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Dissociation Equilibrium and the Activities of Sodium Fluoride and Aluminum(III) Fluoride in Molten Cryolite

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Received November 27, 1972

A method for calculating the stabilities of complex ions in binary molten salt mixtures, based on accurate enthalpy of mixing data, has been developed. As an example two different dissociation models for molten cryolite, (I) $Na_3AlF_6(l) = 3NaF(l) + AlF_3(l)$ and (II) $Na_3AlF_6(l) = 2NaF(l) + NaAlF_4(l)$, have been tested. Good agreement between experimental and calculated data is obtained for model I by use of an enthalpy of dissociation, $\Delta H^{\mathrm{diss}} = 22{,}000$ cal, and a degree of dissociation, $\alpha = 0.31$. This model is also in accordance with calorimetrically measured enthalpies of mixing for the process $^1/_3 NaAlF_6(l) + {}^2/_3 AlF_3(l) = NaAlF_4(l)$.

Introduction

The fairly large negative enthalpies of mixing, which were observed in the system NaF-Na_3AlF_6 by the present author,[1] could at first seem surprising because one would expect rather small enthalpies of mixing in anion mixtures with a common cation.

Kleppa and Melnichack[2] have shown that the enthalpies of mixing in such systems usually are of the order of 0–100 cal. In the following the observed ΔH^{M} will therefore be related to the dissociation of Na_3AlF_6 in the molten state.

Grjotheim[3] made an approach to this problem 15 years ago. He discussed the most probable dissociation schemes for cryolite and also gave equations for the different dissociation models. Of the four models

$$2AlF_6^{3-} = Al_2F_{11}^{5-} + F^-$$

$$AlF_6^{3-} = AlF_5^{2-} + F^-$$

$$AlF_6^{3-} = AlF_4^- + 2F^-$$

$$AlF_6^{3-} = Al^{3+} + 6F^-$$

he concluded that the dissociation scheme $AlF_6^{3-} = AlF_4^- + 2F^-$ would be the most probable model for molten cryolite.

Different approaches to this problem by Foster and Frank[4] (density), Frank and Foster[5] (electrical conductivity), and Rolin[6] (thermodynamic calculations) have given further evidence for the credibility of this dissociation scheme. However, it should be pointed out that *all* approaches to the problem of dissociation of the cryolite anion until now have been based on assumptions, like ideality of the molten mixture.

Method of Calculation

In Figure 1 is shown enthalpy of mixing curves for a system consisting of two molten salts AX and BX_m with an intermediate compound A_nBX_{m+n}. Curve I corresponds to the curve one would obtain if the compound A_nBX_{m+n} was formed without dissociation of the complex $(BX_{m+n})^{n-}$. In this case the enthalpy of mixing is equal to the enthalpy of formation of the complex

$$nAX(l) + BX_m(l) = A_nBX_{m+n}(l)$$

with

$$\Delta H_r = \Delta H^{\mathrm{M}} \qquad (1)$$

If, however, the complex is not a very strong one, one would obtain a curve like the one shown as curve II. Enthalpy of mixing curves of this type were for instance found by Kleppa and McCarty[7] in the three systems KCl-$MgCl_2$, $RbCl$-$MgCl_2$, and $CsCl$-$MgCl_2$. The complex A_nBX_{m+n} may, for instance, dissociate in the molten state as given by equilibrium I or equilibrium II

$$\begin{array}{llll} BX_{m+n}{}^{n-} = & BX_{m+1}{}^{-} + & (n-1)X^- & \\ 1-\alpha_0 & \alpha_0 & (n-1)\alpha_0 & \qquad (I) \end{array}$$

$$\begin{array}{llll} BX_{m+n}{}^{n-} = & BX_m + & nX^- & \\ 1-\alpha_0 & \alpha_0 & n\alpha_0 & \qquad (II) \end{array}$$

where α_0 is the degree of dissociation. The corresponding equilibrium constants K_{I} and K_{II} are

$$K_{\mathrm{I}} = C_{\mathrm{I}} \cdot \frac{\alpha_0}{1-\alpha_0}\left[\frac{(n-1)\alpha_0}{1+(n-1)\alpha_0}\right]^{n-1} \qquad (2)$$

$$K_{\mathrm{II}} = C_{\mathrm{II}} \cdot \frac{\alpha_0}{1-\alpha_0}\left[\frac{n\alpha_0}{1+n\alpha_0}\right]^{n} \qquad (3)$$

Here the factors C_{I} and C_{II} contain the product of the activity coefficients.

