

Cryoscopy in Solvents with Dystectic Melting

I. PROKS, V. DANĚK, M. CHRENKOVÁ, F. ŠIMKO, and Z. PÁNEK

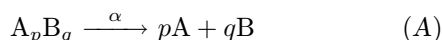
*Institute of Inorganic Chemistry, Slovak Academy of Sciences,
SK-842 36 Bratislava
e-mail: uachdane@savba.sk*

Received 11 June 2001

Theoretical derivation of relations valid for cryoscopic measurements in solvents with dystectic mode of melting, *i.e.* solvents, which undergo at melting a more or less extended thermal dissociation, when chemical reaction between solvent and solute takes place, is presented. When one of the products of this chemical reaction is identical with the product of thermal dissociation of the solvent, the problem of defining the number of “foreign” substances, originating in the reaction between the solvent and the admixture arises. The presented approach shows that the partially dissociated solvent cannot distinguish originating own dissociation products as foreign substances, which made it easier to determine the nature of the probable chemical reaction.

The presented approach is applied in the systems $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3$, $\text{Na}_3\text{AlF}_6\text{—Fe}_2\text{O}_3$, and $\text{Na}_3\text{AlF}_6\text{—Al}(\text{PO}_3)_3$, which are of great importance in the fundamentals of aluminium electrolysis.

In binary systems of alkali metal halides and other metal halides, sulfates, molybdates, tungstates, like NaF—AlF_3 , KF—NbF_5 , $\text{KF—K}_2\text{SO}_4$, *etc.*, originate additive complex compounds, which undergo at melting a more or less extended thermal dissociation according to the general scheme



Evidences of such behaviour for $p = q = 1$ may be found *e.g.* in [1, 2].

Due to the thermal dissociation of the complex compound AB, its liquidus curve exhibits at the temperature of fusion a curvature with the slope at the composition of AB equal to zero. Such phenomenon is called the dystectic mode of melting (Fig. 1). Thus at the temperature of fusion the following equation is fulfilled

$$\left(\frac{dT}{dx_w(\text{AB})} \right)_{x_w(\text{AB})=1} = 0 \quad (\text{1})$$

The radius of curvature of the liquidus curve depends on the degree of dissociation α of the complex compound AB. The flatter is the liquidus curve, the higher is the dissociation degree. Very interesting from the theoretical point of view is the evaluation of cryoscopic measurements made in such solvents, when a chemical reaction takes place between the solvent and solute. In such a case there arises the problem of defining the number of foreign particles in order to determine the nature of the probable chemical reaction.

Typical example of such systems of great technological importance is the system NaF—AlF_3 , in which

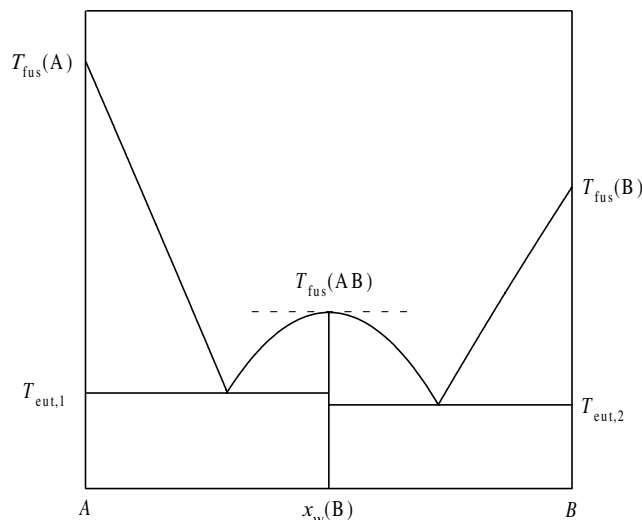


Fig. 1. Phase diagram of the system A—B with dystectic melting of component AB.

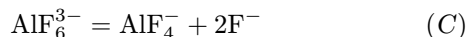
the compound cryolite, Na_3AlF_6 , originates with dystectic mode of melting. The main consumer of cryolite is the aluminium industry, where it serves as solvent for aluminium oxide, the main source of aluminium in the electrochemical production of aluminium, as well as for other oxides introduced into the electrolyte as impurities.

In spite of extensive investigations over six decades the structure of cryolite-based melts is still not sufficiently understood. As it is well known, cryolite undergoes at melting a substantial thermal dissociation.

