

Dissociation of the cryolite anion in the transition point on the liquidus line of barium chloride

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The dissociation of the complex hexafluoroaluminate anion in the systems BaCl_2 — Na_3AlF_6 and BaCl_2 — Li_3AlF_6 was investigated. For the determination of the unknown $k_{\text{Na}_3\text{AlF}_6/\text{BaCl}_2}$ and $k_{\text{Li}_3\text{AlF}_6/\text{BaCl}_2}$ from the course of the experimental liquidus line of BaCl_2 the rule of constancy of the product of Stortenbeker correction factor and of the composition of the added component* was applied. The objectivity of the measured values was verified by means of the criteria of thermodynamic consistency (CTC I and CTC III). The system BaCl_2 — Li_3AlF_6 was measured in the whole composition range; it was found to be a simple eutectic system with the following coordinates of the eutectic point: 62 mole % BaCl_2 , 38 mole % Li_3AlF_6 , and $T_E = 650 \pm 1^\circ\text{C}$. The position of the transition point on the liquidus line of BaCl_2 in systems with cryolites indicates that both $k_{\text{Na}_3\text{AlF}_6/\text{BaCl}_2}$ and $k_{\text{Li}_3\text{AlF}_6/\text{BaCl}_2}$ equal 9, the number of particles decreasing with increasing cryolite concentration. At about 5 mole % Na_3AlF_6 (Li_3AlF_6) the number of particles indicates the presence of the complex cryolite anion AlF_6^{3-} .

Изучалась диссоциация комплексного гексафтороалюминатного аниона в системах BaCl_2 — Na_3AlF_6 и BaCl_2 — Li_3AlF_6 . Было использовано правило о постоянстве произведения корректирующего фактора Стортенбекера и состава добавляемой компоненты для определения неизвестных параметров $k_{\text{Na}_3\text{AlF}_6/\text{BaCl}_2}$ и $k_{\text{Li}_3\text{AlF}_6/\text{BaCl}_2}$ из формы экспериментальной линии ликвидуса BaCl_2 . Измеренные данные были проверены на объективность при помощи «критериев термодинамического согласия». Система BaCl_2 — Li_3AlF_6 была измерена в целом интервале концентраций и было найдено, что она представляет собой простую эвтектическую систему с координатами эвтектики: 62 мол. % BaCl_2 , 38 мол. % Li_3AlF_6 и $T_E = 650 \pm 1^\circ\text{C}$. Положение точки превращения на линии ликвидуса BaCl_2 в системах с криолитами говорит о том, что $k_{\text{Na}_3\text{AlF}_6/\text{BaCl}_2}$ и $k_{\text{Li}_3\text{AlF}_6/\text{BaCl}_2} = 9$ и число частиц уменьшается с растущей концентрацией криолитов. На основании числа частиц для 5 мол. % Na_3AlF_6 (Li_3AlF_6) можно сделать вывод о присутствии комплексного аниона криолита AlF_6^{3-} .

The dissociation of cryolites Na_3AlF_6 and Li_3AlF_6 at both high and low concentrations belongs to the significant problems of the theory of the electrolytic production and refining of aluminium.

* Further on only: the rule of constancy.

Recently, in analyzing the equilibrium "solidus—liquidus" for systems with polymorphous transformation regularities determining the composition coordinate of the transition point x^{tr} have been established [1]. The method of calculation of the hypothetical melting temperature of the low-temperature modification of the studied component was presented [2], this value being necessary for the calculation of the liquidus line. These regularities may be used for the solution of the above-mentioned problems.

Let us consider the binary system A—B without solid solutions, where the component B exists in two enantiotropic modifications. If for the composition coordinate of the transition point x_{B}^{tr} the relation holds

$$0.9 \leq x_{\text{B}}^{\text{tr}} < 1,$$

then

$$k_{\text{A/B}}^{\text{St}} \cdot x_{\text{A}}^{\text{tr}} \doteq \text{const.} \quad (1)$$

From relation (1) it follows that with changing *Stortenbeker* correction factor $k_{\text{A/B}}^{\text{St}}$ [3] also the composition coordinate of the transition point and the course of the liquidus line of both modifications of the studied component B are changing.

