

Calculation of the phase diagrams of multicomponent systems containing cryolite*

P. FELLNER, M. CHRENKOVÁ-PAUČÍROVÁ, and K. MATIAŠOVSKÝ

*Institute of Inorganic Chemistry, Slovak Academy of Sciences,
809 34 Bratislava*

Received 1 September 1976

Liquidus diagrams of the cryolite-based ternary and quaternary systems are calculated using the estimation of the excess Gibbs energy. The systems LiF—NaF—AlF_3 , $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3\text{—NaCl}$, $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3\text{—NaCl—CaF}_2$, and $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3\text{—AlF}_3\text{—NaCl}$ were investigated. Main attention was paid to the region of primary crystallization of cryolite which is important in electrowinning of aluminium. It was found that in spite of a strong interaction among the components of these melts there is a good agreement between the calculated and experimental temperatures of primary crystallization.

Была рассчитана диаграмма ликвидуса в тройных и четверных системах на основании криолита, причем использовался метод избыточных функций Гиббса. Были исследованы системы LiF—NaF—AlF_3 , $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3\text{—NaCl}$, $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3\text{—NaCl—CaF}_2$, $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3\text{—AlF}_3\text{—NaCl}$. Главное внимание уделялось области первичной кристаллизации криолита, что важно с точки зрения электролитического получения алюминия. Было установлено хорошее совпадение между рассчитанными и измеренными значениями температуры первичной кристаллизации, вопреки сильному взаимодействию среди составляющих в этой системе.

Molten salts and their mixtures are studied with respect to their contemporary and perspective application in technical praxis, mainly in electrometallurgy, anticorrosion protection, and power supply problems. For an effective application of molten salts it is necessary to know their structure and physicochemical properties. One of the most important parameters of molten salt mixtures is apparently their temperature of the primary crystallization (temperature of solid—liquid equilibrium). This temperature determines the region of existence of liquid phase, which is important in the study of the other physicochemical parameters. Moreover, these parameters depend to a great extent upon the overheating of the melt (the difference between the temperature of the melt and the temperature of primary crystallization). In multicomponent melts this effect

* Presented at the 1st Conference of Socialist Countries on Chemistry and Electrochemistry of Molten Salts, Smolenice, November 24—26, 1975.

may be even more important than a change in chemical composition of the melt. (It is obvious that the overheating is also a function of composition.) In some cases this influence can be described quantitatively, *e.g.* in the study of transport properties of molten salts [1] or in the investigation of current efficiency of molten salt electrolysis [2].

The experimental study of phase equilibria in multicomponent systems is usually laborous. In the paper [3] we have proposed a method for calculation of the liquidus diagrams of ternary systems of salt mixtures based on the known values of excess Gibbs energy of binary systems. The method was applied to different types of ternary systems and the agreement between calculated and experimental diagrams was very good. In this work the applicability of this way of estimation of "liquidus" of ternary and quaternary systems containing sodium cryolite as the major component is discussed. As the other components, Al_2O_3 , AlF_3 , CaF_2 , NaCl , and LiF were chosen. These systems are close to those used in the electrolytic production of aluminium and, therefore, the corresponding phase equilibria were studied in numerous works. From the theoretical point of view it was interesting to investigate if the proposed method of calculation of "liquidus" (which proved to be successful in the calculation of ternary systems) would be successful also in the quaternary systems with strong interactions among components.

Theoretical

The chemical potential μ_i of the substance i in a condensed mixture of non-electrolytes may be defined as

$$\mu_i = \mu_i^0 + RT \ln(x_i \gamma_i), \quad (1)$$

where μ_i^0 is the standard chemical potential of component i identical with the chemical potential of pure component i , R is gas constant, T is absolute temperature, x_i is mole fraction of the substance i in a mixture, and γ_i is the activity coefficient of the component.

