The Lattice Energy and Thermochemical Properties of the Compound NaAlF$_4$, Sodium Tetrafluoroaluminate

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The author's earlier phase investigations show that NaAlF$_4$ does not exist as a stable compound in the solid phase in the system NaF-AlF$_3$. Lattice energy calculations of the hypothetical compound NaAlF$_4$, sodium tetrafluoroaluminate, with a tetrahedral AlF$_4^-$ ion have been carried out. On the basis of these calculations some recommended enthalpies of reaction between compounds in the system sodium fluoride-aluminium fluoride at 298 and 1300 K in the solid, liquid, and gaseous state are given.

The phase diagram of the system NaF-AlF$_3$ has been investigated by a number of workers throughout the last 50 years, with different conclusions. Even recent investigations of the phase diagram of this system are in disagreement.[1-6]

The present author[2] was not able to detect any stable phase which could correspond to NaAlF$_4$. He therefore revised Grjotheim's[1] diagram and presented a phase diagram[2,3] which is shown in Fig. 1. In the course of this work[2] samples of the composition 50 mol % NaF + 50 mol % AlF$_3$ were examined both by X-ray and microscopy. All samples examined contained very well-formed crystals of chiolite, Na$_5$Al$_3$F$_{14}$, which could easily be detected under a microscope. In addition, two other phases were observed, one phase corresponding to the eutectic mixture and another to a so-called "corroded" phase. This phase consisted of powder which had not melted. It was possible to pick out some very tiny crystals from this phase. These crystals were identified in the microscope as AlF$_3$. The 50:50 composition was examined by DTA, and only one exothermic peak was observed on cooling, at 695°C, corresponding to the eutectic temperature in the system Na$_5$Al$_3$F$_{14}$ – AlF$_3$. It was confirmed that the NaAlF$_4$ compound could be obtained as a *metastable* phase by quenching the vapour, in agreement with Howard's[4] results.

It was shown by DTA and X-ray studies[2] of the quenched metastable NaAlF$_4$ that it disproportionates to chiolite, Na$_5$Al$_3$F$_{14}$, and aluminium fluoride upon heating. This dissociation will take place slowly even at room temperature. *E.g.*, a sample quenched by Howard[4] and shown to be NaAlF$_4$,
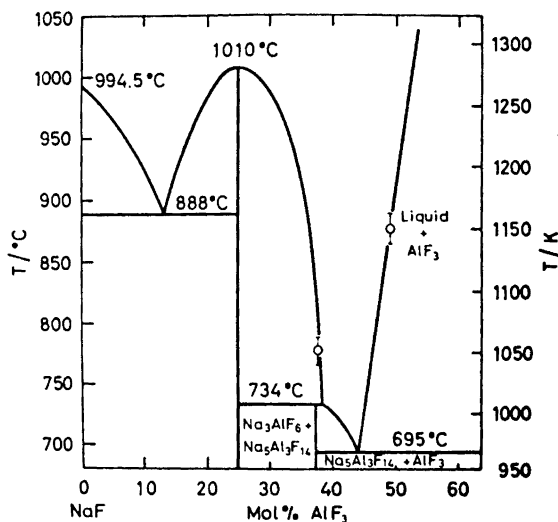
Fig. 1. The revised phase diagram of the system NaF-AlF$_3$. Circles with vertical bars denote points determined for Na$_5$Al$_3$F$_{14}$ and NaAlF$_4$ by drop calorimetry.[8]

was contained by the present author in a desiccator for 2 – 3 years. After this period, new X-ray examinations showed that only Na$_5$Al$_3$F$_{14}$ and AlF$_3$ were present.

Ginsberg and Wefers [5] in a more recent work claim that the compound NaAlF$_4$ is stable in a very narrow temperature range, 680 – 710°C. They were, however, not able to prove the existence of this compound by phase studies by high-temperature X-ray diffraction or other methods.

Foster [6] reexamined the AlF$_3$-side of the system by DTA and quenching, and reached the same conclusion as the present author and also Phillips *et al.*[7] did, namely that there is no sign of any stability range for NaAlF$_4$ in the system NaF-AlF$_3$ at any temperature and at normal pressure.