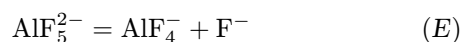
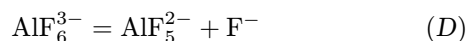
The most accepted dissociation scheme of molten cryolite consists of electrolytic dissociation



and the simultaneous thermal dissociation of the AlF_6^{3-} anion [3]



The thermal dissociation scheme was modified recently by *Dewing* [4] in order to explain some discrepancies in the heat capacity of the NaF—AlF_3 mixtures and the dissociation constant calculated on the basis of thermodynamic [3] and spectroscopic [5] data. *Dewing* proposed the following dissociation mechanism



He also found that AlF_5^{2-} is the most abundant anionic species at the $x(\text{AlF}_3) = 0.333$ composition. The existence of the AlF_5^{2-} anion in the liquid state was also postulated by *Xiang* and *Kvande* [6] on the basis of liquidus temperature calculations and by *Gilbert* and *Materne* [7] using Raman spectroscopy. An attempt to confirm the presence of AlF_5^{2-} anion in the MF—AlF_3 ($M = \text{Li, Na, K}$) melts on the basis of vapour pressure measurements was also made by *Hehua Zhou* [8].

However, when dissolving some compounds like metal oxides in cryolite, besides formation of new compounds due to the chemical reactions between cryolite and the solute, also the formation of compounds identical with cryolite dissociation products may occur, regardless of the accepted dissociation scheme of cryolite. The theoretical derivation of relations valid for cryoscopic measurements in such systems is the aim of the present paper.

THEORETICAL

Let us consider the dissolution of admixture X in the dystectically melting solvent AB. The course of the liquidus curve of substance AB in the system AB—X (Fig. 2) is described by the LeChatelier—Shreder equation, which in the limit for $x_r(\text{AB}) \rightarrow 1$ we can write in the differential form

$$\begin{aligned} \lim_{x_r(\text{AB}) \rightarrow 1} \frac{dx_r(\text{AB})}{x_r(\text{AB})} \frac{1}{dT} &= \lim_{x_r(\text{AB}) \rightarrow 1} \frac{\Delta_{\text{fus}}H(\text{AB}, T)}{RT^2} = \\ &= \frac{\Delta_{\text{fus}}H(\text{AB}, T_{\text{fus}}(\text{AB}))}{RT_{\text{fus}}^2(\text{AB})} = K_{\text{td}} \end{aligned} \quad (2)$$

where $x_r(\text{AB})$ is the real mole fraction of solvent AB (*i.e.* equilibrium activity) and $T_{\text{fus}}(\text{AB})$ and

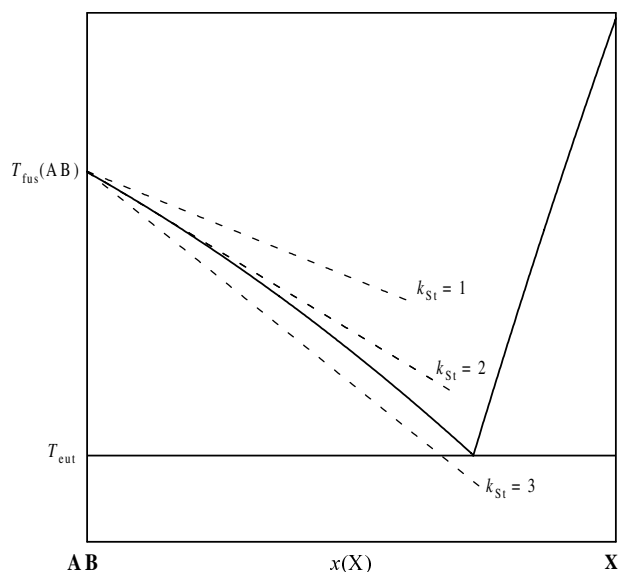


Fig. 2. Phase diagram of the system AB—X with dystecting melting of component AB and chemical reaction between solvent AB and solute X.