In the case of ionic melts, *e.g.* in the system $\text{M}_p\text{A}_q\text{—N}_r\text{B}_s$, molecules M_pA_q or N_rB_s are not present in the melt because they are dissociated into ions M^{q+} , A^{p-} , N^{s+} , B^{r-} . If we denote these particles as α we can write

$$\mu_i = \mu_i^0 + RT \ln(x_i f_i), \quad (2)$$

where x_i is the true mole fraction of the species α in the melt. If we denote the true mole fraction of the species α in the pure liquid component i as $x_{i,\alpha}^0$ and the number of the species α produced by a total dissociation of the component i as $k_{i,\alpha}$ we can write [4, 5]

$$\mu_i = \sum_{\alpha} k_{i,\alpha} \mu_{i,\alpha} \quad (3)$$

$$\mu_i = \mu_i^0 + RT \left[\sum_{\alpha} k_{i,\alpha} \ln(x_{i,\alpha}/x_{i,\alpha}^0) + \sum_{\alpha} k_{i,\alpha} \ln(x_{i,\alpha}^0 f_{i,\alpha}) \right], \quad (4)$$

where

$$\sum_{\alpha} k_{i,\alpha} \ln(x_{i,\alpha}^0 f_{i,\alpha}) = \left(\sum_{\alpha} k_{i,\alpha} \right) \ln f_i \quad (5)$$

Therefore, if we know the difference $\mu_i - \mu_i^0$ for the given composition and temperature of the melt we can calculate (using eqns (4) and (5)) the correction factor f_i which has been introduced by *Haase* [5].

The integral equation of the liquidus curve (or surface) can be written as

$$\mu_i(T) - \mu_i^0(T) = -(\Delta H_{i,l}/T_{i,l})(T_{i,l} - T), \quad (6)$$

where $T_{i,l}$ is the temperature of fusion of pure component i , $\Delta H_{i,l}$ is the enthalpy of fusion of this component, and T is the temperature of solid—liquid equilibrium at the given composition of the system. (Eqn (6) holds exactly if the difference of heat capacities in solid and liquid phases equals zero.)

From the experimental data of solid—liquid equilibrium in binary systems we can calculate (using eqns (4—6)) the activity coefficient for each point on the liquidus curve. Let us assume that the dependence of an excess function Φ^E in binary system can be described with a sufficient accuracy by the relation

$$\Phi^E = x_1 x_2 [A + B(x_2 - x_1)] \quad (7)$$

(If $\mu_i - \mu_i^0$ can be expressed according to eqn (1), the function Φ^E is identical with excess Gibbs energy.)

The function Φ^E is defined in such way that it holds

$$\left(\frac{\partial \Phi^E}{\partial n_i} \right)_{T,P,n_j \neq i} = RT \ln f_i \quad (8)$$

Then

$$\begin{aligned} RT \ln f_1 &= x_2^2 [A + B(4x_2 - 3)], \\ RT \ln f_2 &= x_1^2 [A + B(4x_2 - 1)], \end{aligned} \quad (9)$$

where x_1 and x_2 are mole fractions of the first and the second component, respectively, f_1 , f_2 are the correction factors and A , B are empirical constants that depend only on temperature (or on pressure). Therefore, if we know the values of the correction factors f_1 and f_2 at a certain temperature (they can be obtained e.g. from binary phase diagram) we can calculate the values of constants A , B according to eqns (9). For the estimation of the excess function Φ^E in multicomponent system we use the equation

$$\Phi^E = \sum x_i x_j [A_{ij} + B_{ij}(x_i - x_j)] \quad (10)$$

(Equation (7) is only a special case of equation (10).)

Using definition (8) describing the relation between correction factor and excess function Φ^E we can calculate the correction factors of components in a multicomponent system as a function of composition and temperature (the constants A_{ij} , B_{ij} depend on temperature). Using eqns (4—6), we can further calculate the temperature of primary crystallization of the chosen component in a multicomponent system. It is obvious that this calculation is based on the assumption that the excess function Φ^E in a multicomponent system consists mainly of the contributions of corresponding binary systems and that ternary and quaternary interactions are negligible or mutually compensated.

