diss) species. The solution mechanism of AlF_(g) has been postulated to be of the same type as the solution of CO_{2(g)} in NaF-AlF₃ melts [19,37]. This solubility was measured by Bratland et al. [43] and by Numata and Bockris [44]. Bratland et al. explained the high solubility of CO₂ in these melts by interaction between CO₂ and the melt, forming CO₃²⁻ or CO₂F⁻ complex ions. Numata and Bockris also proposed the formation of CO₃²⁻ complex ions to explain their results. The solubility of O_{2(g)} in NaF-AlF₃ melts is only 1/1000

of the solubility of CO_{2(g)} [44]. This difference was explained by CO₂ being an interacting gas, while O₂ is not. But if AlF_(diss) is postulated to be an important species in the aluminium dissolution reaction, it must be considered as a non-interacting gas species and hence a low solubility in the melt would be expected. However, even if the solubility of AlF_(g) were as large as for CO_{2(g)}, this would account for only 1/20 of the observed concentration of dissolved aluminium in alumina-saturated cryolite at 1000°C. AlF₂⁻ can be treated as the result of the interaction between AlF_(g) and NaF_(l) according to the reaction;



Such a reaction will probably increase the solubility of AlF_(g), but it leads to a different species in the melt that cannot be regarded as being identical to AlF_(diss) in the models. Since AlF_(g) probably has a low solubility in NaF-AlF₃ melts, AlF_(diss) may be questionable as a species of such great importance as models IV and V would indicate. Also the concentration of the AlF₃ species in Model IV and especially in Model V can, as commented before, be regarded as rather high when compared to the concentrations of AlF and AlF₂ in the gas phase over these melts in equilibrium with aluminium.

The partial solubility of Na_(diss) according to models IV, V and VI give 2.24, 2.69 and 2.14 mol% Na respectively, when extrapolated to pure NaF at 1000°C. This agrees well with the estimate from the data by Bredig and Bronstein [30], giving ≈2 mol% Na. However, the partial solubilities of Na_(diss) according to the models are lower than those reported by Haupin [22] and Thonstad [15] for cryolite at 1000°C. The reason for this could be difficulties in preserving the equilibrium between dissolved sodium and aluminium during quenching in their experiments or considerable positive deviation from ideality for dissolved sodium in the NaF-AlF₃ system.

Species of the type Te_{2n}²⁺ (n = 1,2,3,4) has been identified for dissolved tellurium in NaCl-AlCl₃ melts [45]. According to Bjerrum, these species and the corresponding Se_{2n}²⁺ species do not form complexes with the chloride ions. As an analogue to those ions, Al_n⁺ species could also be postulated to explain the dissolution of aluminium in NaF-AlF₃ melts. However, Al_n⁺ species would give a very sharp rise in the concentration of dissolved aluminium at low CR's. Therefore such species can not explain the observed variation in the concentration of dissolved aluminium in the NaF-AlF₃ system.

Among the three models (IV, V and VI) which fit the experimental results well, Model VI seems to be most probable, even though models IV and V cannot be excluded.

Aluminium Solubility in Melts with varying Alumina

Concentration.

The content of dissolved aluminium as a function of the alumina concentration at CR = 2.25 and 1000 ± 1°C is given in Fig. 10, together with some literature data. The decrease in the concentration of dissolved aluminium is ≈ 10% when going from pure NaF-AlF₃ melts to alumina-saturated melts.

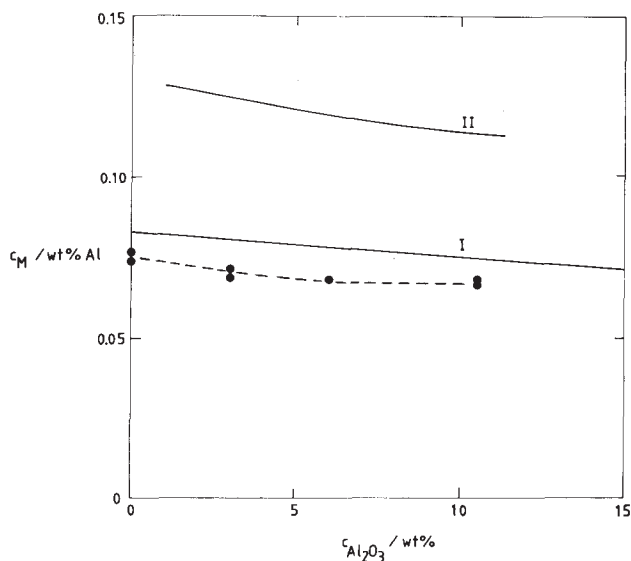


Fig. 10. Concentration of dissolved aluminium as a function of the alumina concentration.