$\Delta_{\text{fus}}H(\text{AB}, T_{\text{fus}}(\text{AB}))$ is the temperature and enthalpy of fusion of AB, respectively. Turning over and extending eqn (2) we get

$$\begin{aligned} \lim_{x_r(\text{AB}) \rightarrow 1} \frac{dT}{dx_r(\text{AB})} x_r(\text{AB}) &= \\ &= \lim_{x_r(\text{AB}) \rightarrow 1} \frac{dT}{dx_w(\text{AB})} \frac{dx_w(\text{AB})}{dx_r(\text{AB})} = \frac{1}{K_{\text{td}}} \end{aligned} \quad (3)$$

Now we have to examine the behaviour of $x_r(\text{AB})$ with regard to $x_w(\text{AB})$, *i.e.* the weighted-in mole fraction of solvent AB, in the limiting region $x_w(\text{AB}) \rightarrow 1$, when X reacts with AB under formation of new, foreign compounds and compounds identical with the products of thermal dissociation of AB *e.g.* according to the scheme $\text{AB} + \text{X} = \text{AX} + \text{B}$. The increase of the activity of substance AB caused by reaction of 1 mol of admixture X with substance AB is denoted by l (l is nonzero only when AB melts dystectically) and the decrease of the activity of substance AB caused by reaction of 1 mol of admixture X with substance AB is denoted as m . For $x_r(\text{AB})$ we get

$$\begin{aligned} \lim_{x_w(\text{AB}) \rightarrow 1} x_r(\text{AB}) &= \\ &= \lim_{x_w(\text{AB}) \rightarrow 1} \left(x_w(\text{AB}) + l[1 - x_w(\text{AB})] - \right. \\ &\quad \left. - m[1 - x_w(\text{AB})] \right) / \left(x_w(\text{AB}) + l[1 - x_w(\text{AB})] - \right. \\ &\quad \left. - m[1 - x_w(\text{AB})] + k_{\text{St}}[1 - x_w(\text{AB})] \right) = \\ &= \lim_{x_w(\text{AB}) \rightarrow 1} \left(x_w(\text{AB}) + \varepsilon[1 - x_w(\text{AB})] \right) / \\ &\quad \left(x_w(\text{AB}) + \varepsilon[1 - x_w(\text{AB})] + k_{\text{St}}[1 - x_w(\text{AB})] \right) = \end{aligned}$$

$$= \frac{x_w(\text{AB})}{x_w(\text{AB})} = 1 \quad (4)$$

where $l - m = \varepsilon$. In the limiting region it is thus possible to substitute $x_r(\text{AB})$ by $x_w(\text{AB})$. Eqn (3) then transforms into the form

$$\lim_{x_w(\text{AB}) \rightarrow 1} \frac{dT}{dx_w(\text{AB})} = \lim_{x_w(\text{AB}) \rightarrow 1} \frac{dx_r(\text{AB})}{dx_w(\text{AB})} \frac{1}{K_{td}} \quad (5)$$

or

$$\lim_{x_w(\text{AB}) \rightarrow 1} \frac{dT}{dx_w(\text{AB})} K_{td} = \lim_{x_w(\text{AB}) \rightarrow 1} \frac{dx_r(\text{AB})}{dx_w(\text{AB})} \quad (6)$$

The right side of eqn (6) can be expressed in the form

$$\begin{aligned} \lim_{x_w(\text{AB}) \rightarrow 1} x_r(\text{AB}) &= \lim_{x_w(\text{AB}) \rightarrow 1} \frac{x_w(\text{AB}) + \varepsilon[1 - x_w(\text{AB})]}{x_w(\text{AB}) + \varepsilon[1 - x_w(\text{AB})] + k_{St}[1 - x_w(\text{AB})]} = \\ &= \lim_{x_w(\text{AB}) \rightarrow 1} \frac{x_w(\text{AB}) + \varepsilon[1 - x_w(\text{AB})]}{F} \quad (7) \end{aligned}$$

Differentiating eqn (7) according to $x_w(\text{AB})$ we get

$$\begin{aligned} \frac{dx_r(\text{AB})}{dx_w(\text{AB})} &= \\ &= \frac{1}{F} - \frac{x_w(\text{AB})F'}{F^2} - \frac{\varepsilon}{F} - \frac{\varepsilon[1 - x_w(\text{AB})]F'}{F^2} = \\ &= \frac{F - F'x_w(\text{AB}) - \varepsilon F - F'\varepsilon[1 - x_w(\text{AB})]}{F^2} \quad (8) \end{aligned}$$

and in the limiting region

$$\begin{aligned} \lim_{x_w(\text{AB}) \rightarrow 1} \frac{dx_r(\text{AB})}{dx_w(\text{AB})} &= \\ &= \lim_{x_w(\text{AB}) \rightarrow 1} \frac{F(1 - \varepsilon) - F'\{x_w(\text{AB}) + \varepsilon[1 - x_w(\text{AB})]\}}{F^2} \quad (9) \end{aligned}$$