Results and discussion

The proposed method of calculation has been applied to the calculation of solid—liquid equilibrium in the quasi-ternary system LiF—NaF—AlF₃ and in

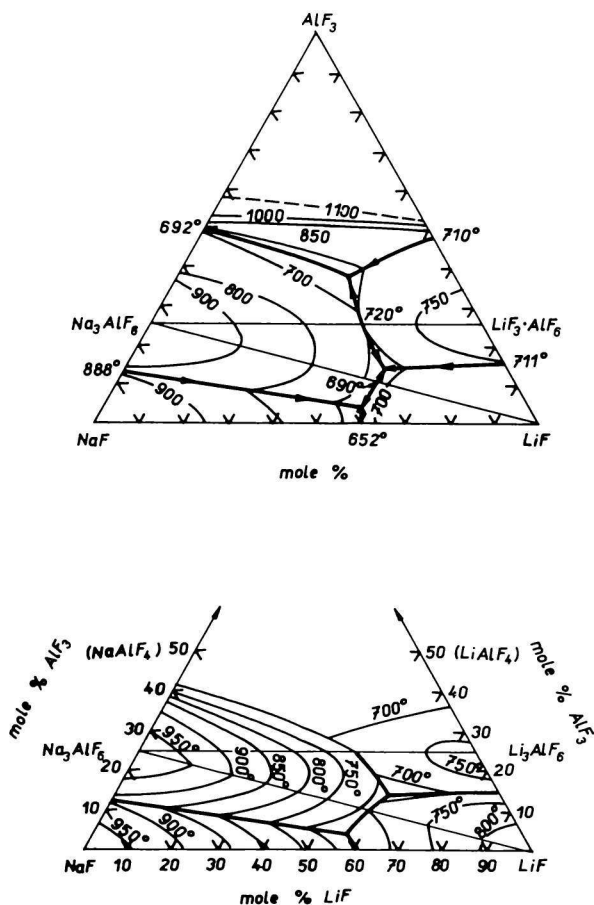


Fig. 1. Phase diagram of the system LiF—NaF—AlF₃,
a) Experimental [8]; b) calculated.

systems Na₃AlF₆—Al₂O₃—NaCl, Na₃AlF₆—Al₂O₃—NaCl—CaF₂, Na₃AlF₆—Al₂O₃—AlF₃—NaCl (only the equilibrium between solid cryolite and melt was studied). In the latter case (the systems containing cryolite), the excess function was estimated only from contributions of binary systems containing sodium cryolite as one component. From a comparison of the calculated and experimental data it follows that in the field of the primary crystallization of cryolite this simplification is justified. The enthalpies and temperatures of fusion of pure components used in the calculation are taken from [6]. The calculations were carried out using a computer CDC 3300 (Research Calculating Centre, Bratislava).

The system LiF—NaF—AlF₃

Generally, the industrial aluminium electrolytes have a cryolite ratio (*i.e.* the ratio between mole fractions of alkali fluorides and of aluminium fluoride) in the range from 2.7 to 3.0. Therefore, it was interesting to verify if also in these systems, where a number of complexes is formed, the surfaces of solid—liquid equilibrium can be calculated only by means of the proposed formal equations without taking into account the dissociation constants of the complexes. In this special case (*i.e.* in cryolite melts) there is enough information on the dissociation of fluoroaluminate complexes [7]. Generally, however, such data are rather scarce. Therefore, the title systems were investigated in order to verify if the proposed method of calculation can be used generally in this class of systems.

In the system LiF—NaF—AlF₃, there are two congruently melting compounds: Na₃AlF₆ and Li₃AlF₆. Therefore, the system was to be divided into three partial systems: LiF—NaF—Na₃AlF₆, LiF—Na₃AlF₆—Li₃AlF₆, and Na₃AlF₆—Li₃AlF₆—AlF₃. The calculations of surfaces of liquidus were based on the following formal assumptions: Cryolites dissociate into alkali cations and AlF₆³⁻ anions which further dissociate to yield fluoride ions required for the formation of AlF₄⁻ ions with AlF₃ if there is any present in the melt (the last subsystem). No free fluoride ions are assumed to exist in the melt. Thus in the subsystem Na₃AlF₆—Li₃AlF₆—AlF₃ only the field of the primary crystallization of cryolite corresponding to the quasi-ternary reciprocal system Li⁺, Na⁺ || AlF₆³⁻, AlF₄⁻ was investigated.