When in the system under consideration A—B, $k_{\text{A/B}}^{\text{St}} = 1$ and at the same time the "condition of concavity"

$$\Delta S_{\text{B}, \alpha}^{\text{tr}} = \frac{\Delta H_{\text{B}, \alpha}^{\text{tr}}}{T_{\text{B}, \alpha}^{\text{tr}}} > 2R,$$

is fulfilled, then it is probable that the liquidus line of the high-temperature modification will be concave against the composition axis. In the system A—B the composition coordinate of the transition point of the minor component has the maximum possible value, if the substance A does not form polymers.

When the component B forms the system B—C, and one molecule of the substance C introduces two new particles into the melt of B, *i.e.* $k_{\text{C/B}}^{\text{St}} = 2$, then according to eqn (1) the composition coordinate of the minor component will have one half of its value.

For the course of the liquidus line of the high-temperature modification of component B in the high-concentration region the relation holds [4]

$$\Delta S_{\text{B}, \alpha}^{\text{tr}} \leq 2R \cdot k_{\text{C}}^{\text{St}}$$

In the case when the value of $\Delta S_{\text{B}, \alpha}^{\text{tr}}$ is higher than $2 \cdot 2R$, also the liquidus line of the high-temperature modification will be concave against the composition axis; in the case of equality it will be practically a straight line and for $\Delta S_{\text{B}, \alpha}^{\text{tr}}$ lower than $4R$ the liquidus line will be convex against the composition axis and it may exhibit an inflection point. On the basis of the thermodynamic parameters of the low-temperature modification of component B we may predict the course of the liquidus

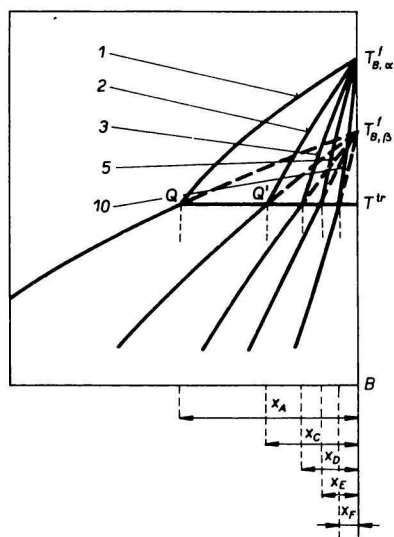


Fig. 1. Schematic presentation of the liquidus lines of the high- and the low-temperature modifications of one component near the transition point for different numbers of particles introduced into component B by the other component.

System A—B	$k_{A/B} = 1$
C—B	$k_{C/B} = 2$
D—B	$k_{D/B} = 3$
E—B	$k_{E/B} = 5$
F—B	$k_{F/B} = 10$

line of this modification. A schematic presentation of the liquidus line of component B in the vicinity of the transition point for various systems is shown in Fig. 1.

These relations may be used for the determination of an unknown Stortenbeker correction factor. If x_A^{tr} in the system A—B is known, we can determine the unknown $k_{C/B}^{St}$ in the system C—B. To secure the objective determination of k^{St} , it is advantageous to measure not only the part of the system C—B near to the transition point, but also a part of the system A—B and to carry out thermodynamic analysis with respect to the correctness of the course of the liquidus lines near the transition and the melting points of the component with a polymorphous transformation [5].

The problem of dissociation of lithium and sodium cryolites has been dealt with in numerous papers; some of them were reviewed in [6] where the number of new particles in the melt of NaCl in dependence on the concentration of Na_3AlF_6 was determined by comparing the experimental liquidus curves with those calculated theoretically by means of the universal relationship for the activity. The paper presents various schemes of dissociation of the complex hexafluoroaluminate anion and the number of particles corresponding to the respective dissociation schemes. From the number of particles formed from one molecule of cryolite, we may judge on the type and degree of the dissociation of AlF_6^{3-} .

For the study of dissociation of AlF_6^{3-} in melts, where the basic component is a substance with a polymorphous transformation, BaCl_2 was chosen. Barium chloride has several advantages: its polymorphous transformation occurs near the melting point ($T_{\text{BaCl}_2,\alpha}^I = 955^\circ\text{C}$, $T^{tr} = 920^\circ\text{C}$); this temperature is comparatively close to that of the aluminium electrolysis and, besides, BaCl_2 is a component of the

electrolyte for aluminium refining. Furthermore, barium chloride was the major component in the systems $\text{BaCl}_2\text{—NaCl}$, $\text{BaCl}_2\text{—NaF}$, and $\text{BaCl}_2\text{—Na}_2\text{SO}_4$ which were used for the experimental verification of the rule of constancy [1]. Here, the validity of relation (1) was fully confirmed.