For F and its first derivative in the limiting region we get

$$\begin{aligned} \lim_{x_w(\text{AB}) \rightarrow 1} F &= \\ &= \lim_{x_w(\text{AB}) \rightarrow 1} \{x_w(\text{AB}) + \varepsilon[1 - x_w(\text{AB})] + \\ &\quad + k_{St}[1 - x_w(\text{AB})]\} = 1 \quad (10) \end{aligned}$$

$$\lim_{x_w(\text{AB}) \rightarrow 1} F' = 1 - \varepsilon - k_{St} \quad (11)$$

and finally for eqn (9)

$$\lim_{x_w(\text{AB}) \rightarrow 1} \frac{dx_r(\text{AB})}{dx_w(\text{AB})} = \frac{1 - \varepsilon - (1 - \varepsilon - k_{St})}{1} = k_{St} \quad (12)$$

The derivative on the left side of eqn (12) is not necessary to calculate separately. Its value is always equal to the number of new substances (k_{St}) originating in the reaction between the solvent AB and the admixture X, distinguishable from the dissociation products of the solvent AB. However, it is necessary to choose such reaction scheme between AB and X for which k_{St} equals the left side of the experimentally determined value of eqn (6).

APPLICATIONS

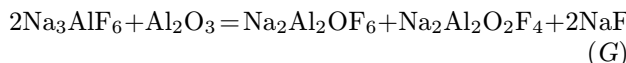
In the application of the proposed thermodynamic approach to cryolite-based melts the general dissociation scheme expressed by eqn (A) transforms into the form (*cf.* dissociation (C))



In the following examples we will confront the common approach with the new one with regard to the above dissociation scheme of cryolite.

a) System $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3$

The melts of the system $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3$ are the basis of the electrolyte used in the aluminium production. The most accepted phase diagram of this system is that published by *Chin and Hollingshead* [9]. According to the recent Raman spectroscopic investigation performed by *Robert et al.* [10] and direct oxygen LECO analysis carried out by *Daněk et al.* [11], aluminium oxide dissolves in cryolite under the formation of two main oxyfluoroaluminates, $\text{Na}_2\text{Al}_2\text{O}_2\text{F}_4$ and $\text{Na}_2\text{Al}_2\text{OF}_6$, according to the general scheme



which indicates the introduction of two new substances when 1 mol of Al_2O_3 is dissolved in an infinite amount of cryolite, *i.e.* $k_{St} = 2$. The phase diagram of this system according to [9] and the calculated slopes of the liquidus curves for three chosen k_{St} are shown in Fig. 3. The material balance involving the above reaction is as follows.

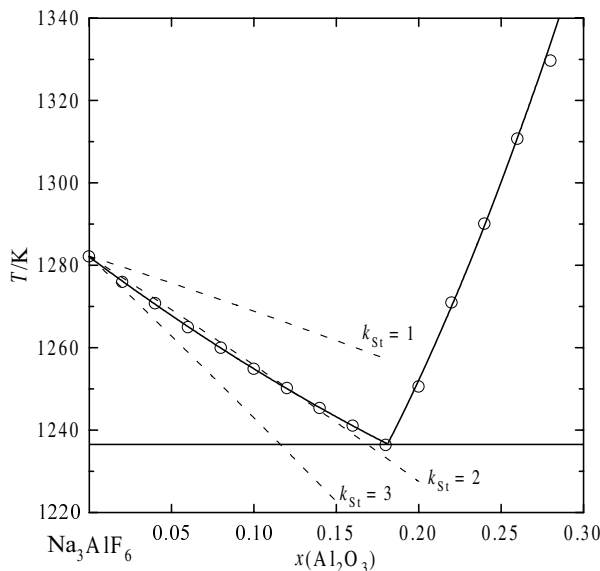


Fig. 3. Phase diagram of the system $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3$ according to [9].