The experimental data (Fig. 1a) are compared with calculated isotherms (Fig. 1b). It is obvious that in the region of "neutral" melts (cryolite, ratio, CR = 3.0) the agreement is very good. For "acid" electrolytes (CR < 3) there is a fair agreement between the calculated and experimental data up to CR ≅ 2.7.

The system Na₃AlF₆—Al₂O₃—NaCl

This system can be considered also as an example of a system with strong interactions among components. This conclusion follows from high values of the enthalpies of dissolution of alumina in cryolite [7] and from a rapid decrease of solubility of alumina with the increasing content of NaCl in the melt. The phase equilibria in binary system Na₃AlF₆—Al₂O₃ have been studied in [9, 10]. The structure of these melts is discussed in [11]. In our calculations we formally assume that Al₂O₃ dissolves in cryolite with the formation of the AlOF₂⁻ anion (Na₃AlF₆ + 2Al₂O₃ = 3NaAlOF₂). This assumption is consistent with the cryoscopic studies from which it follows that the first molecules of alumina added to the cryolite melt dissociate with the formation of 3 new (foreign) particles. The experimental and calculated temperatures of primary crystallization of cryolite in this system are shown in Figs. 2a, b. The agreement between experimental and calculated data is satisfactory.

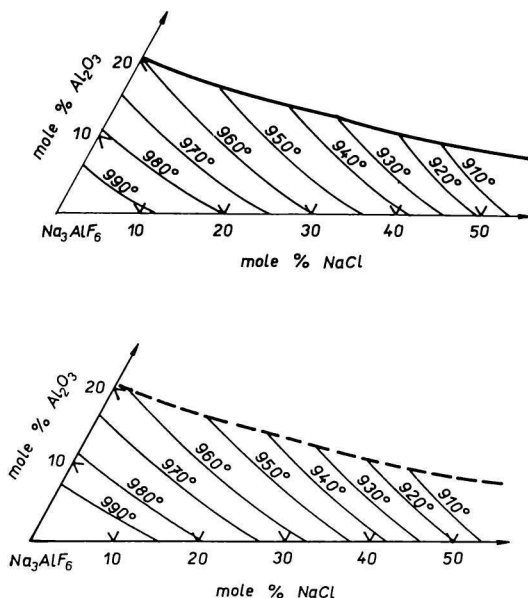


Fig. 2. Phase diagram of the system Na₃AlF₆-Al₂O₃-NaCl.
a) Experimental [10]; b) calculated.

The system Na₃AlF₆-Al₂O₃-NaCl-CaF₂

In the calculation of the equilibrium between solid Na₃AlF₆ and cryolite in the melt the same assumptions as in the former cases were used. The results are summarized in Table 1 (experimental data are those presented in [12]). From a comparison of the experimental and calculated values it is obvious that there is a good agreement between these two sets of data. In the studied range of concentrations the differences between calculated and experimental values are comparable with the accuracy of experimental measurements.

The system Na₃AlF₆-AlF₃-Al₂O₃-NaCl

In the study of the system Na₃AlF₆-Li₃AlF₆-AlF₃ it was found that the proposed method of calculation gives reasonable results only for melts with $CR > 2.7$. As it follows from Table 2, where the experimental and calculated results are summarized, the same phenomenon is observed in the system in question. A good agreement between calculated and experimental data exists only in the region with $CR > 2.7$.

Table 1
The system $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3\text{—NaCl—CaF}_2$

Mole fraction				T_{cal}	T_{exp} [12]	ΔT
Na_3AlF_6	Al_2O_3	NaCl	CaF_2			
0.789	0.000	0.123	0.088	1247.2	1252	-4.8
0.696	0.000	0.226	0.078	1235.2	1235	0.2
0.616	0.000	0.315	0.069	1220.8	1219	0.2
0.548	0.000	0.391	0.061	1203.0	1202	1.0
0.488	0.000	0.457	0.055	1187.0	1184	3.0
0.733	0.066	0.119	0.082	1234.0	1230	4.0
0.681	0.127	0.115	0.076	1215.0	1212	3.0
0.632	0.185	0.112	0.071	1191.0	1194	-3.0
0.649	0.058	0.220	0.073	1217.5	1215	2.5
0.605	0.113	0.214	0.068	1198.0	1195	3.0
0.577	0.052	0.307	0.065	1200.0	1199	1.0
0.540	0.101	0.299	0.060	1180.0	1177	3.0
0.504	0.147	0.292	0.057	1155.0	1163	-5.0
0.514	0.046	0.382	0.058	1183.0	1181	2.0
0.482	0.090	0.374	0.054	1161.8	1162	-0.2
0.460	0.041	0.448	0.051	1167.4	1166	1.4
0.432	0.081	0.439	0.048	1146.5	1147	-0.5

