

DISSOCIATION EQUILIBRIA OF CRYOLITE IN NaF-AlF₃

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The scheme of dissociation of cryolite in NaF-AlF₃ melts was proposed. The constants and heats of dissociation for cryolite were evaluated from experimental data. The mole fractions of each kind of ions at 1298K in NaF-AlF₃ melts were calculated based upon this scheme. The thermodynamic mixing function for liquid NaF and solid AlF₃, and liquidus data of NaF-AlF₃ systems were calculated by using the above evaluated parameters. The results obtained are in good agreement with the experimental data.

KEY WORDS cryolite, thermodynamic function, NaF-AlF₃ melt

1. Introduction

The mixtures of aluminum fluoride with sodium fluoride are very important systems from the theoretical and practical point of view since the NaF-AlF₃ melts are used in aluminum smelting. Because of their industrial interest, the ionic structure of molten cryolite has been discussed extensively for more than seventy years. However, the scheme and the extent of the dissociation of liquid Na₃AlF₆ are still subject to controversy.

A rapid survey shows that in spite of the several experimental techniques used, two schools appear depending on the structural interpretation of the dissociation scheme of cryolite ion. On the one hand, Holm^[1,2] has suggested the presence of the molecular AlF₃ species in the cryolite melts. This dissociation scheme has been confirmed by numerous authors^[3,4]. On the other hand, Piontelli^[5] has proposed the second scheme of dissociation, i.e. the presence of AlF₄⁻ ion in the melts. This hypothesis also has been confirmed by cryoscopic measurements^[6] and density data^[7], and later confirmed by Raman spectroscopy measurements^[8]. Dewing^[9] presented a different dissociation scheme suggesting the presence of AlF₄⁻, AlF₅²⁻ and AlF₆³⁻ in the NaF-AlF₃ melts. This scheme was confirmed by the thermodynamic calculation of Feng^[10] and the spectroscopic study by Gilbert and coworkers^[11]. Mass spectroscopic and vapor pressure measurement have established the presence of Na₂AlF₅, NaAlF₄ and AlF₃ in the vapor phase above the NaF-AlF₃ melts, and these species would be existed in principle in the melts which are equilibrated with the vapor phase.

In this paper, a model of cryolite dissociation has been proposed, and the thermodynamic properties of NaF-AlF₃ systems are calculated in relation to the scheme of dissociation.

2. Basic Consideration

The Na₃AlF₆ in the NaF-AlF₃ melts is completely ionized to Na⁺ and AlF₆³⁻, and the complex ion is partly dissociated in steps, and dissociation reactions of the complex are as

following



In this dissociation scheme, “AlF₃” is supposed to be the inner and most stable part of the distorted AlF₆³⁻ complex and may be not dissociated. This hypothesis was examined by the study of Laurent Joubert^[12]. The equilibrium constants (expressed in mole fraction units) and heats of dissociation reactions written as Eq.(1), Eq.(2) and Eq.(3) are *K*₁ and *H*₁, *K*₂ and *H*₂, and *K*₃ and *H*₃, respectively. The sublattice solution model has been used to express the NaF-AlF₃ melts, and the melts would be expressed by a formula (Na)_{*p*}(F⁻, AlF₃, AlF₄⁻, AlF₅²⁻, AlF₆³⁻)_{*q*}, where *p* and *q* indicate the number of sites on each sublattice. The values of *p* and *q* are obtained that *q* = 1 and *p* = *y*_{F⁻} + *y*_{AlF₄⁻} + 2*y*_{AlF₅²⁻} + 3*y*_{AlF₆³⁻}, where *y* is the site fraction, *i.e.*, the mole fraction of the ions which is indicated by the subscript within the sublattice, and

$$y_{\text{F}^-} + y_{\text{AlF}_3} + y_{\text{AlF}_4^-} + y_{\text{AlF}_5^{2-}} + y_{\text{AlF}_6^{3-}} = 1 \tag{4}$$