●: Present work, CR = 2.25, $t = 1000 \pm 1^\circ\text{C}$.
 Solid lines I: Arthur [14], CR = 3.00, $t = 1020^\circ\text{C}$.
 II: Vetyukov et al. [46], CR = 3.20, $t = 1060^\circ\text{C}$.

The trend in aluminium solubility as a function of the alumina concentration is the same for all works presented in Fig. 10. Vetyukov et al. [46] reported a 12% decrease in the aluminium concentration at CR = 3.20 and 1060°C when the alumina concentration was increased from zero to 11.5 wt%. Arthur [14], in a figure showing aluminium solubility versus temperature, reported data indicating a $\approx 13\%$ decrease in aluminium solubility when going from alumina-free to alumina-saturated cryolite at 1020°C . Both these works are in fair agreement with the present investigation. In the work by Vetyukov et al. [46], there is possibly some aluminium carbide dissolution (BNC-crucibles). Also the solubility of Al_4C_3 decreases with increasing alumina concentration [25]. Thus, the agreement in results may be fortuitous.

Model Fitting for Melts with varying Alumina Concentration.

Sterten and coworkers [1,2] have presented equations for the activities of AlF_3 and NaF for both alumina-free and alumina-saturated NaF-AlF_3 melts. These activities are also given as functions of the alumina concentration for CR = 3.00 [2]. Making the assumption that the shape of activity versus alumina concentration curves is the same at CR = 2.25 as at CR = 3.00, one can estimate the activities of AlF_3 and NaF over the entire alumina concentration range at CR = 2.25.

The concentration dependence of the various models for dissolved aluminium as a function of the alumina concentration was calculated for the various species using the same equilibrium constants that were found to give the best fit in the $\text{NaF-AlF}_3\text{-Al}_2\text{O}_3(\text{sat})$ system. The fit between the experimental results and the solubilities predicted according to models IV, V, and VI (eqs. (18-20)) is shown in Fig. 11.

The models presented in Fig. 11 represent the sum of the partial solubilities of the various species. As seen from Fig. 11, all three models give a fair representation of the aluminium solubility as a function of the alumina concentration. Models IV and VI predict an 8% decrease from alumina-free to alumina-saturated melts, and Model V predicts a 13% decrease. Because of the margin of error in the solubility data, Fig. 11 does not exclude any of the three models (IV, V and VI). However, models IV and VI seem to fit better to the experimental data than Model V does.

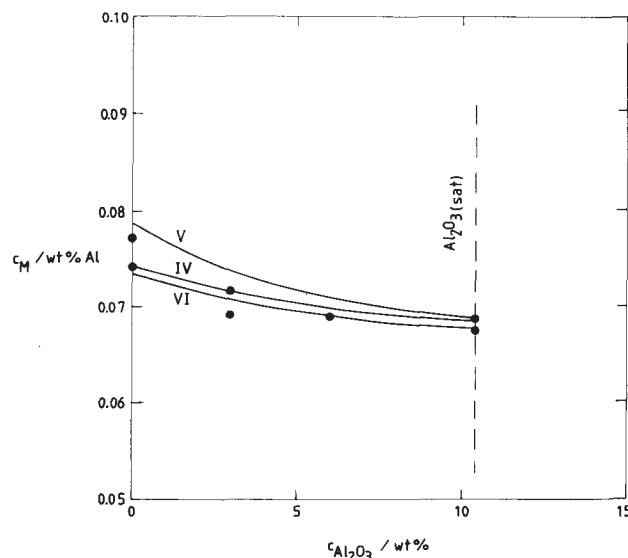


Fig. 11. The concentration of dissolved aluminium as a function of the alumina concentration at CR = 2.25 and 1000°C (●) compared to the solubilities predicted by models IV, V and VI (eqs. (18-20)).

Some Industrial Implications of the Present Work.

From the solubility data in the present work, the following empirical equation for the concentration of dissolved aluminium was derived;

$$\log(c_{\text{Al}}) = 1.8251 - 0.5919/\text{CR} - 3.429 \cdot 10^3/T - 3.39 \cdot 10^{-3} \cdot c_{\text{Al}_2\text{O}_3} - 2.49 \cdot 10^{-2} \cdot c_{\text{LiF}} - 2.41 \cdot 10^{-2} \cdot c_{\text{MgF}_2} - 2.03 \cdot 10^{-2} \cdot c_{\text{CaF}_2} \quad (22)$$

where c_{Al} is the concentration of dissolved aluminium (wt% Al), CR is the NaF/AlF_3 molar ratio, T is the bath temperature (K), $c_{\text{Al}_2\text{O}_3}$ is the concentration of alumina (wt%) and c_{LiF} , c_{MgF_2} , and c_{CaF_2} are the concentrations of LiF, MgF_2 and CaF_2 (wt%).