Let us consider 1 mol of mixture with the composition $x_1(=x_w(\text{Na}_3\text{AlF}_6))$ mol $\text{Na}_3\text{AlF}_6 + x_2(=x_w(\text{X}))$ mol Al_2O_3 , where $x_2 \ll x_1$. Cryolite dissociates according to reaction (C) with the dissociation degree α . The dissolution of Al_2O_3 in cryolite is accompanied with the reaction (G). At equilibrium we get the following amounts of the individual substances

$$\begin{aligned} n(\text{Na}_3\text{AlF}_6) &= [(1-\alpha)x_1 - 2x_2] \text{ mol} \\ n(\text{NaAlF}_4) &= \alpha x_1 \text{ mol} \\ n(\text{NaF}) &= (2\alpha x_1 + 2x_2) \text{ mol} \\ n(\text{Na}_2\text{Al}_2\text{OF}_6) &= x_2 \text{ mol} \\ n(\text{Na}_2\text{Al}_2\text{O}_2\text{F}_4) &= x_2 \text{ mol} \end{aligned}$$

The total amount of all substances is $\sum n_i = [x_1(1+2\alpha) + 2x_2]$ mol. Since we are in the region of diluted solutions, the mole fractions can be set equal to the activities, *i.e.* the real mole fractions of substances. For the real mole fraction of cryolite we then get

$$\begin{aligned} x_r(\text{Na}_3\text{AlF}_6) &= \\ &= \frac{n(\text{Na}_3\text{AlF}_6) + n(\text{NaAlF}_4) + n(\text{NaF})}{\sum n_i} = \\ &= \frac{x_1(1+2\alpha)}{x_1(1+2\alpha) + 2x_2} \end{aligned} \quad (13)$$

Differentiating eqn (13) according to x_1 and inserting the limiting conditions ($x_1 = 1, x_2 = 0$) we get

$$\begin{aligned} \lim_{x_r(\text{Na}_3\text{AlF}_6) \rightarrow 1} \left(\frac{\partial x_r(\text{Na}_3\text{AlF}_6)}{\partial x_1} \right) &= \\ &= \frac{(1+2\alpha)(x_1+2x_1\alpha+2x_2) - (x_1+2x_1\alpha)(1+2\alpha-2)}{(x_1+2x_1\alpha+2x_2)^2} = \\ &= \frac{(1+2\alpha)(1+2\alpha) - (1+2\alpha)(2\alpha-1)}{(1+2\alpha)^2} = \\ &= \frac{2}{(1+2\alpha)} = k_{\text{St}} \end{aligned} \quad (14)$$

Since α attains at 1000°C the value of 0.3 [12], the Stortenbecker's correction factor equals 1.25, which is different from the expected value. Such procedure obviously does not lead to the correct result.

However, as it follows from the theoretical chapter, it is not necessary to take into account the dissociation of cryolite in the calculation of k_{St} , since at the infinite dilution the solvent does not distinguish the originating dissociation product of cryolite as a foreign species. The material balance according to the proposed approach is thus as follows.

The equilibrium amounts of individual substances are then

$$\begin{aligned} n(\text{Na}_3\text{AlF}_6) &= (x_1 - 2x_2 + 2\epsilon x_2) \text{ mol} \\ n(\text{Na}_2\text{Al}_2\text{OF}_6) &= x_2 \text{ mol} \\ n(\text{Na}_2\text{Al}_2\text{O}_2\text{F}_4) &= x_2 \text{ mol} \end{aligned}$$

The total amount of all substances is $\sum n_i = (x_1 + 2\epsilon x_2)$ mol. For the real mole fraction of cryolite we then get the relation

$$\begin{aligned} \lim_{x_1 \rightarrow 1} x_r(\text{Na}_3\text{AlF}_6) &= \frac{n(\text{Na}_3\text{AlF}_6)}{\sum n_i} = \\ &= \frac{x_1 - 2x_2(1-\epsilon)}{x_1 + 2\epsilon x_2} \end{aligned} \quad (15)$$