The mole fraction of Na⁺ is equal to unity since it is only one kind of ions in its sublattice. It is assumed that the mixing of ions in each sublattice is ideal. The equilibrium constants for Eqs.(1)–(3) can be written as

$$K_1 = \frac{y_{\text{F}^-} y_{\text{AlF}_5^{2-}}}{y_{\text{AlF}_6^{3-}}} \tag{5}$$

$$K_2 = \frac{y_{\text{F}^-} y_{\text{AlF}_4^-}}{y_{\text{AlF}_5^{2-}}} \tag{6}$$

$$K_3 = \frac{y_{\text{F}^-} y_{\text{AlF}_3}}{y_{\text{AlF}_4^-}} \tag{7}$$

For the binary system of NaF-AlF₃, the mole fractions of NaF and AlF₃ are expressed as *N*_{NaF} and *N*_{AlF₃}, respectively. The following equation can be obtained.

$$\frac{y_{\text{F}^-} + y_{\text{AlF}_4^-} + 2y_{\text{AlF}_5^{2-}} + 3y_{\text{AlF}_6^{3-}}}{y_{\text{AlF}_3} + y_{\text{AlF}_4^-} + y_{\text{AlF}_5^{2-}} + y_{\text{AlF}_6^{3-}}} = \frac{N_{\text{NaF}}}{N_{\text{AlF}_3}} = C_r \tag{8}$$

where *C_r* is commonly called the cryolite ratio in the study of aluminum electrolysis. Combining Eqs.(4)–(8), we obtain the Eq.(9)

$$C_r + y_{\text{F}^-} \frac{(C_r - 1) - (C_r + 1)K_3}{K_3} + y_{\text{F}^-}^2 \frac{(C_r - 2) - C_r K_2}{K_3 K_2} + y_{\text{F}^-}^3 \frac{(C_r - 3) - (C_r - 1)K_1}{K_3 K_2 K_1} - y_{\text{F}^-}^4 \frac{C_r - 2}{K_3 K_2 K_1} = 0 \tag{9}$$

The value of *y*_{F⁻} can be found by successive iteration for the given parameters of *K*₁, *K*₂ and *K*₃. Then, the values of *y*_{AlF₃}, *y*_{AlF₄⁻}, *y*_{AlF₅²⁻} and *y*_{AlF₆³⁻} can be calculated.

When the equilibrium constants K_1 , K_2 and K_3 at temperature T are known or can be estimated, the constants K'_1 , K'_2 and K'_3 at a different temperature T' may be calculated from Eq.(10)

$$\ln \frac{K'_i}{K_i} = \frac{H_i}{R} \left(\frac{1}{T} - \frac{1}{T'} \right) \quad (i = 1, 2, 3) \quad (10)$$

where it is assumed that the heats of the dissociation, H_i , expressed in Eqs.(1)–(3) are independent of temperature, and R is the universal gas constant.

From the ideal assumption, the activity of NaF can be written as Eq.(11) if pure liquid NaF is selected as the reference state of activities for NaF.

$$a_{\text{NaF}} = y_{\text{Na}^+} y_{\text{F}^-} = y_{\text{F}^-} \quad (11)$$

If the pure solid AlF_3 is taken as the reference state of activities for AlF_3 , the activity of AlF_3 in the NaF- AlF_3 melt saturated with solid AlF_3 is a unit. If the mole fraction of AlF_3 in the NaF- AlF_3 melt saturated with solid AlF_3 is written as $y_{\text{AlF}_3}^s$, the activities of AlF_3 in the NaF- AlF_3 melts with the varying concentration of AlF_3 can be expressed as Eq.(12).

$$a_{\text{AlF}_3} = \frac{y_{\text{AlF}_3}}{y_{\text{AlF}_3}^s} \quad (12)$$

The enthalpy of the mixing of liquid NaF and solid AlF_3 at 1298K may be expressed as Eq.(13)

$$\Delta H = N_{\text{AlF}_3} \Delta H_{m, \text{AlF}_3}^\circ - \frac{N_{\text{AlF}_3} [H_3 y_{\text{AlF}_4^-} + (H_2 + H_3) y_{\text{AlF}_5^{2-}} + (H_3 + H_2 + H_1) y_{\text{AlF}_6^{3-}}]}{y_{\text{AlF}_3} + y_{\text{AlF}_4^-} + y_{\text{AlF}_5^{2-}} + y_{\text{AlF}_6^{3-}}} \quad (13)$$

where $\Delta H_{m, \text{AlF}_3}^\circ$ is the heat of fusion for solid AlF_3 at 1298K.