The dissociation of AlF_6^{3-} was studied in the systems $\text{BaCl}_2\text{—Na}_3\text{AlF}_6$ and $\text{BaCl}_2\text{—Li}_3\text{AlF}_6$ in order to obtain a better picture of the dissociation of fluoride anions, also the system $\text{BaCl}_2\text{—AlF}_3$ was included into the investigation.

$\text{BaCl}_2\text{—Na}_3\text{AlF}_6$

The system was experimentally investigated several times. *Belyaev* [7] classified it as a simple eutectic system with the following coordinates of the eutectic point: 54 mole % BaCl_2 , 46 mole % Na_3AlF_6 , the temperature of eutectic crystallization 710°C . *Guskov* [8] investigated the liquidus line only and found the temperature of the eutectic crystallization to be 700°C . *Khazanov* [9] suggested the formation of a congruently melting compound $\text{Na}_3\text{AlF}_6 \cdot 4\text{BaCl}_2$ with the melting temperature 786°C which forms eutectic systems with both BaCl_2 and Na_3AlF_6 . The above authors do not mention any polymorphous transformation of BaCl_2 , though it was reported by *Sandonini* [10] and *Korring* [11] already in 1914. A part of this system in the range of high BaCl_2 concentrations was studied from the cryometric

Table 1

System $\text{BaCl}_2\text{—Na}_3\text{AlF}_6$
Experimental data on TPC and T''

BaCl_2 mole %	Na_3AlF_6 mole %	TPC $^\circ\text{C}$	T'' $^\circ\text{C}$
100.00	—	955.0	920.0
99.90	0.10	947.5	919.5
99.80	0.20	940.0	919.5
99.70	0.30	934.0	920.0
99.65	0.35	929.5	920.5
99.60	0.40	926.5	920.0
99.55	0.45	923.0	919.5
99.50	0.50	920.0	920.0
99.45	0.55	919.0	—
99.40	0.60	917.5	—
99.30	0.70	915.0	—
99.00	1.00	907.5	—
98.5	1.5	895.0	—
98.0	2.0	882.5	—
97.5	2.5	870.5	—
97.0	3.0	859.5	—
96.0	4.0	844.0	—

standpoint by *Petit and Ngo Tuang* [12] who reported that one molecule of Na_3AlF_6 introduced ten new particles into molten BaCl_2 .

In the investigated systems a part of the liquidus curve of BaCl_2 in the range 0—3 mole % Na_3AlF_6 was measured using the TA method [6]. The experimentally determined values of the liquidus temperatures are listed in Table 1. The composi-

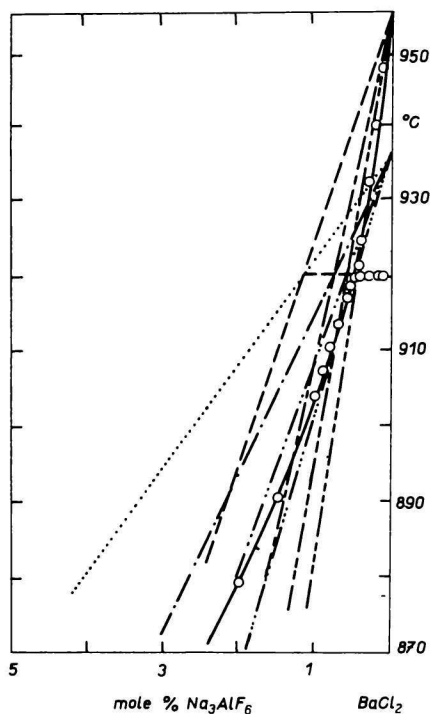


Fig. 2. Part of the phase diagram of the system BaCl_2 — Na_3AlF_6 . Theoretical liquidus lines calculated by means of the universal relationship for different numbers of particles.