Table 2
The system $\text{Na}_3\text{AlF}_6\text{—AlF}_3\text{—Al}_2\text{O}_3\text{—NaCl}$

Mole fraction				T_{cal}	T_{exp} [13]	ΔT
Na_3AlF_6	AlF_3	Al_2O_3	NaCl			
0.743	0.067	0.069	0.120	1237.0	1239	- 2
0.688	0.062	0.133	0.117	1220.5	1218	2.5
0.636	0.058	0.194	0.112	1200.0	1201	- 1
0.655	0.059	0.064	0.222	1219.0	1219	0
0.607	0.055	0.123	0.215	1200.0	1197	3
0.580	0.053	0.059	0.308	1200.0	1203	- 3
0.537	0.049	0.115	0.299	1180.0	1181	- 1
0.515	0.047	0.055	0.383	1181.2	1184	- 2.8
0.476	0.043	0.107	0.373	1161.2	1161	0.2
0.458	0.041	0.052	0.449	1164.4	1168	- 3.6
0.683	0.136	0.066	0.115	1226.0	1239	-13
0.605	0.121	0.061	0.213	1201.5	1222	-20.5
0.634	0.127	0.128	0.112	1202.2	1216	-13.8
0.561	0.112	0.119	0.207	1175.0	1200	-25
0.587	0.117	0.187	0.109	1172.0	1195	-23

Conclusion

From the results of this work it follows that the proposed formalism of calculation of solid—liquid equilibrium can be used also in the systems containing complex ions. In most cases, the agreement between experimental and calculated temperatures of primary crystallization does surpass the experimental error which is in some systems relatively high because of the tendency of cryolite melts containing alumina to undercooling. The method fails in systems with $CR < 2.7$ because the assumptions made in the calculation are not entirely fulfilled. It is presumed that mainly the neglect of the contribution of some binary systems, which do not contain cryolite as one component, to the total value of Φ^E , as required by the relation (10), may be responsible for this failure.

References

1. Fellner, P., *Chem. Zvesti* **28**, 721 (1974).
2. Fellner, P., Grjotheim, K., Matiašovský, K., and Thonstad, J., *Can. Metall. Quart.* **8**, 254 (1969).
3. Fellner, P., Chrenková-Paučírová, M., and Matiašovský, K., *Z. Phys. Chem.* **102**, 175 (1976).
4. Haase, R., in *Physical Chemistry-Thermodynamics*. (H. Eyring, D. Henderson, and W. Jost, Editors.) Vol. 1. Academic Press, London, 1971.
5. Haase, R. and Schönert, H., *Solid—Liquid Equilibrium*. Pergamon Press, Oxford, 1969.
6. Stull, D. R. and Prophet, H., *JANAF Thermochemical Tables*, 2nd Ed. Natl. Bur. Stand. (USA); Coden: NSRDA, 1971.
7. Holm, J. L., *Thesis for a Doctor's Degree*. NTH, Trondheim, 1971.
8. Thoma, R. E., Sturm, B. J., and Guinn, E. H., *ORNL-3594*, p. 32, 1964.
9. Matiašovský, K. and Malinovský, M., *Electrochim. Acta* **11**, 1035 (1966).
10. Yaguchi, H., Pham, H., and Rolin, M., *Bull. Soc. Chim. Fr.* **1970**, 39.
11. Førland, T. and Ratkje, S. K., *Acta Chem. Scand.* **27**, 1883 (1973).
12. Matiašovský, K. and Malinovský, M., *Chem. Zvesti* **14**, 551 (1960).
13. Matiašovský, K. and Malinovský, M., *Chem. Zvesti* **15**, 241 (1961).

Translated by P. Fellner