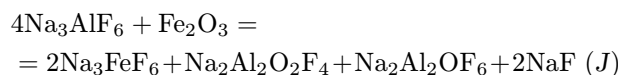
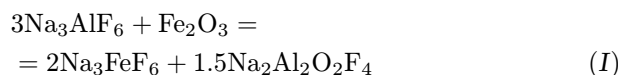
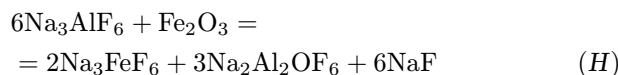
Differentiating eqn (15) according to x_1 and inserting the limiting conditions ($x_1 = 1, x_2 = 0$) we get

$$\begin{aligned} \lim_{x_1 \rightarrow 1} \left(\frac{\partial x_r(\text{Na}_3\text{AlF}_6)}{\partial x_1} \right) &= \\ &= \frac{(1+2(1-\epsilon))(x_1+2\epsilon x_2) - (x_1-2x_2(1-\epsilon))(1-2\epsilon)}{(1+2\epsilon x_2)^2} = \\ &= 2 = k_{\text{St}} \end{aligned} \quad (16)$$

which is in a very good agreement with the experimentally determined value $k_{\text{St}} = 1.99$. This means that 1 mol of Al_2O_3 introduces into infinite amount of cryolite 2 new species, which is in accordance with the assumed reaction (G). The new species are the compounds $\text{Na}_2\text{Al}_2\text{OF}_6$ and $\text{Na}_2\text{Al}_2\text{O}_2\text{F}_4$, since NaF is in cryolite already present due to its thermal dissociation.

b) System Na_3AlF_6 — Fe_2O_3

Fe_2O_3 is introduced into the aluminium electrolyte with raw materials, as well as due to the corrosion of cathode current rods. When dissolved in the electrolyte, Fe_2O_3 reacts with cryolite under formation of Na_3FeF_6 and oxyfluoroaluminates $\text{Na}_2\text{Al}_2\text{OF}_6$ and $\text{Na}_2\text{Al}_2\text{O}_2\text{F}_4$ [13, 14]. The phase diagram of the system was recently measured by *Diep* [13] and by *Šimko* and *Daněk* [14]. The latter authors proposed for the dissolution of Fe_2O_3 in cryolite three different reactions



depending on the concentration of the dissolved Fe_2O_3 . The phase diagram of this system according to [14] and the calculated slopes of the liquidus curves for three chosen k_{St} are shown in Fig. 4.

Using the same procedure as shown in section a), for reactions (H—J) we will obtain different values of the Stortenbecker's correction factor. Consequently, taking into account the degree of thermal dissociation

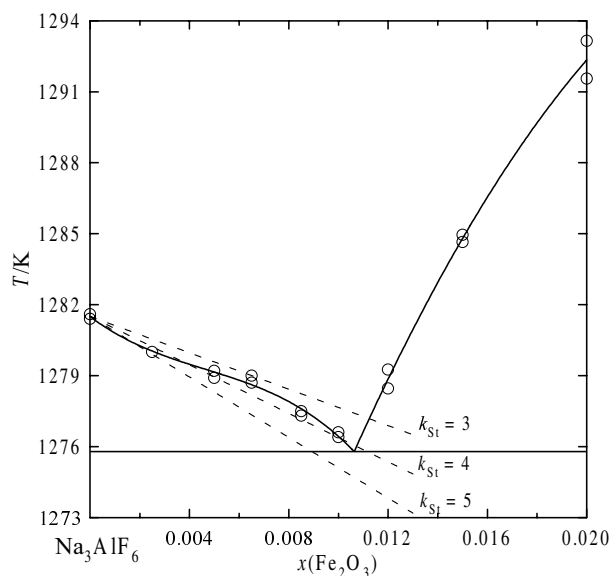
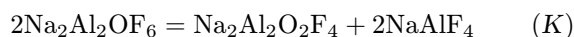


Fig. 4. Phase diagram of the system $\text{Na}_3\text{AlF}_6\text{—Fe}_2\text{O}_3$ according to [14].

of cryolite ($\alpha = 0.3$) we will obtain *e.g.* for the reaction (H) $k_{\text{St}} = 3.1$, which does not agree with the expected value $k_{\text{St}} = 5$. On the other hand, if the degree of thermal dissociation of cryolite is omitted the above-mentioned correct value is obtained, which is in a good agreement with the experimentally determined value $k_{\text{St}} = 5.37$. This means that for reaction (H) 1 mol of Fe_2O_3 introduces into the infinite amount of cryolite 5 new species, which is in accordance with the assumed reaction (H). The new species are two molecules of Na_3FeF_6 and three molecules of $\text{Na}_2\text{Al}_2\text{OF}_6$, since NaF is in cryolite already present due to its thermal dissociation.