In a mixture of the complex A_nBX_{m+n} with either AX or BX_m the dissociation equilibrium I or II will be shifted to the left, and usually the complex will be *less* dissociated in the mixture. The degree of dissociation will change with composition. The enthalpy of mixing as a function of composition, $\Delta H^{\mathrm{M}}{}_{\mathrm{C}}$, is then given by eq 4. Here ΔH^{diss}

$$\Delta H^{\mathrm{M}}{}_{\mathrm{C}} = \Delta H^{\mathrm{diss}} N_0(\alpha_0 - \alpha) \qquad (4)$$

is the enthalpy of dissociation of the pure complex, N_0 is the weighed-in mole fraction of the complex, and α_0 and α are the degrees of dissociation in the pure complex and in the mixture, respectively.

In Figure 1 the dashed curve represents the enthalpy of mixing one would have gotten in the hypothetical case when the degree of dissociation is independent of composition. Curve II represents the curve one obtains if α is smaller than α_0. The difference between the dashed line and curve II therefore represents the enthalpy one will obtain if the pure complex is mixed with one of the components.

Dissociation Models for Molten Cryolite

In the following some of the dissociation models given above will be discussed and tested in connection with the

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[1] J. L. Holm, Ph.D. Thesis, Institute of Inorganic Chemistry, The Technical University of Norway, Nov 1971.

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[5] W. B. Frank and L. M. Foster, *J. Phys. Chem.*, **64**, 310 (1960).

[6] M. Rolin, *Bull. Soc. Chim. Fr.*, 681 (1960).

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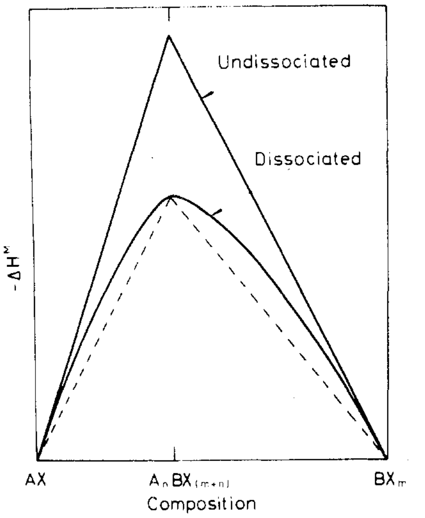

Figure 1. Enthalpy of mixing curves for a system $AX-BX_m$ with an intermediate compound $A_nBX_{(n+m)}$.

measured enthalpies of reactions in the system $NaF-Na_3AlF_6$. Here the discussion will be limited to the two most probable models[1] which are

$$Na_3AlF_6(l) \rightleftarrows 3NaF(l) + AlF_3(l) \qquad (I)$$

$$Na_3AlF_6(l) \rightleftarrows 2NaF(l) + NaAlF_4(l) \qquad (II)$$

In putting up these equations it should be pointed out that according to calculations by the present author[1,8,9] $NaAlF_4$ should be unstable with respect to Na_3AlF_6 and AlF_3, since the enthalpy of the reaction

$$Na_3AlF_6(l) + 2AlF_3(l) = 3NaAlF_4(l) \qquad (III)$$

is of the order 12 ± 4 kcal mol^{-1} at 1273 K. This can very easily be seen from enthalpy cycle 1. The cycle gives eq 5.

