THERMODYNAMICS OF THE SYSTEM LiF - AlF₃

E.W. Dewing
Aluminum Co. of Canada Research Centre
Arvida, P.Q., Canada, G7S 4K8

Abstract

It is demonstrated from the liquidus curve that solid Li₃AlF₆ is stoichiometric. Solid-electrolyte concentration cells have been used to determine the free energy of

\[ 3\text{LiF}(s) + \text{AlF}_3(s) = \text{Li}_3\text{AlF}_6(s) \]

as \( \Delta G^o = -3668 - 7.051T \) cal (870 - 1058 K) and \( \Delta G^o = -4138 - 6.510T \) cal (773 - 870 K) with a standard deviation of ±11 cal. At 1073 K liquid concentration cells with alumina diaphragms have given free energies of mixing for the system, the results being calculated with a transport number of Li⁺ ions of 0.957 ± 0.008 determined by coulometric titration of added AlF₃. For liquid Li₃AlF₆ the discrepancy between the results of the liquid cells and extrapolation of the results from solid cells is 100 cal.

The free energies of mixing at 1073 K can be interpreted in terms of the equilibrium

\[ \text{AlF}_4^- + 2\text{F}^- \rightleftharpoons \text{AlF}_6^{3-} \]

with \( K = 14.9 \) (in terms of anion fractions).

In earlier work, the free energy of the solid compounds Na₃AlF₆ and Na₃AlF₁₄ was determined with solid-electrolyte concentration cells (1), and activities in liquid NaF - AlF₃ mixtures saturated with alumina were determined with concentration cells with alumina diaphragms (2). The object of the present work is to use similar methods on the LiF - AlF₃ system. At the same time a check is made to see whether solid Li₃AlF₆ is non-stoichiometric in the same way that Na₃AlF₆ seems to be (3).

Romberger and Braunstein (4) measured emf's of concentration cells in the system LiF - BeF₂. In that case the activities were already known, so that transport numbers could be calculated. In the present case neither activities nor transport numbers are available; it has thus been necessary to measure the transport number of Li⁺ independently in a Hittorf-type experiment.

338
Solid Li\textsubscript{3}AlF\textsubscript{6}

The check for non-stoichiometry is made by plotting the liquidus curve for Li\textsubscript{3}AlF\textsubscript{6} on the basis of \(\log(C_{n^p} \cdot n^p)\) against \(1/T\) (3). If the compound is stoichiometric the two branches of the liquidus will have at least a common tangent and may be superimposed. Figure 1, based on the results of Jensen (5), Rolin et al (6,7), and Matiasovsky and Malinovsky (8) shows that there is no effective separation of the lines except at the lowest temperature, and that consequently Li\textsubscript{3}AlF\textsubscript{6} may be treated as stoichiometric.

The determination of the free energy of formation of solid Li\textsubscript{3}AlF\textsubscript{6} with a solid electrolyte cell is simple since the lithium analogue of chiolite, Na\textsubscript{2}Al\textsubscript{3}F\textsubscript{14}, does not exist. Hence, one cell

\[
\begin{array}{c|c|c|c}
\text{LiF} & \text{Li}\textsubscript{3}AlF\textsubscript{6} & \text{Li}\textsubscript{3}AlF\textsubscript{6} & \text{Al} \\
\text{Li}\textsubscript{3}AlF\textsubscript{6} & (\text{Li}^+) & \text{AlF}_3 & \text{Al}
\end{array}
\]

(1)

gives the desired result; if its emf is \(E\), then for

\[
3\text{LiF(s)} + \text{AlF}_3(s) = \text{Li}_3\text{AlF}_6(s)
\]

(1)

\[
\Delta G^0 = -3EF/2.
\]
(2)

(The theory of such cells has been given previously (1).)

The electrolyte was Li\textsubscript{3}AlF\textsubscript{6} doped with Mg\textsuperscript{2+}. Crystals were recovered from a slowly-cooled melt containing 8.4% MgF\textsubscript{2} and 7.5% excess AlF\textsubscript{3}. (This AlF\textsubscript{3} is equivalent to 3/2 MgF\textsubscript{2}. The crystals were not analyzed. On each side of the doped material pure Li\textsubscript{3}AlF\textsubscript{6} was placed, and the powders were compacted into 5 mm ID alumina tubes, as in the earlier work. The liquid aluminum electrodes were kept in place by layers of graphite and silver.