$\text{BaCl}_{2,\beta}$

- 4 particles ————
- 6 particles — · · · —
- 8 particles — · · — ·
- 10 particles — · · · — · ·

$\text{BaCl}_{2,\alpha}$

- 4 particles ————
- 6 particles ————
- 8 particles ————
- 10 particles ————

—○—○— experimental data

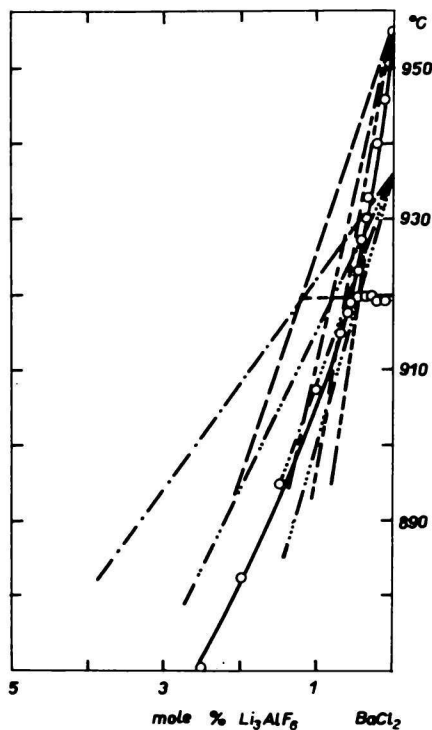


Fig. 3. Part of the phase diagram of the system BaCl_2 — Li_3AlF_6 . Theoretical liquidus lines calculated by means of the universal relationship for different numbers of particles.

$\text{BaCl}_{2,\beta}$

- 4 particles — · · · —
- 6 particles — · · · —
- 8 particles — · · — ·
- 10 particles — · · · — · ·

$\text{BaCl}_{2,\alpha}$

- 4 particles ————
- 6 particles ————
- 8 particles ————
- 10 particles ————

—○—○— experimental data

tion coordinate of the transition point was 99.5 mole % BaCl_2 , 0.5 mole % Na_3AlF_6 , $T^{\text{tr}} = 920^\circ\text{C}$.

In the dissociation of cryolite in a melt without common ion, 6—10 new particles may arise from one molecule [13], with a common alkaline cation it was 3—7 new particles. Since the given system exhibits no common ion, we calculated the theoretical courses of the liquidus lines using the universal relationship [14] for $k_{\text{Na}_3\text{AlF}_6/\text{BaCl}_2}^{\text{St}} = 10, 8, 6, \text{ and } 4$. The calculated results are shown in Fig. 2, together with the experimentally measured course of the liquidus line of BaCl_2 .

The course of the liquidus line of BaCl_2 was verified by means of CTC I and CTC III [15]. In both cases, the deviations were within $\pm 1\%$ range.

$\text{BaCl}_2\text{—Li}_3\text{AlF}_6$

In the available literature we did not find any data on the equilibrium in this system.

Applying the TA method we investigated the system in the whole composition range, viz., 26 mixtures in the region of the liquidus of BaCl_2 and 17 mixtures in that of the liquidus of Li_3AlF_6 [11]. Our attention was directed to the determination of the character of this system and also of the course of the liquidus line in the region of polymorphous transformation of BaCl_2 . The experimentally found values

Table 2

System $\text{BaCl}_2\text{—Li}_3\text{AlF}_6$
Experimental data on TPC and T^{tr}

BaCl_2 mole %	Li_3AlF_6 mole %	TPC $^\circ\text{C}$	T^{tr} $^\circ\text{C}$
100.00	—	955.0	920.0
99.90	0.10	947.5	920.0
99.80	0.20	940.0	920.0
99.70	0.30	932.5	920.0
99.60	0.40	925.5	919.5
99.55	0.45	922.0	920.0
99.50	0.50	920.0	920.0
99.45	0.55	918.5	—
99.40	0.60	917.0	—
99.30	0.70	914.0	—
99.20	0.80	910.5	—
99.10	0.90	907.5	—
99.00	1.00	904.0	—
98.50	1.50	890.5	—
98.00	2.00	879.0	—
97.50	2.50	867.0	—
97.00	3.00	859.0	—

are in Table 2. It has been found that $\text{BaCl}_2\text{—Li}_3\text{AlF}_6$ is a simple eutectic system with the following coordinates of the eutectic point: 62 mole % BaCl_2 , 38 mole % Li_3AlF_6 , $T_E = 650 \pm 1^\circ\text{C}$.

Again this is a system without a common ion and the results obtained for the theoretical course of the liquidus line are the same as for the system $\text{BaCl}_2\text{—Na}_3\text{AlF}_6$. Fig. 3 shows the calculated and the experimental values in the region of the polymorphous transformation of BaCl_2 . The course of the liquidus lines in this system was verified applying CTC I, CTC II, and CTC III [5]. The agreement between the theoretical and the experimental values [15] was found to be very good.