Some new examinations carried out by the present author [8] on the heat content of both the solid and molten mixtures of the composition 50 mol % NaF + 50 mol % AlF$_3$ show that the liquidus point for this composition is at 880 ± 5°C (1150 K). This strongly indicates that the phase diagram presented in Fig. 1 is the correct one.

Attempts to discuss the stability or the thermodynamic properties of solid NaAlF$_4$ in relation to the other fluoroaluminates were made by Sidorov *et al.*[9–11] and later also by Grjotheim *et al.*[12] The main reason why the stability of sodium tetrafluoroaluminate has been of particular interest is the fact that the dissociation scheme

$$Na_3AlF_{6(l)} = 2NaF_{(l)} + NaAlF_{4(l)}$$
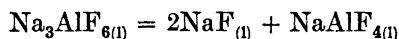
for some time has been suggested as the most probable one for molten cryolite.

This reaction scheme has been suggested on the basis of thermodynamic calculations and also from spectroscopic examinations.[13] The results from the latter are, however, doubtful. It should also be pointed out that the approaches to the problem of dissociation of the cryolite anion based on phase diagram calculations have been built on assumptions like the ideality of the molten mixture. It has been shown by the present author,[14] who measured enthalpies of mixing in the system Na_3AlF_6-NaF, that this assumption is not valid.

In the following, the stability of the compound $NaAlF_4$, both as a tetrahedral compound with isolated AlF_4^- ions and as an octahedral compound, will be calculated by use of enthalpy cycles and thermodynamic data available in the literature.

CALCULATIONS

(a) *Lattice energy calculations.* The fluoride affinity, $Y(AlF_4^-)$, of gaseous aluminium trifluoride is given by the reaction

$$AlF_{3(g)} + F_{(g)}^- = AlF_{4(g)}^-$$
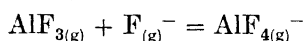
The value of this affinity can be calculated from the following enthalpy cycle (cycle 1):
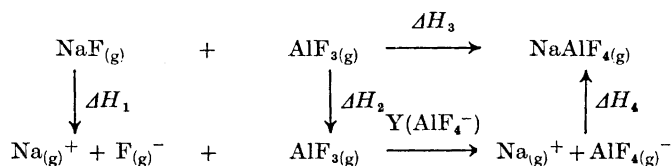
which gives

$$Y(AlF_4^-) = \Delta H_3 - \Delta H_1 - \Delta H_2 - \Delta H_4$$

Here $\Delta H_1 = 152$ kcal (Chao [15])
$\Delta H_2 = 0$
$\Delta H_3 = -76$ kcal (Sidorov *et al.*[9-11] and Grjotheim *et al.*[12]).
The enthalpy change, ΔH_4, has to be calculated. The Coulomb energy is given by

$$\Delta H_4 = -U = -\frac{Z_1 Z_2 e^2}{d_{NaAlF_4}} (1 - \varrho/\varrho_0) \tag{1}$$

By using an interatomic distance, $d = 3.10$ Å, in the gas molecule $NaAlF_4$, one finds from eqn. (1): $\Delta H_4 = -97$ kcal mol^{-1}. The fluoride affinity of gaseous aluminium trifluoride is

$$Y(AlF_4^-) = -76 - 152 + 97 = -131 \text{ kcal}$$

This value should be compared with the fluoride affinity of $BF_{3(g)}$, which is -76 kcal mol^{-1}.[16] Hence, gaseous aluminium trifluoride has a higher affinity for fluoride ions than boron trifluoride.

The lattice energy of $NaAlF_4$, sodium tetrafluoroaluminate, a hypothetical compound with isolated tetrahedral AlF_4^- ions, which is isomorphous with $NaBF_4$, can be calculated from the well-known Kapustinskii [17] equation

$$U_L = 287.2 \frac{vZ_1Z_2}{r_+ + r_-}\left(1 - \frac{0.345}{r_+ + r_-}\right) \text{kcal mol}^{-2} \qquad (2)$$

where v is the number of ions (here 2), $r_+ = 0.98$ Å, and $r_- = 2.60$ Å. The last value is the estimated thermochemical radius of the tetrahedral AlF_4^- ion. This value is reasonable when compared with the thermochemical radius of the BF_4^- ion, which is 2.28 Å.[16] Using these values one obtains a lattice energy of $NaAlF_4$ at 0 K of $U_L = 146$ kcal mol^{-1}. At 298.15 K, this value should be corrected to 145 kcal mol^{-1}.