Similar procedure can be done also for reaction (I), where the calculation yields $k_{\text{St}} = 3.5$, *i.e.* 2 mol of Na_3FeF_6 and 1.5 mol of $\text{Na}_2\text{Al}_2\text{O}_2\text{F}_4$. For reaction (J) the calculation results in $k_{\text{St}} = 4$, *i.e.* 2 mol of Na_3FeF_6 , 1 mol of $\text{Na}_2\text{Al}_2\text{O}_2\text{F}_4$, and 1 mol of $\text{Na}_2\text{Al}_2\text{OF}_6$. The equilibrium between both oxyfluoroaluminates, $\text{Na}_2\text{Al}_2\text{OF}_6$ and $\text{Na}_2\text{Al}_2\text{O}_2\text{F}_4$, is determined by the reaction [11]



c) System $\text{Na}_3\text{AlF}_6\text{—Al}(\text{PO}_3)_3$

The presence of phosphorus in the aluminium cell is unwanted since it lowers the current efficiency of the process and the quality of produced metal. Phosphorus is introduced into the aluminium electrolyte together with raw materials in the form of different phosphates. One of the probable phosphorus compounds is $\text{Al}(\text{PO}_3)_3$. According to the results of cryoscopic measurements performed by *Chrenková et al.* [15], the

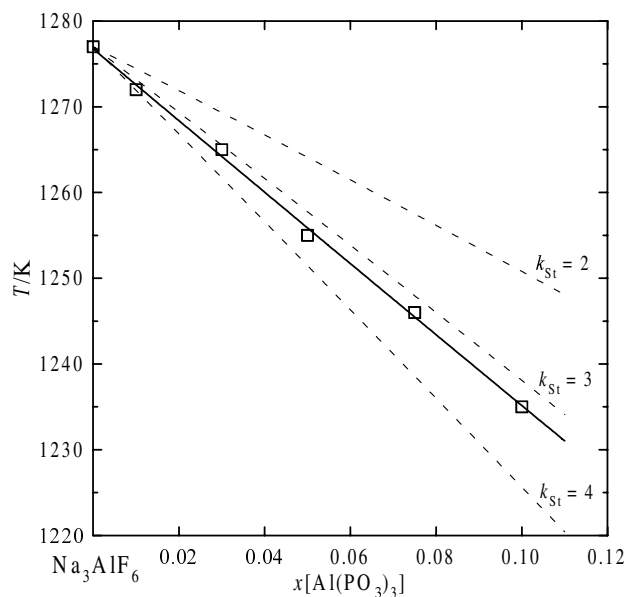
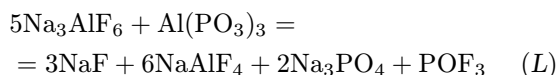


Fig. 5. Cryoscopy in the system $\text{Na}_3\text{AlF}_6\text{—Al}(\text{PO}_3)_3$ according to [15].

reaction between cryolite and $\text{Al}(\text{PO}_3)_3$ can be described by the reaction scheme



which indicates the introduction of three new substances when 1 mol of $\text{Al}(\text{PO}_3)_3$ is dissolved in an infinite amount of cryolite, *i.e.* $k_{\text{St}} = 3$. The liquidus curve of cryolite in the phase diagram of this system according to [15] and the calculated slopes of the liquidus curves for three chosen k_{St} are shown in Fig. 5. Analogically to the previous systems, the correct values of k_{St} are obtained when the dissociation degree of cryolite is not included into the calculation of k_{St} . In such manner calculated value $k_{\text{St}} = 3$ for reaction (L) is close to the experimentally determined value $k_{\text{St}} = 3.3$ [14], in contradiction to the value $k_{\text{St}} = 1.9$, when dissociation degree of cryolite is included into the calculation. This means that 1 mol of $\text{Al}(\text{PO}_3)_3$ introduces into the infinite amount of cryolite 3 new species, *i.e.* 2 mol of Na_3PO_4 and 1 mol of POF_3 . In the very diluted solutions of $\text{Al}(\text{PO}_3)_3$ in cryolite the originating POF_3 remains physically dissolved, while at higher $\text{Al}(\text{PO}_3)_3$ concentrations POF_3 escapes from the melt. This observation is in full agreement also with the results of mass loss measurements in this system [14].