cycle 1

$$\begin{tikzcd}
Na_3AlF_6(s) \arrow[d, "\Delta H_f(Na_3AlF_6)"] & + & 2AlF_3(s) \arrow[d, "2\Delta H_f(AlF_3)"] \arrow[dr, "\Delta H_f(\text{mixture})"] & \\
Na_3AlF_6(l) & + & 2AlF_3(l) \arrow[r, "\Delta H_1"] & 3\text{“}NaAlF_4\text{”}(l)
\end{tikzcd}$$

$$\Delta H_1 = \Delta H_f(\text{mixture}) - \Delta H_f(Na_3AlF_6) - 2\Delta H_f(AlF_3) \qquad (5)$$

By inserting the experimental values $\Delta H_f(\text{mixture}) = 61.5$ kcal,[9] $\Delta H_f(Na_3AlF_6) = 27.1$ kcal mol^{-1},[10,11] and $\Delta H_f(AlF_3) = 11.3$ kcal mol^{-1},[9] one obtains for reaction III $\Delta H_1 = +12.0$ kcal.

For schemes I and II the dissociation constants are

$$K_I = C_I \cdot \frac{\alpha_0}{1 - \alpha_0} \cdot \left(\frac{3\alpha_0}{1 + 3\alpha_0}\right)^3 \qquad (6)$$

$$K_{II} = C_{II} \cdot \frac{\alpha_0}{1 - \alpha_0} \cdot \left(\frac{2\alpha_0}{1 + 2\alpha_0}\right)^2 \qquad (7)$$

In a mixture of cryolite and sodium fluoride, where the mole fractions are $N_0(Na_3AlF_6)$ and $N_1(NaF)$, the degree of dissociation is α_1.

For this mixture the dissociation constants for the two schemes are given by

$$K^\circ{}_I = \frac{\alpha_1}{1 - \alpha_1} \cdot \left(\frac{3N_0\alpha_1 + N_1}{1 + 3\alpha_1 N_0}\right)^3 \qquad (8)$$

$$K^\circ{}_{II} = \frac{1}{1 - \alpha_1} \cdot \left(\frac{2N_0\alpha_1 + N_1}{1 + 2N_0\alpha_1}\right)^2 \qquad (9)$$

The theoretical enthalpy of mixing, $\Delta H^M{}_C$, can be calculated from the following expression

$$\Delta H^M{}_C = -\Delta H^{diss} N_0(\alpha_0 - \alpha_1) \qquad (10)$$

where ΔH^{diss} is the enthalpy for the dissociation of Na_3AlF_6, according to scheme I or II.

In writing the expression for the equilibrium constants, eq 8 and 9, the mole fractions have been used instead of the activities. The correct equilibrium constants are given by eq 11 and 12.

$$K_I = K^\circ{}_I \cdot \frac{\gamma_{NaF}{}^3 \cdot \gamma_{AlF_3}}{\gamma_{Na_3AlF_6}} \qquad (11)$$

$$K_{II} = K^\circ{}_{II} \cdot \frac{\gamma_{NaF}{}^2 \cdot \gamma_{NaAlF_4}}{\gamma_{Na_3AlF_6}} \qquad (12)$$

It has been assumed that the change with composition in the term containing the product of the activity coefficients is negligible. As shown in the Appendix, this is indeed the case. For model I the true equilibrium constant is given by

$$K_I{}^a = K_I \cdot 10^{-3.75 \pm 0.1} \qquad (13)$$

For the calculation of $\Delta H^M{}_C$ a computer program was made. The calculations were performed in the following manner. A set of values was chosen for ΔH^{diss}. For each of these values of ΔH^{diss} the following operation was performed for each of a set of values of α_0. The equation 6 = 8 or 7 = 9 was solved with respect to α_1 for values of N_0 from 0 to 1. This value of α_1 was then used to calculate $\Delta H^M{}_C$ as a function of ΔH^{diss}, α_1, N_0, and α_0. From the results could be found the combination of values for α_0 and ΔH^{diss} which gave the best fit between the experimental enthalpies of mixing and the calculated curve.