(b) *The enthalpy of formation of NaAlF$_4$.* When both the lattice energy and the fluoride affinity are known, the enthalpy of formation of the hypothetical compound $NaAlF_4$ can be calculated at 298.15 K, from the following enthalpy cycle (cycle 2):
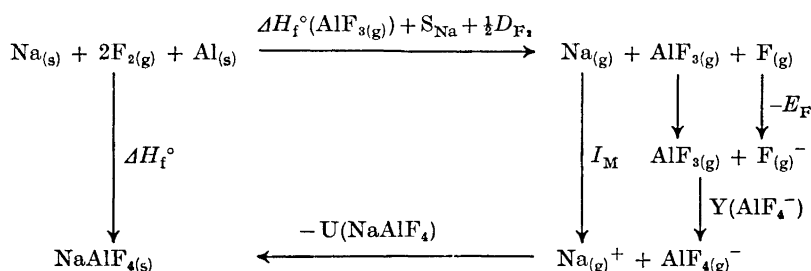
$$\Delta H_f^\circ{}_{298.15} = \Delta H_f^\circ(AlF_{3(g)}) + S_{Na} + \tfrac{1}{2}D_{F_2} + I_{Na} - E_{F^-} - Y(AlF_4^-) - U(NaAlF_4)$$

After inserting the values given in Table 1, one optains for the enthalpy of formation of $NaAlF_{4(s)}$

$$\Delta H_f^\circ{}_{298.15} = -290 + 26 + 18 + 118 - 80 - 131 - 145 = -482 \text{ kcal mol}^{-1}.$$

Table 1. Some lattice energy and enthalpy data in kcal mol^{-1} for $NaBF_4$ and $NaAlF_4$. (From Waddington,[16] JANAF,[18] and this work.)

Comp.	$Na_{(s)} \to$ $Na_{(g)}$	$M_{(s)} +$ $\tfrac{3}{2}F_{2(g)} \to$ $MF_{3(g)}$	$\tfrac{1}{2}F_{2(g)} \to$ $F_{(g)}$	$F_{(g)} +$ $e^- =$ $F_{(g)}^{-\,a}$	$MF_{3(g)} +$ $F_{(g)}^- =$ $MF_{(g)}^-$	$Na_{(g)} =$ $Na_{(g)}^+$ e^-	$-U_{NaMF_4}$	$\Delta H_f^\circ{}_{(NaMF_4)}$
$NaBF_4$	26	−271	18	−80	−76	118	−160	−425
$NaAlF_4$	26	−290	18	−80	−131	118	−145	−482

a From Ladd, M. F. C. and Lee, W. H. *Progr. Solid State Chem.* 1 (1963) 37 and 2 (1965) 378.

In Table 1 the values for $NaAlF_4$ are compared with the corresponding enthalpy data for sodium tetrafluoroberyllate. $NaBeF_4$, which is a stable compound in the solid state. The data are the same as those given in the review by Waddington.[16]

Table 2. Enthalpies of formation, ΔH_f, in kcal mol^{-1} for some important compounds in the system $NaF-AlF_3$ at 298.15 and 1300 K. (From JANAF [18] and this work [a]).

Phase	Temp/K	NaF	AlF₃	Na₃AlF₆	NaAlF₄ tetrahedral	NaAlF₄ octahedral
Solid	298.15	− 137.5	− 361	− 793	− 482 [a]	− 498 [a]
	1300	− 159.1	− 360	− 851.5	− 509 [a]	− 523 [a]
Liquid	298.15	− 130.5	− 353 [a]	− 774 [a]	− 478 [a]	
	1300	− 151.1	− 349 [a]	− 824 [a]	− 502 [a, b]	
Gas	298.15	− 69.4	− 289		− 435	
	1300	− 95.6	− 293		− 464	

[a] Estimated uncertainties for the new values 1 − 2 kcal.
[b] See Ref. 22.

It is now possible to calculate more accurate enthalpies of reaction for the compounds in the binary system $NaF-AlF_3$, by use of the new values. These results are summarized in Table 2. The enthalpy of fusion of AlF_3 at 1300 K, $\Delta H_f = 11$ kcal, is a hypothetical value which has been determined by the author.[14] This value has been added to the enthalpy of formation of solid AlF_3 to give the enthalpy of formation of liquid AlF_3.