Emf's were measured with a Guildline potentiometer and a Keithley 600 B electrometer as null-detector. The latter has an internal impedance of 10\textsuperscript{14} ohm and a recorder output, so that out of balance current could be recorded continuously with a sensitivity of 10 mV full scale. The emf's were in fact steady to a few tenths of a mV. The results are shown in Figure 2.

According to Jensen (5) Li\textsubscript{3}AlF\textsubscript{6} has transitions at 870 and 783 K. With the exception of the point at 745 K, which is well below the lower transition, the data were fitted by least squares to two straight lines intersecting at the upper transition point. The two equations are
The enthalpy of transition is 470 cal. The standard deviation of the points from the line is 11.5 cal, corresponding to 0.33 mV.

For comparison, Figure 2 also shows the free energy given by the JANAF Tables (9). It differs by 0.9 kcal from this work.

**Liquid LiF - AlF₃ Mixtures**

The basis of the thermodynamic measurements is concentration cells with transport of the type

\[
\begin{array}{c|c|c|c}
\text{Al} & \text{LiF} & \text{LiF} & \text{Al} \\
\text{AlF₃ (sat)} & \text{AlF₃} & & \\
\end{array}
\]

The left-hand side has a fixed composition since it is always saturated with AlF₃; the right-hand side is variable. The mixtures were held in alumina tubes; since these are penetrated by cryolite melts the liquid junctions were formed within them. The electrodes were tungsten rods previously dipped in molten aluminum; effectively, for a period of minutes, they acted as reversible aluminum electrodes.

Mixtures were made up by weight from Reagent Grade LiF (Baker & Adamson - Allied Chemical) and AlF₃ purified by sublimation. The latter contained 0.08 wt % NaF. They were put into 5 mm ID x 8 mm OD alumina tubes, enough to give 1 - 2 cm depth when melted. The tubes were immersed in a LiF - Li₃AlF₆ eutectic mixture (64.6 wt % LiF, 35.4 wt % AlF₃) in a graphite crucible of two inches ID (Figure 3). Seven tubes in all were immersed; five containing mixtures, one in the centre containing a Pt - 10% Rh thermocouple, and the other containing liquid aluminum. The latter served for coating and re-coating the tungsten rods (1.5 mm diameter) used as electrodes.

A few additional results were obtained in the course of the transport number work described below.

To make a measurement the two tungsten rods were taken out of the aluminum and placed in the reference mixture (~60 mol% AlF₃ - saturated with AlF₃) and the one to be studied. An emf steady to within a millivolt or so was usually obtained within a few minutes. The electrodes were then removed, cleaned of electrolyte with a file, and replaced in the aluminum.

The theory of cells of this type has been given previously (2,4, 10,11). Activities are derived from emf's by
\[
\frac{d \ln a_{\text{LiF}}}{dt} = -\frac{3F}{RT} \cdot \frac{dE}{r + 3t}
\]

and

\[
\frac{d \ln a_{\text{AlF}_3}}{dt} = \frac{3F}{RT} \cdot \frac{r}{r + 3t} \cdot dE
\]

where \( r \) is the molar ratio \( \text{LiF}/\text{AlF}_3 \) and \( t \) is the transport number of \( \text{Li}^+ \) ions. (It is assumed that the transport number of \( \text{F}^- \) ions is \( 1-t \), and hence that \( \text{AlF}_3^{3+} = 0 \), which is reasonable if it is entirely complexed as \( \text{AlF}_6^{3-} \) and \( \text{AlF}_4^- \) (12)). Since these are differential equations they involve integrations and bring in unknown integration constants. These can be fixed if the integration can be started at a phase boundary where the activity is known.

From the phase diagram (5,7) the LiF liquidus at 1073 K may be taken to lie at 8.1 mol\% \( \text{AlF}_3 \). The activity with respect to liquid LiF may be calculated from the JANAF (9) free energy of fusion as \( \Delta G_{\text{LiF}} = -283 \text{ cal} \), and \( a_{\text{LiF}} = 0.876 \). This provides the necessary integration constant for equation (5).