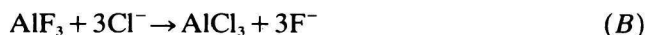
$\text{BaCl}_2\text{—AlF}_3$

This system was studied by *Kuvakin* [16]. The presented data are, however, somewhat disputable since no polymorphous transformation has been reported. The investigation of this system in the region of low AlF_3 concentrations allowed us to confront the character of the dissociation of AlF_3 with the dissociation of the complex hexafluoroaluminate anion.

If the dissociation of AlF_3 followed the scheme

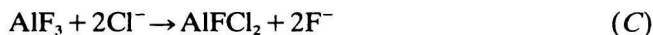


or the scheme



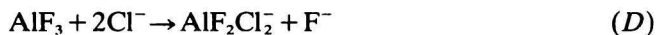
then one molecule of AlF_3 would introduce four new particles in the melt of BaCl_2 .

Should the F^- ions be partly eliminated according to the scheme



then one molecule of AlF_3 would give three new particles.

In the study of the molten cryolite—chloride mixtures the possibility of the formation of the complex $\text{AlF}_2\text{Cl}_2^-$ anion might be encountered at low concentration of cryolite (as *e.g.*, in the system $\text{NaCl—Na}_3\text{AlF}_6$ in the range 0.25—1.2 mole % Na_3AlF_6 [6]) according to the scheme



In such a case, one molecule of AlF_3 would introduce only two new particles into molten BaCl_2 .

The system was investigated using the TA method [11] in the range 0—10 mole % AlF_3 where eighteen mixtures were measured. The results are presented in Table 3.

The calculation of the liquidus curve of BaCl_2 was made using the universal relationship [14] for 4, 3, and 2 particles. The results of the calculation are

Table 3

System $\text{BaCl}_2\text{—AlF}_3$
Experimental data on TPC and T^{tr}

BaCl_2 mole %	AlF_3 mole %	TPC °C	T^{tr} °C
100.00	—	955.0	920.0
99.8	0.2	950.0	921.0
99.6	0.4	948.0	920.0
99.4	0.6	943.7	920.5
99.2	0.8	941.2	920.5
99.0	1.0	936.5, 937.0	919.2, 920.7
98.8	1.2	934.2	920.7
98.6	1.4	933.0, 930.7	920.0, 920.5
98.4	1.6	929.5, 927.7	920.7, 920.0
98.2	1.8	924.0	918.7
98.0	2.0	921.7	919.2
97.8	2.2	917.5	—
97.6	2.4	918.0	—
97.4	2.6	914.4, 916.5	—
97.2	2.8	916.7	—
97.0	3.0	914.8	—
96.8	3.2	915.2	—
95.0	5.0	897.5	—
90.0	10.0	878.0	—

confronted with the experimental data in Fig. 4. The course of the experimental liquidus curve was verified using CTC *I* and CTC *III*. Because of the agreement between the experimental and the calculated liquidus curve for two particles, $k_{\text{AlF}_3/\text{BaCl}_2}^{\text{St}} = 2$ was used for CTC *I*. The criterion was fulfilled with a deviation of less than 8%, while CTC *III* showed a deviation of 1.5% [15]. The transition point has the following coordinates: 97.9 mole % BaCl_2 , 2.1 mole % AlF_3 , $T^{\text{tr}} = 920^\circ\text{C}$.

Discussion

Though *Grjotheim* has applied the classical thermodynamic method to the determination of the dissociation of the hexafluoroaluminate anion as early as in 1956 [17], this problem remains to be a topical subject of the research. *Malinovský* [18] pointed out that this method would give exact results only provided that the course of the liquidus line was measured with a high accuracy. Another method for the determination of the character of dissociation of the hexafluoroaluminate anion AlF_6^{3-} was presented in [6]; the dissociation of the AlF_6^{3-} anion was