The enthalpy values given for solid $NaAlF_4$ with octahedral coordination at 298.15 and 1300 K are taken as the most probable ones, giving the enthalpy of the reaction
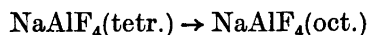
$$NaF_{(s)} + AlF_{3(s)} = NaAlF_{4(s)}(oct.)$$
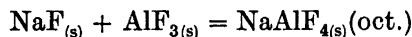
as follows:

$$\Delta H° = +1 \text{ kcal at } 298.15 \text{ K}$$

and

$$\Delta H° = -4 \text{ kcal at } 1300 \text{ K}.$$

Hence one gets for the solid state reaction

$$NaAlF_4(tetr.) \rightarrow NaAlF_4(oct.)$$

$\Delta H_{298.15} = -16$ kcal showing a strong preference for octahedral co-ordination of aluminium with respect to fluorine.

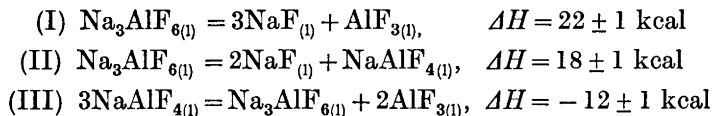From the enthalpies given in Table 1 it is possible to calculate the enthalpy for the reaction

$$3NaAlF_{4(s)} = Na_3AlF_{6(s)} + 2AlF_{3(s)}$$
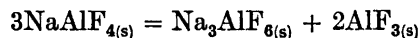
At 298.15 K one obtains $\Delta H = -21$ kcal. This result clearly shows the unstability of $NaAlF_4$ with respect to Na_3AlF_6 and AlF_3, in complete agreement with the phase diagram investigations.

The enthalpy of fusion of the hypothetical compound $NaAlF_4$ with tetrahedral AlF_4^- ions was taken as 7 kcal mol^{-1} at 1300 K and 5 kcal mol^{-1} at 298.15 K. These values should be of the same magnitude as the enthalpy of fusion of the compound $NaBF_4$, which is 5 kcal mol^{-1} according to Dworkin and Bredig.[19] The enthalpy of fusion of $NaAlF_4$ with octahedral structure was taken as 19 kcal mol^{-1}, the value which has been determined by the author [8] for a mixture of $\frac{1}{3}Na_3AlF_6$ and $\frac{2}{3}AlF_3$.

The enthalpy of fusion of cryolite, Na_3AlF_6, was taken as $\Delta H_f = 27.5$ kcal mol^{-1}, a value which was obtained by the present author [14] in good agreement with the value given by O'Brien and Kelley,[20] 27.64, kcal mol^{-1}. From these values one can calculate enthalpies of reaction in the liquid state. Here the following three reactions are of particular interest:

$$(I) \quad Na_3AlF_{6(l)} = 3NaF_{(l)} + AlF_{3(l)}, \qquad \Delta H = 22 \pm 1 \text{ kcal}$$

$$(II) \quad Na_3AlF_{6(l)} = 2NaF_{(l)} + NaAlF_{4(l)}, \quad \Delta H = 18 \pm 1 \text{ kcal}$$

$$(III) \quad 3NaAlF_{4(l)} = Na_3AlF_{6(l)} + 2AlF_{3(l)}, \quad \Delta H = -12 \pm 1 \text{ kcal}$$

The enthalpies given for the three reactions are those calculated at 1300 K from the data in Table 1. These results give new and important information about the *thermodynamically* most probable dissociation scheme for molten cryolite in the system NaF-Na_3AlF_6[21] as well as about the stability of the AlF_4^- ion in the system Na_3AlF_6-AlF_3.[8,12]

In the gas phase the enthalpy for the reaction

$$NaF_{(g)} + AlF_{3(g)} = NaAlF_{4(g)} \quad \Delta H = -74 \text{ kcal}$$

given by Sidorov et al.[9-11] and also by Grjotheim et al.[12] has been adopted as the most probable value. It has been shown by Kvande [23] that this value is nearly temperature independent.

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