Figure 4 is a plot of the results. Examination shows that the line is not quite straight (there is no reason why it should be); and it has been represented by three straight-line segments:

\[
\begin{align*}
n_{\text{AlF}_3} &< 0.25 \\
E & = 524 - 123.1 \, n_{\text{AlF}_3} \, \text{mV}
\end{align*}
\]

\[
\begin{align*}
0.25 &< n_{\text{AlF}_3} < 0.30 \\
E & = 554 - 135.2 \, n_{\text{AlF}_3} \, \text{mV}
\end{align*}
\]

\[
\begin{align*}
n_{\text{AlF}_3} &> 0.30 \\
E & = 494 - 115.3 \, n_{\text{AlF}_3} \, \text{mV}
\end{align*}
\]

The last of these extrapolates to zero at 42.8 mol\% \( \text{AlF}_3 \), about 1.5 mol\% higher than would be expected from the liquidus curve (5,6) but hardly beyond experimental uncertainty.

The overall standard deviation of the points from the lines is \( \pm 5.6 \) mV.

341
Integration of equations (5) and (6) was first carried out numerically with the assumption that t = 1; step size was 1 mol%. It was found that the AG° of formation of a 25 mol% AlF₃ mixture (i.e., for .75 LiF + .25 AlF₃) was -3009 cal (starting from liquid LiF and solid AlF₃). This may be compared with the value derived from the free energy of formation of solid Li₃AlF₆ (equation 3). With the enthalpy of fusion of Li₃AlF₆ of 21,000 ± 300 cal at 1058 K given by Holm and Grønvold (13) this gives for

\[3\text{LiF}(s) + \text{AlF}_3(s) = \text{Li}_3\text{AlF}_6(\ell)\]  (7)

\[\Delta G^0 = 17,332 - 26.900T,\]  (8)

and at 1073 K, \(\Delta G^0 = -11,532\). To make comparison with the integral \(\Delta G\) of mixing this value must be divided by 4 (to put it on the basis of 1 mole total), and then \(-283 \times 0.75\) cal must be added to transfer to the liquid standard state for LiF. The final result is \(\Delta G = -3,095\) cal. The discrepancy of 86 cal corresponds to 344 cal in the free energy of formation of Li₃AlF₆, and is an error of the order of 10 mV in the emf's. One therefore questions whether the assumption of unit transport number for Li⁺ ions is valid. If it be assumed that t is independent of composition a value of 0.94 is needed to get rid of the discrepancy.

The transport number of Li⁺ was determined by the direct coulometric titration of AlF₃. The procedure was that a melt was made up by weight to have a molar ratio LiF/AlF₃ of 3. It was placed in an alumina tube which was in turn immersed in a LiF - Li₃AlF₆ eutectic melt, as in the earlier work. The only difference was that the tube was 12 mm ID and the reference electrode was in a tube 8 mm ID. Dry argon was passed via a narrow alumina tube into the tube to exclude moisture; the top was plugged with glass wool. Aluminum-plated tungsten electrodes were used as before, except that the main one was not subsequently removed for re-plating. Aluminum was added to the crucible to act as anode.

At the start of a run, the emf between the two electrodes was found. A carefully weighed piece of coarsely crystalline AlF₃ was then dropped in, and the emf was redetermined. A current was then passed between the graphite crucible and the main electrode (cathodic) until the emf was above (or at least close to) the initial value. The duration of current was carefully timed and its value was measured with a calibrated resistor. (Since it had a small temperature coefficient and since it heated when current was passed, its value was determined with a Kelvin bridge immediately after use. The current, from a Hewlett-Packard 6200B Power Supply, was kept flowing through the resistor at all times to ensure that it stayed at steady state.) Linear interpolation was made on the emf - time line to determine the number of coulombs passed when the potential was restored to its original value. More AlF₃ was dropped in, and the process repeated. In this way a plot of coulombs vs wt AlF₃ added was obtained.
Figure 5 shows part of the emf - coulombs sequence, and Figure 6 is the final plot of moles of AlF₃ added vs equivalents of charge passed. The slope of the least squares line is 1.5317 with a standard error of ± 0.0025 equiv/mole. The standard deviation is ±0.079 m equiv, or ±7.6 coulombs. This is based on 9 points, including the origin. If the origin is omitted the standard deviation increases, showing that it is a valid point. If, on the other hand, a tenth point is brought in the standard deviation again increases (by a factor of 1.6), implying that something is wrong with it. Possibly a fragment of the AlF₃ failed to reach the bottom of the tube. It has been omitted from the final result.