From phase diagram theory, the activity of Na_3AlF_6 can be expressed by Eq.(14).

$$\ln a_{\text{Na}_3\text{AlF}_6} = -\frac{\Delta H_{m, \text{hyp}}^\circ}{R} \left(\frac{1}{T} - \frac{1}{T^\circ} \right) - \frac{1}{RT} \int_{T^\circ}^T \Delta C_p dT + \frac{1}{R} \int_{T^\circ}^T \frac{\Delta C_p}{T} dT \quad (14)$$

where $\Delta H_{m, \text{hyp}}^\circ$ is the heat of fusion of pure, hypothetical, undissociated cryolite at the melting point T° , ΔC_p is the heat capacity difference between pure liquid and solid Na_3AlF_6 , and T is the absolute temperature of liquidus. Since the assumption of ideal mixing, the activity of Na_3AlF_6 can be replaced by the mole fraction of Na_3AlF_6 . $\Delta H_{m, \text{hyp}}^\circ$ can be expressed as Eq.(15)

$$\Delta H_{m, \text{hyp}}^\circ = \Delta H_m^\circ - \frac{[H_1 y_{\text{AlF}_5^{2-}} + (H_1 + H_2) y_{\text{AlF}_4^-} + (H_3 + H_2 + H_1) y_{\text{AlF}_3}]}{y_{\text{AlF}_3} + y_{\text{AlF}_4^-} + y_{\text{AlF}_5^{2-}} + y_{\text{AlF}_6^{3-}}} \quad (15)$$

where ΔH_m° is the heats of fusion of pure cryolite.

If $a_{\text{Na}_3\text{AlF}_6}$ is known at its real melting point T_r , T° can be calculated by Eq.(14).

The calculation procedure is as follows: A set of parameters of K_1 and H_1 , H_2 and K_2 , and K_3 and H_3 at 1298K for the reactions Eqs.(1)–(3) is evaluated from the experimental data. Then, the mole fraction of ion F^- in the NaF- AlF_3 melts can be calculated from Eq.(9). Substituting the values of the mole fraction of F^- to Eqs.(4)–(7), the mole

fractions of each kind of ions in the NaF-AlF₃ melts can be calculated out. Using Eq.(10), the constants of dissociation at a different temperature can be calculated, and the mole fractions of each kind of ions can be also calculated at the different temperature. When the mole fraction of Na₃AlF₆ is obtained at T_r temperature, that at the temperature T° is calculated by Eq.(14). The liquidus temperature and thermodynamic mixing function for NaF(l) and AlF₃(s) at 1298K can be calculated too. In order to obtain the optimization of the parameters, some experimental data of NaF-AlF₃ are considered including the enthalpies of mixing of NaF(l) and AlF₃(s)^[13], the enthalpies and temperature of fusion for Na₃AlF₆^[14], the phase diagrams of NaF-AlF₃^[6], and thermodynamic properties of pure NaF^[15,16].

3. Results and Discussion

All the above experimental data are used as input into the optimization program in order to find the parameters of K_1 and H_1 , K_2 and H_2 , and K_3 and H_3 , which are list in Table 1. The mole fractions of each kind of ions are calculated and the results are shown in Fig.1, in which the concentration of AlF₃ for NaF-AlF₃ melts is extended to saturating level. The mole fractions of the complex ions AlF₄⁻, AlF₅²⁻ and AlF₆³⁻ are increased with increasing concentration of AlF₃ in NaF-AlF₃ systems up to the stoichiometric compositions where correspond to the maximum fraction for the each kind of complex ions.

The hypothetical melting point, and heats of pure and undissociated Na₃AlF₆ are 1555K and 73.0kJ/mol, respectively. The melting point for pure and undissociated Na₃AlF₆ from this work is some higher than that of other researches^[6]. The reason may be that ΔC_p was implicitly assumed to be negligible when Eq.(14) was used to calculate the hypothetical melting point in this work. The calculated and measured liquidus temperatures for NaF-AlF₃ are shown in Fig.2. The better fit between calculated and measured enthalpies of mixing of NaF(l) and AlF₃(s) can be seen from Fig.3.