For scheme I, $AlF_6{}^{3-} = AlF_3 + 3F^-$, the best fit is found for $\alpha_0 = 0.31 \pm 0.01$ and $\Delta H^{diss} = 22{,}000 \pm 1000$ cal (Table I). As can be seen from Figure 2 the agreement between the calculated and experimental results is good. The value for ΔH^{diss} is in excellent agreement with that calculated from a thermodynamic cycle by the present author[1] (cycle 2).

cycle 2

$$\begin{tikzcd}
Na_3AlF_6(s) \arrow[r, "\Delta H_2"] \arrow[d, "\Delta H_f(Na_3AlF_6)"] & 3NaF(s) \arrow[d, "3\Delta H_f(NaF)"] & + & AlF_3(s) \arrow[d, "\Delta H_f(AlF_3)"] \\
Na_3AlF_6(l) \arrow[r, "\Delta H_2{}^M"] & 3NaF(l) & & AlF_3(l)
\end{tikzcd}$$

$$\Delta H_2{}^M = \Delta H_2 + 3\Delta H_f(NaF) + \Delta H_f(AlF_3) - \Delta H_f(Na_3AlF_6) \qquad (14)$$

By inserting $\Delta H_2 = 13.8$ kcal mol^{-1},[12] $\Delta H_f(Na_3AlF_6) = 27.1$ kcal mol^{-1},[1,10,11] $\Delta H_f(NaF) = 8.0$ kcal mol^{-1},[10,11] and $\Delta H_f(AlF_3) = 11.3$ kcal mol^{-1},[9] one obtains $\Delta H_2{}^M = 22.0$ kcal. For scheme II, $AlF_6{}^{3-} = AlF_4{}^- + 2F^-$, ΔH^{diss} has been set equal to 18,000 cal, which is the difference between the enthalpies calculated from cycle 1 and cycle 2. The best fit is obtained for $\alpha_0 = 0.35$. As can be seen from Figure 2, however, the $\Delta H^M{}_C$ values calculated for this scheme are less negative than the experimental enthalpies of mixing. Hence, this model does not explain the rather large negative enthalpies of mixing which are observed in the system.

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Table I. Dissociation Degrees and Calculated Enthalpies of Mixing, in cal mol^{-1}, on the NaF Side

		Composition, mol fraction of Na_3AlF_6									
Scheme		0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.00
I	α	0.064	0.086	0.115	0.149	0.183	0.216	0.245	0.270	0.291	0.310
	ΔH^M, cal	−540	−984	−1286	−1421	−1397	−1247	−1008	−709	−368	0
II	α	0.101	0.122	0.148	0.178	0.210	0.242	0.273	0.301	0.327	0.350
	ΔH^M, cal	−448	−820	−1090	−1240	−1263	−1168	−974	−702	−373	0

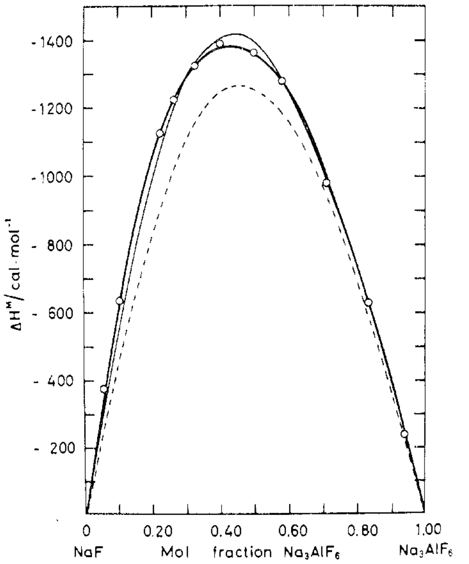

Figure 2. Experimental and calculated ΔH^M curves for molten mixtures of Na_3AlF_6 and NaF: ○, experimental values; heavy line, least-squares ΔH^M curve; thin line, best calculated ΔH^M curve for dissociation scheme $AlF_6^{3-} = AlF_3 + 3F^-$, $\alpha_0 = 0.31$ and $\Delta H^{diss} =$ 22,000 cal; dotted line, best calculated ΔH^M curve for dissociation scheme $AlF_6^{3-} = AlF_4^- + 2F^-$, $\alpha_0 = 0.35$ and $\Delta H^{diss} = 18000$ cal.