Equation (22) was derived by multiple regression analysis, assuming that the activation energy for the aluminium dissolution reaction is independent of the composition, that the additives have the same relative effect at all CR's and temperatures and that the effects of additions of LiF, MgF₂, CaF₂ and Al₂O₃ can be linearized. The variation of the concentration of dissolved aluminium as a function of the CaF₂ concentration is in fact not linear (see Fig. 3). Equation (22) was therefore based on the measurements with 10 wt% CaF₂ addition.

With the given assumptions eq. (22) applies for CR's up to 4, for the whole available range of temperatures and alumina concentrations and for additions of LiF, MgF₂ and CaF₂ up to 5 wt%. The correlation coefficient of equation (22) for all 23 solubility measurements in the NaF-AlF₃-Al₂O₃(sat) system without additives at 1000°C is 0.9938. This gives a relative standard deviation of less than 5% at all CR's.

As mentioned above, eq. (22) is based on the assumption that the effects of LiF, MgF₂, CaF₂ and Al₂O₃ are additive. This assumption is probably not strictly valid. However, the deviation from eq. (22) due to interaction effects cannot be estimated without having activity data for NaF and AlF₃ in cryolitic melts with additives. Such data are not available for alumina-containing melts.

Eq. (22) shows that the equilibrium concentration of dissolved aluminium can be lowered by decreasing the CR (increasing the excess AlF₃ content), lowering the bath temperature, increasing the concentration of additives (Al₂O₃, CaF₂, MgF₂, LiF) in the bath, or a combination of these measures. If the conditions in Hall-Héroult cells are identical in all other respect, a decreased equilibrium concentration of dissolved aluminium in the boundary layer at the cathode will give a higher current efficiency [9]. The trends given by eq. (22) regarding temperature and excess AlF₃ agree with current efficiency data reported for industrial cells [47] and with the present practice of operating the Hall-Héroult cells with increasingly higher excess content of AlF₃ and lower temperature. The effect of the alumina concentration on current efficiency is disputable since a change in the alumina concentration influences also the size of the gas bubbles and hence the rate of the "back reaction" [9]. This effect may be more important than the influence of the alumina concentration on the aluminium solubility, especially at low alumina concentrations [8].

Additions of LiF, MgF₂ and CaF₂ to aluminium cells have been reported to be beneficial for CE [3]. However, the experimental data on the magnitude of the improvements in current efficiency with these additives are partly in conflict [3]. An extensive discussion of the reported industrial current efficiencies in view of the present solubility data is therefore hardly warranted.

REFERENCES

1. Å. Sterten, K. Hamberg and I. Mæland, *Acta Chem. Scand.*, A36(1982), 329.
2. Å. Sterten and I. Mæland, *Acta Chem. Scand.*, A39(1985), 241.
3. K. Grjotheim, C. Krohn, M. Malinovsky, K. Matiasovksy and J. Thonstad, *Aluminium Electrolysis*, 2nd ed., Aluminium-Verlag GmbH, Dusseldorf, 1982.
4. R.F. Robl, W.E. Haupin and D. Sharma, *Light Metals 1977*, 106th Annual Meeting of AIME, Atlanta, 1977, Vol.1., p.185.
5. B. Lillebuen, S.A. Ytterdahl, R. Huglen and K.A. Paulsen, *Electrochim. Acta*, 25(1980), 131.
6. J.W. Evans, Y. Zundelvich and D. Sharma, *Metall. Trans.*, 12B(1981), 353.
7. S. Rolseth and J. Thonstad, *Light Metals 1981*, 110th Annual Meeting of AIME, Chicago, 1981, p.289.
8. B. Lillebuen and T. Møllerud, *Light Metals 1985*, 114th Annual Meeting of AIME, New York, 1985, p.637.
9. K. Grjotheim, W.E. Haupin and B.J. Welch, *Light Metals 1985*, 114th Annual Meeting of AIME, New York, 1985, p.679.
10. M. Rolin, *L'electrolyse de l'aluminium*, Publication de L'Institut National des Sciences Appliquées de Lyon, Villeurbanne, France, 1981.
11. K. Motzfeldt, "Means of attending and controlling temperature", in *Physicochemical Measurements at High Temperature*, Eds.: J.O'M. Bockris, J.L. White and J.D. Mackenzie, Butterworths, London, 1959, p.51.
12. P.S. Rogers, D.J.M. Bevan and J.W. Tomlinson, *Mikrochim. Acta*, 12(1956), 1839.
13. K. Yoshida and E.W. Dewing, *Metall. Trans.*, 3(1972), 1817.
14. A.M. Arthur, *Metall. Trans.*, 5(1974), 1225.
15. J. Thonstad, *Can. J. Chem.*, 43(1965), 3429.
16. M.M. Vetyukov and V.B. Vinokurov, *Physical Chem. and Electrochem. of Molten Salts and Slags*, Kiev, 1969, p.367.
17. M.M. Vetyukov and V.B. Vinokurov, *Tsvet. Met.*, 44(6)(1971), 5.
18. M.M. Vetyukov and V.B. Vinokurov, *Tsvet. Met.*, 47(6)(1974), 39.
19. H. Kvande, *Thermodynamics of the System NaF-AlF₃-Al₂O₃-Al*, Dr. techn. thesis, The University of Trondheim, NTH, Norway, 1979.
20. S. Rolseth, *Tilbakereaksjonen i aluminiumelektrolysen*, Dr.ing. thesis, The University of Trondheim, NTH, Norway, 1980. (in Norwegian).
21. A. Bjørgum, Å. Sterten, J. Thonstad, R. Tunold and R. Ødegård, *Electrochim. Acta*, 29(1984), 975.
22. W.E. Haupin, *J. Electrochem. Soc.*, 107(1960), 232.
23. A.I. Zhurin, *Legk. Met.*, 6(5-6)(1937), 27.
24. E.W. Dewing, *Trans. Metall. Soc. AIME*, 245(1969), 2181.
25. R. Ødegård, Å. Sterten and J. Thonstad, *Proceedings of the Fifth International Symposium on Molten Salts*, Las Vegas, USA, October 13-18, 1985, p.361.