Table 1 Constants and heats of dissociation of complex ion AlF₆³⁻ in NaF-AlF₃ at 1298K

Dissociation reaction	Dissociation const.	Dissociation heat, kJ/mol
AlF ₆ ³⁻ → AlF ₅ ²⁻ + F ⁻	1.56×10^{-1}	37.8
AlF ₅ ²⁻ → AlF ₄ ⁻ + F ⁻	5.32×10^{-1}	48.1
AlF ₄ ⁻ → AlF ₃ + F ⁻	4.91×10^{-2}	107.1

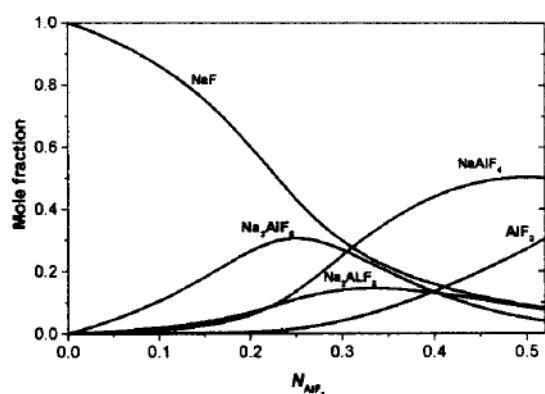


Fig.1 Distribution curves for the different species in NaF-AlF₃ melt vs. AlF₃ mole fraction at 1298K.

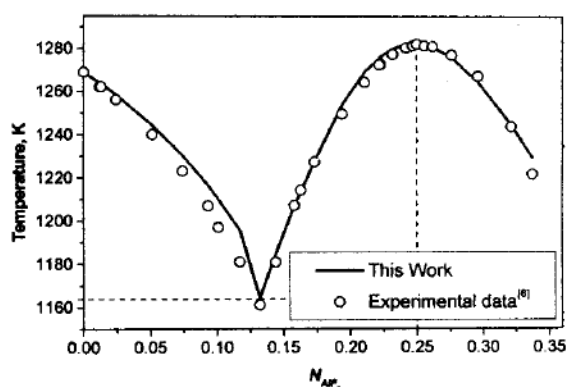


Fig.2 Calculated and experimental temperatures of primary crystallization of the system NaF-AlF₃.

The activities of NaF and AlF₃ are calculated by using the Eq.(11) and Eq.(12) and compared with the results of Dewing^[17], as shown in Fig.4. The difference of them is related with the different scheme of dissociation used and different constants of dissociation estimated here.

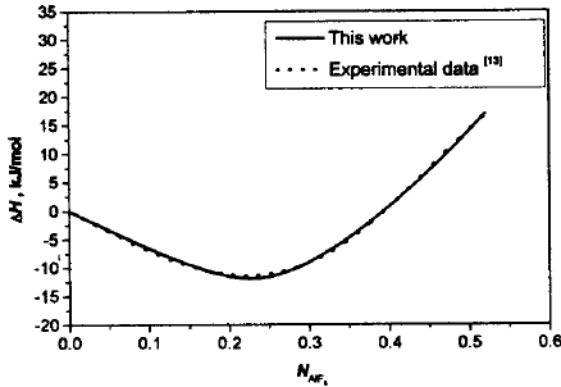


Fig.3 Calculated and experimental ΔH curves for the mixing enthalpies of the liquid NaF and solid AlF₃ at 1298K.

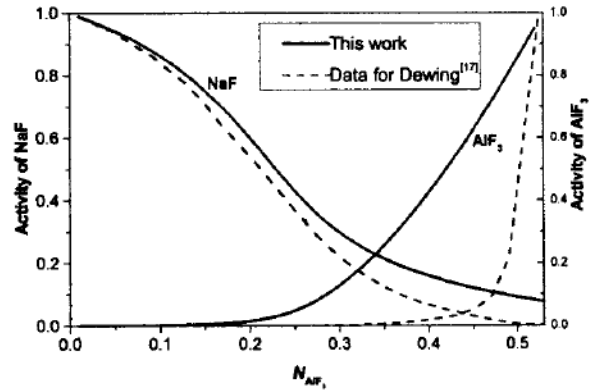


Fig.4 Activities of NaF and AlF₃ at 1298K.