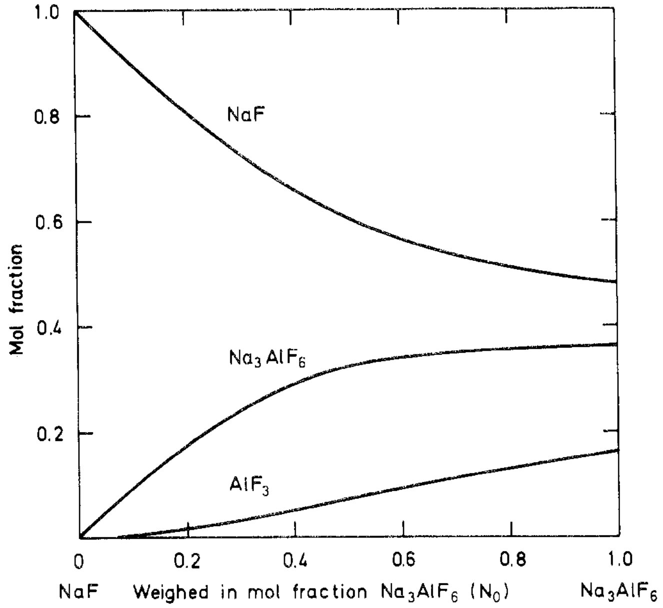

Figure 3. Mole fractions of NaF, Na_3AlF_6, and AlF_3 in molten mixtures of NaF and Na_3AlF_6 according to scheme I, $AlF_6^{3-} =$ $AlF_3 + 3F^-$, $\alpha_0 = 0.31$, $\Delta H^{diss} = 22000$ cal.

The calculated mole fractions of NaF, Na_3AlF_6, and AlF_3 in NaF-Na_3AlF_6 melts at 1011°, for $\alpha_0 = 0.31$ and $\Delta H^{diss} =$ 22,000 cal (scheme I), are plotted in Figure 3 as a function of composition. Hence, of the two most probable dissociation schemes for molten cryolite

$$Na_3AlF_6(l) = 3NaF(l) + AlF_3(l) \qquad (I)$$

$$Na_3AlF_6(l) = 2NaF(l) + NaAlF_4(l) \qquad (II)$$

scheme II seems to be of minor importance on the NaF side of the system. The main species present in basic (NaF rich) melts will be Na^+, AlF_6^{3-}, F^-, *and* "AlF_3." (In this dissociation scheme "AlF_3" is not supposed to be a separate species, but rather the inner and most stable part of the distorted AlF_6^{3-} complex.)

The dissociation equilibrium $AlF_6^{3-} = AlF_3 + 3F^-$ with a calculated dissociation constant of 10^{-5} at 1011° (see Appendix) is written *thermodynamically.* This preferred dissociation indicates that the Al-F vibrations in the AlF_6^{3-} complex follow a model of type I

$$\underset{\text{octahedral}}{(AlF_6^{3-})} \rightleftarrows \underset{\text{distorted octahedral}}{[(AlF_3)(F^-)_3]}$$

rather than type II.

$$\underset{\text{octahedral}}{(AlF_6^{3-})} \rightleftarrows \underset{\text{tetrahedral}}{[(AlF_4)^- + 2F^-]}$$

Spectroscopically one would therefore expect to observe AlF_6^{3-} in a distorted octahedral field as illustrated above. The more or less free AlF_3 which is formed could be compared to BF_3, a planar molecule with an incomplete octet around the boron atom. As there is not a full octet, there will be fewer repulsions between the electrons, and the length of the Al-F bond will be somewhat shortened. Consequently, in the deformed or distorted AlF_6^{3-} complex there should be three shorter and three longer Al-F bonds, as illustrated in Figure 4.

