Stability of AlF_5^{2-} anion in the system CaF_2—AlF_3

[a]J. VRBENSKÁ and [b]M. MALINOVSKÝ

[a]Department of Electrotechnology, Slovak Technical University,
880 19 Bratislava

[b]Department of Inorganic Technology, Slovak Technical University,
880 37 Bratislava

The degree of the thermal dissociation of the complex AlF_5^{2-} anion of the compound $CaAlF_5$ formed in the binary system CaF_2—AlF_3 was determined by means of the classical thermodynamic proceeding. Approximate value of the enthalpy of fusion of $CaAlF_5$, ca. 96 kJ mol⁻¹, was determined. The degree of the thermal dissociation of AlF_5^{2-} anion ranges within 5—10%. This result agrees with the assumption of a high stability of the complex AlF_5^{2-} anion in the given system within the temperature interval 800—900°C.

При помощи классического термодинамического подхода определена степень термической диссоциации комплексного аниона AlF_5^{2-} соединения $CaAlF_5$, образующегося в бинарной системе CaF_2—AlF_3. Получено ориентировочное значение энтальпии плавления $CaAlF_5$ (приблизительно 96 кДж моль⁻¹). Степень термической диссоциации аниона AlF_5^{2-} приблизительно 5—10%. Этот результат находится в соответствии с предположением высокой устойчивости комплексного аниона AlF_5^{2-} в данной системе в температурной области между 800 и 900°C.

The study of the phase equilibria in systems related to aluminium electrolysis led to the discovery of the incongruently melting compound, $CaAlF_5$, in the system CaF_2—AlF_3 [1]. In our previous work [2] the existence of this compound was confirmed and the course of the liquidus of $CaAlF_5$ was measured. Also the respective composition and temperature of the eutectic and peritectic points were determined. In the experimental measurements carried out using the thermal analysis an extremely large undercooling was detected at the primary crystallization of the compound $CaAlF_5$ between the peritectic and eutectic points (down to 80 K). This extreme undercooling was observed in two cases: on the first record of the cooling curve when a solid mixture of CaF_2 and AlF_3 was melted, or on the repeated record if the temperature of the melt before cooling was higher than the peritectic temperature (1166 K). An exact measurement without undercooling was possible only when the cooling curve was recorded for the second time under the

condition that the temperature of the molten sample did not surpass the temperature of the peritectic reaction.

This phenomenon is related evidently to the thermal stability of the AlF$_5^{2-}$ anion. The thermal stability of AlF$_5^{2-}$ anion below the temperature 1166 K ($<900°C$) can be of practical significance with respect to the tendency to decrease the working temperature in aluminium electrolysis.

Indirect determination of the degree of the thermal dissociation of AlF$_5^{2-}$

A direct experimental determination of the degree of dissociation of AlF$_5^{2-}$, *e.g.*, by Raman spectroscopy has been inaccessible to the authors. In the literature [3] a proceeding for the determination of the degree of thermal dissociation of a congruently melting compound based on a classical thermodynamic approach is described. This proceeding was applied to the determination of the degree of thermal dissociation of AlF$_6^{3-}$ in molten Na$_3$AlF$_6$ [4] and recently also in Li$_3$AlF$_6$ [5].

In this work the proposed proceeding was applied to the determination of the degree of thermal dissociation of an incongruently melting compound since it can be assumed that the same thermodynamic regularities hold both for the liquidus curves of a congruently as well as of an incongruently melting compound (between the peritectic and the eutectic points in the latter case).

For this purpose the course of the liquidus curve of the given compound as well as its melting temperature and the change of its enthalpy of fusion are to be known. The degree of dissociation is determined by a comparison of the experimental liquidus curve with the curve calculated on the basis of the above data. The melting temperature and the change of the enthalpy of fusion of CaAlF$_5$ were calculated using the experimental data determined in the measurement of liquidus in the system CaF$_2$—AlF$_3$ and converted to the system CaF$_2$—CaAlF$_5$. As no solid solutions were observed in this system, the liquidus curve could be described by the generalized Le Chatelier—Shreder equation

$$\ln a_i = \frac{\Delta H_i^f}{R}\left[\frac{1}{T_i^f}-\frac{1}{T}\right]+f(\Delta C_{P_i}) \tag{1}$$

Subsequently, the data were presented in the coordinates log x_i *vs.* $1/T$. The value of the hypothetic melting point of the compound CaAlF$_5$, 1179 K, was determined by extrapolation of this almost linear dependence to log $x_i = 0$.

From the slope of this linear dependence also the value $\Delta H_{CaAlF_5}^f \cong 96$ kJ mol^{-1} could be determined. The physical justification of this value can be verified approximately by a comparison with the values of ΔH_{CaF_2} and ΔH_{AlF_3} at the same temperature. The corresponding values at 1178 K are: $\Delta H_{CaF_2} = 40.86$ kJ mol^{-1} [6] and $\Delta H_{AlF_3} = 42.60$ kJ mol^{-1} [7]. The difference between the sum of these values

and the above-determined value 96 kJ mol^{-1} corresponds to *ca.* 13%, this being a fair agreement for this method of verification.

It could be assumed that $f(\Delta C_P) = 0$ since the investigated liquidus curve lies within a temperature interval of less than 100 K. Also it was assumed that the melt behaves as an ideal solution, hence $a_i = x_i$ ($i = \text{CaAlF}_5$).

