

Application of the theory of regular ionic solution to calculation of the liquidus course in the system $\text{LiF}-\text{Na}_3\text{AlF}_6$ in the region of high concentration of LiF

^{a, b}J. KALOUSEK and ^cG. KALOUSKOVÁ

^a Department of Physical Chemistry, Technical University of Mining and Metallurgy, CS-708 33 Ostrava

^b Institute of Theory of Metallurgical Processes, Czechoslovak Academy of Sciences, CS-703 00 Ostrava

^c Department of Inorganic Chemistry, Technical University of Mining and Metallurgy, CS-708 33 Ostrava

Received 5 February 1986

The paper deals with the calculation of the liquidus course in the region of high concentration of LiF. The *Kozheurov's* theory of the regular ionic solution [1] has been used to express the activity and activity coefficient and necessary modifications of the Le Chatelier—Shreder's equation have been performed. The applied theory has been verified on the experimental data gained by *Koštenská, Čorba, and Malinovský* [2] with a very good agreement.

В статье подается вычисление кривой ликвидуса в области высокой концентрации LiF. Для выражения активности и коэффициента активности *Кожеуров* использовал модель регулярного ионтового раствора [1] с проведением коррекции по уравнению Ле Шательер—Шредера. Теорию подтвердили экспериментальные результаты полученные *Коштенской, Чорбой и Малиновским* [2].

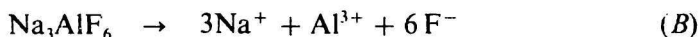
The above-mentioned system is of great importance in electrolytic production of aluminium. It has been therefore several times experimentally investigated as far as the liquidus course, eutectic point, and thermodynamical quantities of the components are concerned [3—8]. Because of serious discrepancies between the results [3—8] the authors of paper [2] have made an experimental revision of the temperatures of the primary crystallization through the whole concentration region. The accuracy of the temperature measurement was ± 1 K. An eutectic point (85 ± 1) mole % LiF, $T_E = (1121 \pm 1)$ K ($(696 \pm 1)^\circ\text{C}$) has been found. The melting temperature of the pure LiF is $T = 1121$ K (848°C). The difference between the melting temperature of LiF and the eutectic temperature is 147 K.

The system is quasi-binary, no solid solutions are present in the region: pure LiF—eutectic point. The change of the enthalpy of fusion at standard pressure for pure LiF is $\Delta H_{\text{fus}}^{\circ} = 26\,138\text{ J mol}^{-1}$. These data have been used for further purposes of this work.

Theoretical

Generally, in the molten system LiF— Na_3AlF_6 the simple ions Li^+ , Na^+ , F^- , complex anion AlF_6^{3-} and most probably also complex anion AlF_4^- are present [9, 10]. The degree of dissociation of AlF_6^{3-} into AlF_4^- was thermodynamically proved [11–13], experimentally proved by means of Raman spectrometry [14]. The mathematical analysis of the dissociation of cryolite anions is presented in paper [15]. According to [16, 17] the dissociation of the complex anion AlF_6^{3-} is practically total.

Let us further consider the concentration region pure LiF—eutectic point of the system only. In this region with high concentration of LiF the dissociation equations for both components may be suggested



In addition to the literature references the dissociation equations can be supported by reasoning taking into account the properties of cations present in the molten system, as follows:

If the concentration of LiF in the system is high, total dissociation according to eqn (A) yields Li^+ ($r_{\text{Li}^+} = 0.068\text{ nm}$, electronegativity $\text{Li} = 1.0$). The interactive forces between the cation Li^+ and anion F^- ($r_{\text{F}^-} = 0.136\text{ nm}$, electronegativity $\text{F} = 4.0$) are prevailing in comparison with the interactive forces between cation Al^{3+} ($r = 0.051\text{ nm}$, electronegativity $\text{Al} = 1.5$) and anion F^- . The complex anions containing Al and F are therefore disintegrated and the dissociation equation (B) may be considered acceptable.

If the total dissociation according to eqns (A) and (B) is valid, the *Kozheurov's* theory of the regular ionic solution [1] developed for the systems with only one common ion, may be applied in order to estimate the necessary thermodynamical quantities. The *Kozheurov's* theory yields for the activity coefficient γ_l (at the constant temperature) of the l -th component in the k -component system the general expression

$$RT \ln \gamma_l = v_l \left[\sum_{i=1}^{l-1} x_i Q_{il} + \sum_{j=l+1}^k x_j Q_{lj} - \sum_{i=1}^{k-1} \sum_{j=i+1}^k x_i x_j Q_{ij} \right] \quad (I)$$

The symbols x_i , x_j represent the mole (ionic) fractions of the ions, Q_{il} , Q_{lj} , Q_{ij} (J mol^{-1}) the energies of mixing. These quantities include the interactive forces between the ions. They are related to a solution containing one mole of all cations, if the common ion is an anion, or one mole of all anions, if the common ion is a cation. The quantity ν_l relates to the number of ions in the dissociation equation.