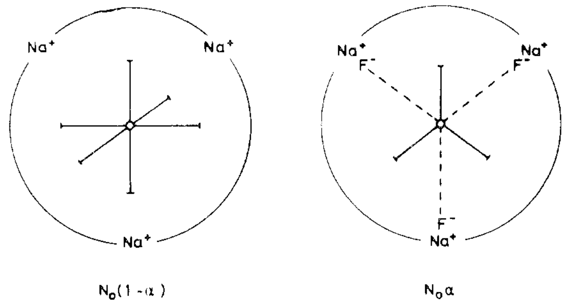

Figure 4. Dissociation model for molten cryolite, $AlF_6^{3-} =$ "AlF_3" + $3F^-$.

Registry No. NaF, 7681-49-4; AlF_3, 7784-18-1; Na_3AlF_6, 13775-53-6; cryolite, 15096-52-3.

Acknowledgment. Thanks are due to Norges Teknisk-Naturvitenskapelige Forskningsrad for financial support. Dr. Birgit Jenssen Holm is acknowledged for her assistance with computer programs and calculations.

Appendix

a. Activity Coefficients γ_{NaF}, γ_{AlF_3}, and $\gamma_{Na_3AlF_6}$ in Liquid Ternary NaF-AlF_3-Na_3AlF_6 Mixtures. The partial excess Gibbs free energy for component A in a ternary mixture A-B-C can be calculated from the expression

$$\overline{G}^E{}_A = R'T \log \gamma_A = (1 - X_A)(X_B\lambda_{AB} + X_C\lambda_{AC}) - X_BX_C\lambda_{BC} \qquad (15)$$

Table II. Activity Coefficients of NaF, AlF_3, and Na_3AlF_6 in Molten Mixtures of Sodium Fluoride and Cryolite

Weighed-in mol fraction of Na_3AlF_6, N_0	Log γ_{NaF}	Log γ_{AlF_3}	Log $\gamma_{Na_3AlF_6}$	$\frac{\gamma_{NaF}^3 \cdot \gamma_{AlF_3}}{\gamma_{Na_3AlF_6}}$
0.2	$(-0.01)^a$	$(-4.0)^a$	$(+0.07)^a$	$(10^{-4.1})$
0.4	−0.090	−3.18	+0.167	$10^{-3.7}$
0.6	−0.215	−2.72	+0.284	$10^{-3.7}$
0.3	−0.337	−2.35	+0.351	$10^{-3.8}$
1.0	−0.436	−2.12	+0.407	$10^{-3.8}$

[a] Uncertain value.

(see, for instance, ref 13 and 14). Here X_A, X_B, and X_C are the ternary mole fractions of the components in the system, while the λ's are the interaction parameters in the component binaries. Equation 15 has been used to calculate the activity coefficients γ_{NaF}, γ_{AlF_3}, and $\gamma_{Na_3AlF_6}$ in the ternary mixture at different compositions.

The binary interaction parameters λ_{AC} and λ_{BC} [A = NaF, B = AlF_3, C = Na_3AlF_6 (undissociated)] have been assumed to be small compared to λ_{AB} (*i.e.*, $\lambda_{AC} = \lambda_{BC} = 0$). The interaction parameter in the NaF-rich part of the system NaF-AlF_3 has been calculated from enthalpy data obtained by the present author[9] and follows the expression

$$\lambda_{NaF-AlF_3} = -28{,}410 - 42{,}130X_{AlF_3} + 176{,}280X_{AlF_3}{}^2 \text{ cal} \qquad (16)$$

The mole fractions used in the calculations have been taken from Figure 3. The calculated activity coefficients are given in Table II. Using these values, one can now calculate the activities of sodium fluoride and aluminum fluoride in pure molten cryolite.

$$a_{NaF} = N_{NaF} \cdot \gamma_{NaF} = 0.48 \times 10^{-0.436} = 0.176 \qquad (17)$$

$$a_{AlF_3} = N_{AlF_3} \cdot \gamma_{AlF_3} = 0.16 \times 10^{-2.12} = 1.2 \times 10^{-3} \qquad (18)$$