If the slope of the line is n equiv/mole, the transport number is calculated as follows. Of 1 mole AlF₃ added, n/3 is destroyed by plating out Al onto the cathode. To restore the composition to the original molar ratio of 3, 3(1-n/3) moles LiF must be transported in. The transport number is thus

\[ t = \frac{3(1 - n/3)}{n} \]

\[ = \frac{3}{n} - 1 \]

\[ = 0.9586 \pm 0.0032. \]

If it be assumed that the 0.082% NaF is the only impurity in the AlF₃ (it is the most likely one), the value of t is reduced to 0.957.

The error quoted is a statistical standard error; systematic errors are much harder to estimate. The resistor was measured in situ with a precision of about ±0.2%, timing the duration of the current is, say, ±1 s in 10 minutes or about 0.17%. The overall precision on the coulombs is thus about ±0.26%. This will make ±0.52% in the value of t. If one takes this and two standard errors the overall uncertainty is \[ \sqrt{0.0064^2 + 0.0052^2} = \pm 0.0083. \] We may thus take \( t = 0.957 \pm 0.008. \)

Since t is very close to unity it is unlikely that a significant variation with composition could be determined experimentally, and it is assumed that it is constant. Integration of equations (5) and (6) is then straightforward, and the result is shown in Table 1. The ΔG for (.75 LiF, .25 AlF₃) is now -3070 cal; the ±0.008 uncertainty in the transport number makes ±11 cal. The discrepancy with the calculated value of -3095 cal is 25 cal, which is not really big enough to worry about. It would correspond to 3 mV in the emf's.

**Discussion**

That solid Li₃AlF₆ is the only one of the alkali metal cryolites which does not show pre-melting effects (13) is probably associated with the fact demonstrated here that it is stoichiometric. The implication could be that the others are not.
It has been assumed in this work that alumina is essentially insoluble in lithium cryolite. Rolin and Muhlethaler (6) stated that the solubility was less than 1%; in fact their figures (14) indicate that it is about 0.2% at 1073 K. There was no obvious attack on the alumina tubes used in the concentration cells, and it is not believed that the solubility is high enough to have affected the thermodynamic values.

Although the values obtained are completely independent of any model of the melts it is interesting to see if they can be fitted to a reasonable model. One which has been adopted by numerous authors is the equilibrium

\[ 2F^- + AlF_4^- \rightleftharpoons AlF_6^{3-}, \]  \hspace{1cm} (9)

it being assumed that the various anionic species mix ideally. In the past it has been necessary to calculate for temperatures and compositions along the liquidus curve, but now isothermal data covering the whole composition range are available.

Since Li\(^+\) is the only (uncomplexed) cation present, and since we are assuming that the anionic species are mixing ideally, we may identify the activity of LiF as measured with the anion fraction of F. Having found that, and knowing the overall composition, we can calculate the anion fractions of AlF\(_6\)\(^{3-}\) and F\(^-\), and then see if the model is working insofar as the equilibrium constant

\[ K = \frac{a_{LiAlF_6}}{a_{LiAlF_4} \cdot a_{LiF}} \]  \hspace{1cm} (10)

is constant.