CONCLUSION

The evaluation of cryoscopic measurements in solvents with dystectic mode of melting, accompanied with chemical reaction between solvent and solute under formation of new compounds and the products

of the thermal dissociation of the solvent, yields correct results only when the thermal dissociation of the solvent is not incorporated into the material balance of the considered reaction scheme. This is due to the fact that the solvent does not distinguish the product of thermal dissociation from the identical product of chemical reaction.

Acknowledgements. The present work was financially supported by the Scientific Grant Agency VEGA of the Ministry of Education of the Slovak Republic and the Slovak Academy of Sciences under the No. 2/1032/21.

SYMBOLS

$x_r(\text{AB})$	real mole fraction of solvent AB (equilibrium activity)
$x_w(\text{AB})$	weighted-in mole fraction of solvent AB
$x_w(\text{X})$	weighted-in mole fraction of solute X
k_{St}	Stortenbecker's correction factor (number of new compounds different from dissociation products of solvent AB introduced into the system by the solute X)
l	increase of the amount of solvent AB caused by reaction of 1 mol of admixture X with solvent AB (l is nonzero only when AB in the presence of reaction products with X melts dystectically)
m	decrease of the amount of solvent AB caused by reaction of 1 mol of admixture X with solvent AB
α	degree of thermal dissociation of the solvent AB
T	thermodynamic temperature
$T_{\text{fus}}(\text{AB})$	temperature of fusion of solvent AB
$\Delta_{\text{fus}}H(\text{AB}, T_{\text{fus}}(\text{AB}))$	enthalpy of fusion of solvent AB at its temperature of fusion
$\Delta_{\text{fus}}H(\text{AB}, T)$	enthalpy of fusion of solvent AB at temperature T

R	gas constant
K_{td}	constant of thermal depression of the solvent AB

REFERENCES

1. Daněk, V. and Cekovský, R., *Chem. Pap.* 46, 161 (1992).
2. Daněk, V. and Proks, I., *J. Mol. Liq.* 83, 65 (1999).
3. Grjotheim, K., Krohn, C., Malinovský, M., Matiašovský, K., and Thonstad, J., *Aluminium Electrolysis: The Chemistry of the Hall-Héroult Process*. Chap. 3, p. 75. Aluminium-Verlag, Düsseldorf, 1977.
4. Dewing, E. W., *Proc. Electrochem. Soc.* 86, 262 (1986).
5. Gilbert, B., Mamantov, G., and Begun, G. M., *J. Chem. Phys.* 62, 950 (1975).
6. Xiang, F. N. and Kvande, H., *Acta Chem. Scand.* A40, 622 (1986).
7. Gilbert, B. and Materne, T., *Appl. Spectrosc.* 44, 299 (1990).
8. Hehua Zhou, *Dr. Ing. Thesis No. 63*. Institute of Inorganic Chemistry, Norwegian Institute of Technology, Trondheim, 1991.
9. Chin, D. A. and Hollingshead, E. A., *J. Electrochem. Soc.* 113, 736 (1966).
10. Robert, E., Olsen, J. E., Daněk, V., Tixhon, E., Østvold, T., and Gilbert, B., *J. Phys. Chem.* B101, 9447 (1997).
11. Daněk, V., Gustavson, Ø. T., and Østvold, T., *Can. Metall. Quart.* 39, 153 (2000).
12. Grjotheim, K., Krohn, C., Malinovský, M., Matiašovský, K., and Thonstad, J., *Aluminium Electrolysis. Fundamentals of the Hall-Héroult Process*. 2nd Edition. Aluminium-Verlag, Düsseldorf, 1982.
13. Diep, B. Q., *Dr. Ing. Thesis*. Department of Electrochemistry, Norwegian University of Science and Technology, Trondheim, 1998.
14. Šimko, F. and Daněk, V., *Chem. Pap.*, in press.
15. Chrenková, M., Silný, A., Daněk, V., and Staš, M., *Chem. Pap.*, in press.