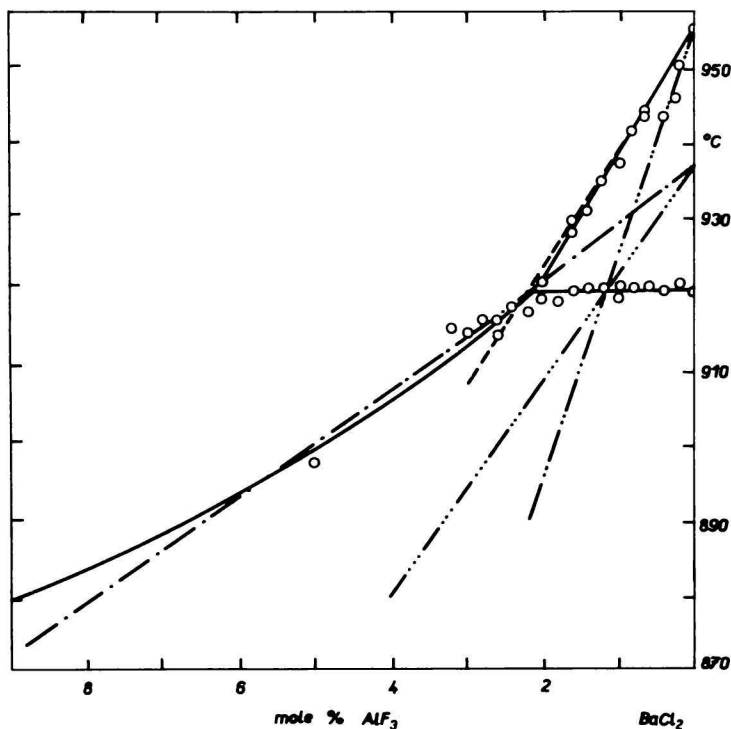


Fig. 4. Part of the phase diagram of the system BaCl₂—AlF₃. Theoretical liquidus lines calculated by means of the universal relationship for different numbers of particles.

BaCl _{2,β}	BaCl _{2,α}
2 particles — · — · —	2 particles - - - - -
4 particles — · — · —	4 particles — · — · —
—○—○— experimental data	

determined on the basis of the course of the liquidus curve of component A in the system A—cryolite. This method of investigation of the dissociation of AlF_6^{3-} shows some advantages compared with the one used in [6]. The dissociation is determined on the basis of the course of the liquidus line of the component with polymorphous transformation, at temperatures between the melting point of the substance B and temperatures slightly lower than that of the transformation. The existence of the transition point on the liquidus line enables us to apply not only CTC I, but also CTC III. This makes possible a better verification of the objectivity of the measured values. Owing to its thermodynamic parameters, barium chloride used in this work is very advantageous for such a study since here the rule of constancy holds accurately.

The experimentally determined composition of the transition point in the

systems $\text{BaCl}_2\text{—Na}_3\text{AlF}_6$ (Li_3AlF_6) is 0.5 mole % Na_3AlF_6 (Li_3AlF_6) and 99.5 mole % BaCl_2 .

Let us apply the rule of constancy of the product $k_{A/B}^{\text{St}} \cdot x_A^{\text{tr}}$. The dissociation of AlF_6^{3-} and consequently also the number of particles, introduced by one molecule of cryolite into molten BaCl_2 , depends on the concentration of cryolite [6]. We replace $k_{A/B}^{\text{St}}$ in the rule of constancy by the coefficient $k_{A/B}$ from the universal relationship for the activity of the component B: $a_B = x_B^{k_{A/B}}$ [14]. Then the coefficient for the transition point in the measured systems will be

$$k_{\text{cryolite}/\text{BaCl}_2} = 0.0459/0.005 = 9.$$

The constancy of the product $k_{A/\text{BaCl}_2} \cdot x_A = 0.0459$ was experimentally verified in [1].

In [6] we proposed a scheme for very low concentrations of cryolite in chloride melts, which depending upon the degree of dissociation of $\text{AlF}_2\text{Cl}_2^-$ into AlCl_4^- and F^- gives 8—10 new particles. If the dissociation degree is 0.5 then one molecule of Na_3AlF_6 introduces nine new particles into the melt without a common ion. Experimental study of the system $\text{BaCl}_2\text{—AlF}_3$ shows that in the range of low AlF_3 concentrations the dissociation follows the Scheme (D) with the formation of $\text{AlF}_2\text{Cl}_2^-$ since the number of new particles determined by means of the relation (I) was found to be two.

If the coefficient $k_{\text{cryolite}/\text{BaCl}_2}$, i.e. the number of new particles formed from one molecule of cryolite in the melt of BaCl_2 , decreases under the value 6, then AlF_6^{3-} from AlF_4^- and F^- should be formed. This type of dissociation which involves the presence of the AlF_6^{3-} ion in molten BaCl_2 occurs in the system $\text{BaCl}_2\text{—Na}_3\text{AlF}_6$, at a content of Na_3AlF_6 higher than 4.8 mole %, and in the system $\text{BaCl}_2\text{—Li}_3\text{AlF}_6$ beginning with 4.6 mole % Li_3AlF_6 .

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