The activity coefficients can be checked by calculating the activity of Na_3AlF_6 in a pure cryolite melt, which should be 1.0. From the data given in this paper one obtains

$$a_{Na_3AlF_6} = 0.36 \times 10^{0.407} = 0.92 \qquad (19)$$

This shows that the activity coefficients given are somewhat uncertain. These uncertainties in the activities are mainly due to the interaction parameter which has been used (eq 15). This interaction parameter is based on enthalpy data and not, as it more correctly ought to be, on Gibbs free energy data. Even so, these data are probably the best activity values for the cryolite melt reported until now, as the errors are certainly less than 10%.

Kvande[15] has reported a vapor pressure of AlF_3 above a cryolite melt, $p_{AlF_3} = 0.012$ Torr, while the total pressure of AlF_3 above solid AlF_3 at the same temperature, according to Kuxmann and Tillessen,[16] is $p = 10.5$ Torr. This gives an activity of AlF_3 in molten cryolite of the order of 10^{-3}, in good accordance with the value 1.2×10^{-3} given above.

One may therefore with good accuracy use an equilibrium constant of

$$K_{eq} = \frac{a^3{}_{NaF} \cdot a_{AlF_3}}{a_{Na_3AlF_6}} = [(0.176)^3]1.2 \times 10^{-3} \simeq 10^{-5} \qquad (20)$$

for the dissociation equilibrium of molten cryolite $Na_3AlF_6(l) \rightleftarrows 3NaF(l) + AlF_3(l)$.

b. An Equation for Calculating Liquidus Curves on the Cryolite Side of Phase Diagrams. In calculations of phase diagrams where cryolite is the main component, it is necessary to have a correct expression for the mole fraction of cryolite in the mixture. This mole fraction can be expressed as

$$N_{Na_3AlF_6} = k \cdot N_{Na^+}{}^3 \cdot N_{AlF_6{}^{3-}} \qquad (21)$$

In pure molten cryolite $N_{Na_3AlF_6} = 1$, $N_{Na^+} = 1$, and $N_{AlF_6{}^{3-}} = (1 - \alpha_0)/(1 + 3\alpha_0)$. By use of the dissociation degree for the scheme $AlF_6{}^{3-} = AlF_3 + 3F^-$, $\alpha_0 = 0.31$ at 1011°, one finds $k = 2.80$ and therefore

$$N_{Na_3AlF_6} = 2.80N_{Na^+}{}^3 \cdot N_{AlF_6{}^{3-}} \qquad (22)$$

The partial Gibbs free energy of cryolite is given by the well-known expression

$$\overline{G}_{Na_3AlF_6} = -\Delta H_f(1 - T/T_f) = \overline{H}_{Na_3AlF_6} - T\overline{S}_{Na_3AlF_6} \qquad (23)$$

The liquidus curve in systems without solid solution can be calculated from

$$T = \frac{\Delta H_f + \overline{H}_{Na_3AlF_6}}{\Delta S_f + \overline{S}_{Na_3AlF_6}} \qquad (24)$$

Here $\overline{H}_{Na_3AlF_6}$ is the partial enthalpy of mixing and ΔS_f is the entropy of fusion of cryolite. In this expression the partial entropy of mixing, $\overline{S}_{Na_3AlF_6}$, has also been introduced. In calculations the partial molar entropy, $\overline{S}$, is usually set equal to the configurational entropy, which in this case is

$$\overline{S}_{Na_3AlF_6} = -R \ln N_{Na_3AlF_6} \qquad (25)$$

By combining eq 22, 24, and 25 one obtains the following expression

$$T = \frac{\Delta H_f + \overline{H}_{Na_3AlF_6}}{\Delta S_f - R \ln (2.80 \cdot N_{Na^+}{}^3 \cdot N_{AlF_6{}^{3-}})} \qquad (26)$$

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