The applied method further requires to choose an appropriate scheme of dissociation for the studied system. It was assumed that 1 mole of CaAlF$_5$ entirely dissociates electrolytically according to the scheme
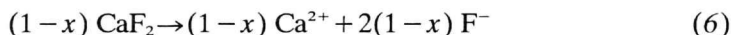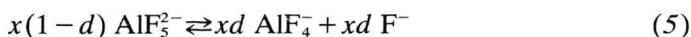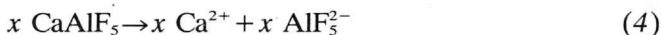
$$\text{CaAlF}_5 \rightarrow \text{Ca}^{2+} + \text{AlF}_5^{2-} \tag{2}$$

and subsequently a partial thermal dissociation of the complex anion takes place

$$(1-b)\ \text{AlF}_5^{2-} \rightleftarrows b\ \text{AlF}_4^- + b\ \text{F}^- \tag{3}$$
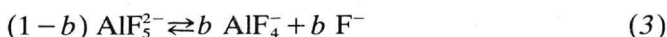
where b denotes the degree of dissociation of the AlF$_5^{2-}$ anion in a hypothetical pure congruently melting CaAlF$_5$.

In a mixture with CaF$_2$ the degree of dissociation will be different and will be denoted by d. For the system formed by x moles of CaAlF$_5$ and $(1-x)$ moles of CaF$_2$ it holds analogically

$$x\ \text{CaAlF}_5 \rightarrow x\ \text{Ca}^{2+} + x\ \text{AlF}_5^{2-} \tag{4}$$

$$x(1-d)\ \text{AlF}_5^{2-} \rightleftarrows xd\ \text{AlF}_4^- + xd\ \text{F}^- \tag{5}$$

$$(1-x)\ \text{CaF}_2 \rightarrow (1-x)\ \text{Ca}^{2+} + 2(1-x)\ \text{F}^- \tag{6}$$

Another schemes of dissociation based on the assumption of an interaction between F$^-$ and Ca^{2+} ions with the formation of CaF$^+$ ions could not be applied in this case as it was impossible to express the dissociation constants of relation (3) and (5). Also it could not be suggested that CaAlF$_5$ dissociates according to the scheme

$$\text{CaAlF}_5 \rightarrow \text{CaF}^+ + \text{AlF}_4^- \tag{7}$$

In this case it would be impossible to explain the great undercooling observed at the crystallization which is related evidently to the formation of the complex anion from an overheated melt.

The existence of CaF$^+$ ion was not suggested in the investigated system in spite of the fact that the study of the system Li$_3$AlF$_6$—CaF$_2$ [8] indicated the likelihood of the dissociation CaF$_2 \rightarrow$ CaF$^+ +$ F$^-$. However, the liquidus curve of Li$_3$AlF$_6$ in this system lies within the temperature interval 1055—987 K, which might explain this difference.

The curve of the primary crystallization of CaAlF$_5$ was calculated according to the Le Chatelier—Shreder equation, the dissociation being considered in the activity term which was expressed according to Temkin's theory of ideal ionic solutions. The proceeding is fully described, *e.g.*, in [3—5] and elsewhere.

Results and discussion

From a comparison of the calculated and experimental liquidus curves (Table 1) it follows that the best agreement with the experiment was achieved for the degree of dissociation of pure $CaAlF_5$ $b = 0.05$—0.10. This comparison shows that in the

Table 1

Comparison of the experimental and calculated liquidus curve of $CaAlF_5$ in the mixtures with CaF_2

Mole % $CaAlF_5$	T_{exp} K	$b = 0.25$		$b = 0.10$	
		T_{calc}	d	T_{calc}	d
90.5	1166	1164.4	0.014	1169.2	0.047
88.7	1165	1161	0.012	1166	0.042
85.2	1160	1153	0.009	1159	0.035
81.8	1155	1145	0.008	1150	0.030
78.6	1150	1138	0.007	1145	0.027

peritectic point the thermal dissociation of the complex AlF_5^{2-} anion is very small and it decreases with the increasing concentration of CaF_2. This indicates that the F^- ions introduced by CaF_2 into the electrolyte shift the equilibrium $AlF_5^{2-} \rightleftarrows AlF_4^- + F^-$ towards the left. The results of this comparison confirm the high degree of stability of AlF_5^{2-}, which simultaneously explains the high undercooling observed at the primary crystallization of $CaAlF_5$ in the mixtures with CaF_2.

References

1. Holm, J. L., *Acta Chem. Scand.* **19,** 1512 (1965).
2. Malinovský, M., Vrbenská, J., and Čakajdová, I., *Chem. Zvesti* **23,** 35 (1969).
3. Glasstone, S., *Textbook of Physical Chemistry*, 2nd Ed., p. 757. Van Nostrand, New York, 1946.
4. Grjotheim, K., *Contribution to the Theory of the Aluminium Electrolysis*, p. 26. Kgl. Norske Vidensk. Selsk. Skr., No 5. F. Bruns, Trondheim, 1956.
5. Vrbenská, J. and Malinovský, M., *Collect. Czech. Chem. Commun.* **38,** 659 (1971).
6. Kelley, K. K., *Contributions to the Data on Theoretical Metallurgy, XIII.* U.S. Bureau of Mines. Bulletin 584, Washington, 1960.
7. Holm, J. L., *Dr Thesis*, p. 84. The Technical University of Norway, Trondheim, 1971.
8. Vrbenská, J., Koštenská, I., and Malinovský, M., *Chem. Zvesti* **27,** 577 (1973).

Translated by K. Matiašovský