26. JANAF Thermochemical Tables, 2.ed., Dow Chemical Co., Midland, Michigan, 1971.
27. G.N. Lewis and M. Randall, Thermodynamics, revised by K.S. Pitzer and L. Brewer, McGraw-Hill, New York, 1961.
28. D. Phan-Xuan, R. Castanet and M. Lafitte, Light Metals 1975, 104th Annual Meeting of AIME, New York, 1975, Vol.1., p.159.
29. M.A. Bredig, in Molten Salt Chemistry, Ed.: M. Blander, Interscience Publishers, New York, 1964, p.367.
30. M.A. Bredig and H.R. Bronstein, J.Phys.Chem., 64(1960), 64.
31. M.M. Makansi, C.H. Muendell and W.A. Selke, J.Phys.Chem., 59,(1955), 40.
32. JANAF Thermochemical Tables, 1978 Supplement, Eds.: M.W. Chase Jr., J.L. Curnutt, R.A. McDonald and A.N. Syverud, J.Phys.Chem.Ref.Data 7(3)(1978), 793.
33. J.P. Saget, V. Plichon and J. Badoz-Lambling, Electrochim.Acta, 20(1975), 825.
34. R. Ødegård, On the Solubility and Electrochemical Behaviour of Aluminium and Aluminium Carbide in Cryolitic Melts, Dr.Techn. thesis, The University of Trondheim, NTH, Norway, 1986.
35. C.A. Angell, Ann.Rev.Phys.Chem., 22(1971), 429.
36. T. Hertzberg, Modifit user's guide, SINTEF Report STF21 A83001, SINTEF, Trondheim, Norway, 1983.
37. H.Kvande, "Light Metals 1980", 109th Annual Meeting of AIME, Las Vegas, 1980, p.171.
38. K. Yoshida, T. Ishihara and M. Yokoi, Trans.Metall.Soc.AIME, 242(1968), 231.
39. A. Sterten, Electrochim.Acta, 25(1980), 1673.
40. J.L. Holm, Thermodynamic Properties of Molten Cryolite and Other Fluoride Mixtures, Dr.techn. thesis, The University of Trondheim, NTH, Norway, 1971.
41. W. Zachariasen, J.Am.Chem.Soc., 54(1932), 3841.
42. S. Julsrud, Some Oxy-Anion Complexes in Alkali Fluoride Melts, Dr.techn. thesis, The University of Trondheim, NTH, Norway, 1983.
43. D. Bratland, K. Grjotheim, C. Krohn and K. Motzfeldt, J.Metals, 19(10)(1967), 13.
44. H. Numata and J.O'M. Bockris, Light Metals 1984, 113th Annual Meeting of AIME, Los Angeles, 1984, p.759.
45. N. J. Bjerrum, The Chalcogens in Chloroaluminate Melts, Dr.Techn. thesis, The Technical University of Denmark, 1981.
46. M.M. Vetyukov, Saber Abu-Zeid, Yu.V. Borisoglebskii and L.V. Krylov, Sov.Non-Ferrous Met.Research, 26(4)(1978), 154.