The activity of the l -th component may be defined

$$a_l = \gamma_l \cdot x_l^{\nu_l} \quad (2)$$

The mole (ionic) fractions in eqns (1) and (2) are related to Temkin's model. The mole (ionic) fraction of the common ion equals to one. If $\gamma_l = 1$ (*i.e.* all the energies of mixing are equal to zero), the Kozheurov's model transits into Temkin's model of the perfect ionic solution [18]. The activity of the i -th component and the temperature of the liquidus are connected by the generalized Le Chatelier—Shreder's equation [19]

$$\ln a_i = \frac{\Delta H_{\text{fus},i}^\circ}{R} \left(\frac{1}{T_{\text{fus}}} - \frac{1}{T} \right) + \frac{1}{R} \int_T^{T_{\text{fus}}} \frac{dT}{T^2} \int_T^{T_{\text{fus}}} \Delta C_p dT \quad (3)$$

The symbol ΔC_p represents the change of the heat capacity for the i -th component from the solid to the liquid phase. If the difference $T_{\text{fus}} - T$ is not too high, the second term on the right-hand side of eqn (3) may be neglected.

Using this condition and eqns (1—3), then after rearrangement it generally holds

$$T = \frac{\Delta H_{\text{fus},i}^\circ + \varphi_l}{\frac{\Delta H_{\text{fus},i}^\circ}{T_{\text{fus}}} - R \ln(a_l)_{\text{id}}} = \frac{\Delta H_{\text{fus},i}^\circ + \varphi_l}{\Delta S_{\text{fus},i}^\circ - R \ln(a_l)_{\text{id}}} \quad (4)$$

Eqn (4) describes the liquidus curve. The symbols represent: φ_l — abbreviation of the expression on the right-hand side of eqn (3), $\Delta S_{\text{fus},i}^\circ$ — the change of entropy of fusion of the l -th component, $(a_l)_{\text{id}}$ — the activity of the l -th component according to the Temkin's model of the perfect ionic solution [17].

Let us now simplify the general relations. With respect to eqns (A) and (B) the cations are Li^+ , Al^{3+} , Na^+ , $k = 3$, the common anion is F^- . If the mole (ionic) fractions of cations are x_1 , x_2 , x_3 , it holds

$$x_1 + x_2 + x_3 = 1 \quad (5)$$

For the component LiF according to eqn (1) and the definition of the quantity φ_l in eqn (4) it holds

$$RT \ln \gamma_1 = (1 - x_1) (x_2 Q_{12} + x_3 Q_{13}) - x_2 x_3 Q_{23} \doteq \varphi_1 \quad (6)$$

According to eqn (A)

$$\nu_l = \nu_i = 1$$

If the mole fractions for the components LiF and Na_3AlF_6 are x_1^* , x_2^* , it is possible to derive further relations

$$x_1^* + x_2^* = 1 \quad (7)$$

The mole (ionic) fractions according to Temkin's model are

$$x_1 = \frac{x_1^*}{x_1^* + 4x_2^*} = \frac{x_1^*}{4 - 3x_1^*} \quad (8)$$

$$x_2 = \frac{x_2^*}{x_1 + 4x_2^*} = \frac{1 - x_1^*}{4 - 3x_1^*} \quad (9)$$

$$x_3 = \frac{3x_2^*}{x_1 + 4x_2^*} = \frac{3(1 - x_1^*)}{4 - 3x_1^*} \quad (10)$$

The relations (8—10) take into account the dissociation equations (A) and (B). From eqns (9), (10), and (5) it holds

$$x_1 + 4x_2 = 1 \quad (11)$$

From eqns (6—11) it holds

$$\varphi_l = (1 - x_1)^2 \frac{1}{4} \left[Q_{12} + 3Q_{13} - \frac{1}{4} Q_{23} \right] \quad (12)$$

The expression in brackets, however, remains unknown. It must be estimated by means of the experimental data.

Calculation of the liquidus course

Let us — for the sake of higher clarity and simplicity — introduce the dimensionless quantities

$$\tau = \frac{T}{T_{\text{fus},l}}; \quad \lambda = \frac{Rv_l}{\Delta H_{\text{fus},l}^\circ}; \quad \xi = \frac{1}{4} \frac{Q_{12} + 3\left(Q_{13} - \frac{1}{4} Q_{23}\right)}{\Delta H_{\text{fus},l}^\circ} \quad (13)$$

Eqns (2), (4), and (13) lead after rearrangement to the dimensionless description of the liquidus curve

$$\tau = \frac{1 + (1 - x_1)^2 \xi}{1 - \lambda \ln x_1} \quad (14)$$

Let us introduce new coordinates

$$Y = \tau[1 - \lambda \ln x_1] - 1; \quad X = (1 - x_1)^2 \quad (15)$$

The transformation of eqn (14) by means of eqn (15) yields the equation of a line

$$Y = \xi X \quad (16)$$

The method of the linear regression can be applied in order to estimate the unknown dimensionless parameter ξ . If this parameter is already estimated, the temperature of the liquidus can be calculated according to the relation

$$T \equiv T_{\text{fus}} \frac{1 + (1 - x_1)^2 \xi}{1 - \lambda \ln x_1} \quad (17)$$

Results

From experimental data [2] $\lambda = 0.356567$, $\xi = 0.17146$, with respect to the linear regression error $\xi = 0.171 \pm 0.006$.