In this work, $\Delta H_{m,AlF_3}^\circ$, the heat of fusion for solid AlF₃ at 1298K, is evaluated to be 108kJ/mol, which is in excellent agreement with 111.9 ± 3.4 kJ/mol, the result of Kleppa^[13]. It is found that the mole fraction of complex AlF₃ in the NaF-AlF₃ melts which are saturated with solid AlF₃ is near to 0.29 at 1298K, as shown in Fig.1. These results can be used to calculate $\Delta G_{m,AlF_3}^\circ$, the free energy of fusion of solid AlF₃ at 1298K, by Eq.(16).

$$\Delta G_{m,AlF_3}^\circ = RT \ln \frac{a_{AlF_3}}{y_{AlF_3}} \quad (16)$$

Since the activity of AlF₃ is equal to unity when the melts are saturated with solid AlF₃, the Eq.(16) can be written as

$$\Delta G_{m,AlF_3}^\circ = 8.314 \times 1298 \times \ln \frac{1}{0.29} = 13.3 \text{kJ/mol} \quad (17)$$

The difference between the heat capacity of liquid and solid AlF₃ is so small^[18] that it can be neglected, and T_{m,AlF_3} , the melting point of solid AlF₃, can be calculated by Eq.(18).

$$\Delta G_{m,AlF_3}^\circ = \Delta H_{m,AlF_3}^\circ \left(1 - \frac{1298}{T_{m,AlF_3}}\right) \quad (18)$$

T_{m,AlF_3} is about 1479K, which is higher than 1263K, the result of Phillips^[19]. However, some researchers^[20] thought the melting point of AlF₃ which is 1263K would seem too low.

4. Conclusion

This work gives the scheme of dissociation of cryolite. There are several kinds of complex ions in the NaF-AlF₃ melts since the complex ion AlF_6^{3-} is dissociated into AlF_5^{2-} , AlF_4^- and AlF₃ in steps. The constant and heat of dissociating reaction for each step are

estimated from experimental data. The mole fractions of each kind of ions in the melts and thermodynamic mixing function for NaF(l) and AlF₃(s), as well as the activities of NaF and AlF₃, are calculated based upon the scheme of dissociation. The liquidus temperature of NaF-AlF₃ is calculated and agreement with experimental data.

REFERENCES

- 1 J.L. Holm, *Inorg. Chem.* **12** (1973) 2062.
- 2 J.L. Holm, *High Temp. Sci.* **6** (1974) 12.
- 3 W.B. Frank, *J. Phys. Chem.*, **62** (1961) 2081.
- 4 M. Rolin, *J. Four. Electr. Ind. Electrochim.* **3** (1953) 83.
- 5 R. Piontelli, *Chim. Ind.* **22** (1940) 501.
- 6 K. Grjotheim, *Det. Kgl. Norske Videnskabens Selskabs Skrifter* (Trondheim, Norway, 1956, No.5).
- 7 W.B. Frank and L.M. Foster *J. Phys. Chem.* **64** (1960) 95.
- 8 B. Gilbert, G. Mamantov and G.M. Begum, *J. Chem. Phys.* **62** (1975) 950.
- 9 E.D. Dewing, *Proceedings of the Fifth International Symposium on Molten Salts* (The Electrochemical Society Inc., Pennington, NJ, 1986, Vol.86(1)) p.262.
- 10 N.X. Feng and H. Kvande, *Nacta. Chem. Scand.* **A40** (1986) 622.
- 11 B. Gilbert and T. Materne, *Appl. Spectrosc.* **40(2)** (1990) 299.
- 12 L. Joubert, G. Picard, *et al.*, *J. Electrochem. Soc.* **146(6)** (1999) 2180.
- 13 K.C. Hong and O.J. Kleppa, *J. Phys. Chem.* **82** (1978) 176.
- 14 B.J. Holm and F. Gronvold, *Acta. Chem. Scand.* **27A** (1973) 2043.
- 15 I. Borin, O. Knacke and O. Kubaschewski, *Thermochemical Properties of Inorganic Substances* (Supplement, Spring-Verlag, New York, 1977).
- 16 I. Borin, and O. Knacke, *Thermochemical Properties of Inorganic Substances* (Spring-Verlag, New York, 1973).
- 17 E.W. Dewing, *Metall. Trans. B* **21B** (1990) 285.
- 18 B.J. Holm, Thesis, The University of Trondheim (NTH Trondheim, Norway, 1971) p.84.
- 19 B. Phillips, C.M. Warshaw and I. Mockrin, *J. Am. Ceram. Soc.* **49(12)** (1966) 631.
- 20 S. Scharmm, L. Rabardel, *et al.*, *CALPHAD* **14(4)** (1990) 631.