If we start with an overall composition \(n_{LiF}\) and \(n_{AlF_6}\) (the total = 1), and \(x_{LiF}\), \(x_{LiAlF_4}\), and \(x_{LiAlF_6}\) denote numbers of moles of the individual species present, then

\[ x_{LiAlF_4} + x_{LiAlF_6} = n_{AlF_6} \]  \hspace{1cm} (11)

\[ x_{LiF} + x_{LiAlF_4} + 3x_{LiAlF_6} = n_{LiF} \]  \hspace{1cm} (12)

By substituting (11) in (12)

\[ x_{LiF} = n_{LiF} - n_{AlF_3} - 2x_{LiAlF_6} \]

\[ = 2n_{LiF} - 1 - 2x_{LiAlF_6} \]  \hspace{1cm} (13)

since \(n_{AlF_3} = 1 - n_{LiF}\). The sum of the \(x\)'s is from (12)
\[ x_{LiF} + x_{LiAlF_4} + x_{Li_3AlF_6} = n_{LiF} - 2x_{Li_3AlF_6} \]  

Hence,

\[ a_{LiF} = \frac{2n_{LiF} - 1 - 2x_{Li_3AlF_6}}{n_{LiF} - 2x_{Li_3AlF_6}} \]  

and, rearranging,

\[ x_{Li_3AlF_6} = \frac{n_{LiF}(2 - a_{LiF}) - 1}{2(1 - a_{LiF})} \]

Once this is known, insertion into (11) gives \( x_{LiAlF_4} \), and division by the sum of the x's (equation (14)) gives the activities of \( Li_3AlF_6 \) and \( LiAlF_4 \).

If the model is working, and the equilibrium constant is constant, then a plot of \( a_{LiF} \) against \( \sqrt{a_{LiAlF_4}/a_{LiAlF_4}} \) should be straight. In Figure 7 the results for \( n_{AlF_3} > 0.25 \) are plotted. The line is remarkably straight. For \( n_{AlF_3} < 0.25 \) problems arise because the quantity of \( AlF_4 \) present is so small that accuracy is lost, and another approach must be tried.

Fundamentally, the problem is: given the experimental emf's and assuming the model is applicable, what is the value of the equilibrium constant \( K \) which will minimize the scatter of the calculated and experimental emf's? The problem can be treated directly without doing any integrations since, for any composition, if \( K \) is specified the activities can be calculated uniquely and hence emf's with respect to some arbitrary standard composition. The only adjustment necessary is a constant to bring the arbitrary standard in line with the real one. In making the calculation it is of course necessary to insert the same transport number as used previously.

The best value of \( K \) is found to be 14.9. The resulting line is shown for comparison in Figure 7 and the calculated emf composition curve is compared with the experimental points in Figure 8. The standard deviation is ±8.5 mV, which may be compared with the ±5.6 mV standard deviation from the straight line segments. On the AlF_3 -side of Li_3AlF_6 the fit is very good (as it is also in Figure 7), but on the LiF - side there is a bend in the calculated curve which is not reproduced by the experimental values.

The simple dissociation model thus looks like a good first approximation, and is not inconsistent with Ratkje and Rytter's (15) finding that by Raman spectroscopy of LiF - Li_3AlF_6 eutectic mixture (15 mol% AlF_3) they could detect distorted AlF_6^2- groups but no AlF_4. With the value of the dissociation constant of 14.9 the composition is expected to be
74 mol\% \text{F}^-, 23 \text{ mol\% AIF}_6^{3-}, \text{ and } 2.8 \text{ mol\% AIF}_4^- . \text{ It is thus perhaps not surprising that it was not detected. On the other hand, Gilbert, Mamantov and Begun (16) did not see any AIF}_4^- \text{ in a Li}_2\text{AlF}_6 - \text{ Na}_2\text{AlF}_6 \text{ eutectic at } 790^\circ\text{C. If K is around 15, then there should be 19 mol\% AIF}_4^- . \text{ It is therefore quite possible that cation effects are not negligible, and that K varies with both the cation and the temperature. The assumption of ideal mixing of the anionic species may also be of limited application.}

Now that thermodynamic functions are available it would be very interesting to have Raman spectra for the whole range of composition of LiF - AIF_4 mixtures at 1073 K. A direct comparison between activities and concentrations of various species would then be possible.

References

(1) Dewing, E.W. Met. Trans., 1, 2211-15 (1970).

(2) Yoshida, K., and Dewing, E.W. Met. Trans., 3, 682-86 (1972).

(3) Dewing, E.W. Met. Trans. 3, 2699-2702 (1972).