Table 1

Comparison of the experimental [2] and calculated values of the liquidus course in the system $\text{LiF}-\text{Na}_3\text{AlF}_6$

Column 3 — Temkin's model, column 4 — Kozheurov's model

Experimental		Calculated	
$\frac{1}{x_1^*(\text{LiF})}$	$\frac{2}{T/\text{K}}$	$\frac{3}{T/\text{K}}$	$\frac{4}{T/\text{K}}$
0.9975	1116	1117.03	1117.04
0.9950	1113	1113.10	1113.17
0.9925	1109	1109.22	1109.39
0.9900	1106	1105.39	1105.67
0.9800	1092	1090.49	1091.55
0.9700	1080	1076.24	1078.48
0.9600	1068	1062.59	1066.31
0.8600	976	950.96	976.32
0.8500	969	941.67	969.32
$\Sigma \Delta^2$	—	674.18	6.94

The correlation coefficient of the line (16) is $r = 0.995 \pm 0.002$. The experimental data [2] and calculated values according to the experimental and calculated temperature have been evaluated according to the equation

$$\Delta = T_{\text{exp}} - T_{\text{calc}} \quad (18)$$

The columns 1, 2 in Table 1 include the experimental data [2]. The column 3 includes the calculated temperatures (eqn (17)) related to the Temkin's model ($\xi = 0$), the column 4 is related to the Kozheurov's model ($\xi \neq 0$). The last line relates to the eutectic temperature.

The high value of the correlation coefficient, the low sum of the square differences (18), and the good agreement between experimental and calculated temperatures support the application of the theory of regular ionic solutions; furthermore, this makes the dissociation equation (B) acceptable.

This paper is based on a more detailed analysis applying the theory of the regular ionic solution to the molten electrolytes [20, 21].

References

1. Kozheurov, L. A., *Termodinamika metallurgicheskikh shlakov*. (Thermodynamics of Metallurgical Slags.) Metallurgizdat, Sverdlovsk, 1956.
2. Koštenská, I., Čorba, J., and Malinovský, M., *Chem. Zvesti* 28, 546 (1974).
3. Chu, Y. I. and Belyaev, A. I., *Izv. Vyssh. Ucheb. Zaved., Tsvet. Met.* 1959, 59.
4. Holm, J. L., *Thesis*. The Technical University of Norway, Trondheim, 1963; cited from [2].
5. Jenssen, B., *Thesis*. The Technical University of Norway, Trondheim; cited from [2].
6. Kuvakin, M. A., *Zh. Neorg. Khim.* 14, 282 (1969).
7. Matiašovský, K. and Malinovský, M., *Hutn. Listy* 24, 515 (1969).
8. Holm, J. L., *Dr. Thesis*. The Technical University of Norway, Trondheim, 1971; cited from [2].
9. Malinovský, M. and Vrbenská, J., *Collect. Czechoslov. Chem. Commun.* 36, 567 (1961).
10. Grjotheim, K., Krohn, C., Malinovský, M., Matiašovský, K., and Thonstad, J., *Aluminium Electrolysis*, p. 183. Aluminium-Verlag, Düsseldorf, 1982.
11. Grjotheim, K., *Contribution to the Theory of the Aluminium Electrolysis*. Det. Kgl. Norske Vidensk. Selsk. Skr., No. 5. F. Burns Bokhandel, Trondheim, 1956.
12. Frank, W. B. and Foster, L. M., *J. Phys. Chem.* 61, 1531 (1957).
13. Rolin, M. and Bernard, M., *Bull. Soc. Chim. Fr.* 1962, 429.
14. Solomons, C., Clarke, J. H. R., and Bockris, J. O. M., *J. Chem. Phys.* 49, 445 (1968).
15. Řeháková, J., Vrbenská, J., and Malinovský, M., *Chem. Zvesti* 28, 523 (1974).
16. Dewing, E. W., *Met. Trans.* 3, 495 (1972).
17. Dewing, E. W., *Met. Trans.* 3, 2699 (1972).
18. Temkin, M., *Acta Physicochim. USSR* 20, 411 (1945).
19. Malinovský, M. and Kašíková-Svobodová, S., *Sborník vědeckých prací VŠB v Ostravě*. (Collection of Scientific Papers of the Technical University of Mining and Metallurgy in Ostrava.) 18, 33 (1972).
20. Kalousek, J., unpublished results, 1983.
21. Malinovský, M. and Kašíková-Svobodová, S., *Sborník vědeckých prací VŠB v Ostravě*. (Collection of Scientific Papers of the Technical University of Mining and Metallurgy in Ostrava.) Part II, 27 (1985).

Translated by J. Kalousek