(4) Romberger, K.A., and Braunstein, J. Inorg. Chem., 9, 1273-75 (1970).

(5) Jensen, B. Phase and structure relations for some alkali aluminium fluorides. Norges tekniske høgskole, Trondheim, October 1969.

(6) Rolin, M., and Muhlethalter, R. Bull. Soc. Chim. Fr., 2593-99 (1964).

(7) Rolin, M., Latreille, H., and Pham, H. Bull. Soc. Chim. Fr., 2271-76 (1969).

(8) Matiasovsky, K., and Malinovsky, M. Collection Czech. Chem. Comm., 36, 3746-51 (1971).

(9) JANAF Thermochemical Tables, 2nd edn. U.S. National Standard Reference Data System, NSRDS-NBS 37, Washington, DC, 1971.

(10) Wagner, C. Advan. Electrochem. Electrochem. Eng., 4, 1-45 (1966).

(11) Behl, K.B., and Egan, J.J. J. Phys. Chem., 71, 1764-69 (1967).

(12) Kachanovskaya, I.S. Tr. Vses, Nauch.-Issled. Proekt. Inst. Alyum., Magn. Elek. Prom. 1970, 69-74.

(13) Holm, B.J., and Grønvold, F. Acta Chem. Scand., 27, 2043-50 (1973).
(14) Rolin, M. Private communication.

(15) Ratkje, S.K., and Rytter, E. J. Phys. Chem., 78, 1499-1502 (1974).

(16) Gilbert, B., Mamantov, G., and Begun, G.M. J. Chem. Phys., 62, 950-55 (1975).
THERMODYNAMIC FUNCTIONS FOR LiF - AlF₃ MIXTURES AT 1073 K
(Transport Number for Li⁺ = 0.957)

| n₃AlF₃ | ΔG₃AlF₃ (cal) | ΔG₃LiF (cal) | ΔG (cal) | a₃AlF₃ | a₃LiF |
|--------|---------------|--------------|----------|--------|-------|
| .425   | 0             | -5077        | -2919    | 1.000  | .092  |
| .420   | -129          | -4983        | -2944    | .941   | .097  |
| .400   | -661          | -4613        | -3032    | .733   | .115  |
| .380   | -1224         | -4253        | -3102    | .563   | .136  |
| .360   | -1818         | -3904        | -3153    | .426   | .160  |
| .340   | -2445         | -3567        | -3185    | .318   | .188  |
| .320   | -3106         | -3241        | -3198    | .233   | .219  |
| .300   | -3803         | -2928        | -3191    | .168   | .253  |
| .280   | -4673         | -2573        | -3161    | .112   | .299  |
| .260   | -5581         | -2237        | -3106    | .0730  | .350  |
| .250   | -6052         | -2076        | -3070    | .0585  | .378  |
| .240   | -6502         | -1930        | -3027    | .0474  | .405  |
| .220   | -7419         | -1656        | -2924    | .0308  | .460  |
| .200   | -8386         | -1399        | -2796    | .0196  | .519  |
| .180   | -9404         | -1161        | -2644    | .0122  | .580  |
| .160   | -10476        | -941         | -2467    | .00735 | .643  |
| .140   | -11607        | -741         | -2263    | .00433 | .706  |
| .120   | -12799        | -563         | -2032    | .00247 | .768  |
| .100   | -14057        | -408         | -1773    | .00137 | .826  |
| .081   | -15316        | -283         | -1501    | .00076 | .876  |
1. Liquidus curve for Li$_3$AlF$_6$.

2. Free energy
   of 3LiF(s) + AlF$_3$(s) = Li$_3$AlF$_6$(s)

3. Apparatus.
4. Emf at 1073 K of the cell

\[
\text{Al} | \text{LiF} | \text{LiF} \text{ (sat)} | \text{AlF}_3 | \text{AlF}_3 | \text{Al}
\]

5. Part of emf - coulombs sequence.
5. Part of emf - coulombs sequence

7. Plot of $a_{LiF}$ vs $(x_{Li_3AlF_6}/x_{LiAlF_4})^{1/2}$

8. Calculated emf - composition curve