Thermodynamic Calculation of Phase Diagrams of Systems in which One Component Undergoes Thermal Dissociation

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Thermodynamically consistent calculation of the phase diagram of systems, in which one component thermally dissociates, is proposed. For the calculation of the activity of the component, undergoing thermal dissociation, the standard state of the dissociated pure compound was chosen. The expressions for the activity of components were derived.

The proposed thermodynamic approach was verified by calculation of the phase diagram of the systems $MF-M_2SO_4$ (M = Na, K), where the congruently melting compounds M_3FSO_4 are formed. It was found that the degrees of thermal dissociation of these compounds, calculated in the proposed way, attain the values $\alpha_*(Na_3FSO_4) = 0.71$ and $\alpha_*(K_3FSO_4) = 0.76$, which are the same values as obtained by means of conventional methods.

In the binary systems of alkali metal fluorides and other salts of alkali metals, such as sulfates, chromates, molybdates, tungstates, transition metal fluorides, *etc.*, complex compounds like Na_3FSO_4, K_3FMoO_4, K_3TiF_7, K_3ZrF_7, *etc.* are formed. These compounds exhibit a lowered symmetry of the crystal structure probably due to either the repulsive forces of both anions or the lowered symmetry of the coordination sphere of the central atom of the complex anion. Owing to this fact and obviously to a relatively high energetic state such compounds undergo often at melting a more or less extended thermal dissociation, in some cases they melt even incongruently. Evidence of such behaviour may be found *e.g.* in [1, 2].

The calculation of the phase diagrams of systems, in which one component undergoes thermal dissociation at melting was treated till now in three different ways.

Grjotheim [3] used the model of *Roozeboom* and *Aten* [4] and other authors and chose for systems mentioned above the standard state of the hypothetical fluid comprised in the undissociated component only and according to *Kremann* [5] he introduced the hypothetical temperature and heat of fusion of such substance.

Brynestad [6] improved the preceding approach introducing formally two chemical equilibria between undissociated compound in solid and liquid phases and between solid undissociated compound and the products of dissociation in the melt. From the physical point of view this approach is not exactly correct since both chemical equilibria may not be considered as independent.

Bale and *Pelton* [2] used the theory of regular solutions and using the transformation of coordinates they obtained for the pure component undergoing the dissociation the unique activity. They did not consider the thermal dissociation of this component.

In the present work the thermodynamic analysis of this problem was solved in a new, physically more realistic way.

THEORETICAL

Let us consider a melt formed from $y(ABw,T)$ mol of the substance AB and $(1 - y(ABw,T))$ mol of the substance A ($y(ABw,T)$ denotes the weighed-in substance AB). Assuming the substance AB dissociates according to the scheme

$$AB \overset{\alpha}{=} A + B \qquad (A)$$
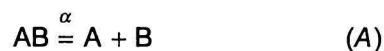
$(1 - \alpha(T))$ mol of the undissociated constituent ABu, $\alpha(T)$ mol of the constituent A and simultaneously $\alpha(T)$ mol of the constituent B originate from 1 mol of the component AB. In the next we shall strictly distinguish between the weighed-in substance ABw, which we call component, and the dissociation products ABu, A, B, which we call constituents.

For the equilibrium mole fractions of the constituents in the mixture we get from the material balance

$$x(ABu,eq,T) = \frac{y(ABw,T) \cdot (1 - \alpha(T))}{1 + \alpha(T) \cdot y(ABw,T)} \qquad (1)$$

$$x(A,eq,T) = \frac{1 - y(ABw,T) \cdot (1 - \alpha(T))}{1 + \alpha(T) \cdot y(ABw,T)} \qquad (2)$$

$$x(B,eq,T) = \frac{\alpha(T) \cdot y(ABw,T)}{1 + \alpha(T) \cdot y(ABw,T)} \qquad (3)$$

At equilibrium the chemical potentials of components in the solid and liquid phases are equal, and for the dissociated component ABw in the mixture we get

$$\mu^\circ(ABw,s,T) = \mu(ABw,dis,l,T) \qquad (4)$$

where

$$\mu(ABw,dis,l,T) = (1 - \alpha(T))\cdot\mu(ABu,eq,T) + \\ + \alpha(T)\cdot\mu(A,eq,T) + \alpha(T)\cdot\mu(B,eq,T) \qquad (5)$$

As the standard state the "PURE DISSOCIATED COMPONENT AB IN THE UNDERCOOLED LIQUID AT THE TEMPERATURE T" (marked with asterisk) is chosen for all constituents. Then for the chemical potential of the undissociated constituent ABu in the mixture we get

$$\mu(ABu,eq,T) = \mu^*(ABu,eq,T) + \\ + RT\ln a_{rel}(ABu,eq,T) = \\ = \mu^*(ABu,eq,T) + RT\ln\frac{f(ABu,eq,T)}{f_*(ABu,eq,T)} = \\ = \mu^*(ABu,eq,T) + RT\ln\frac{\dfrac{f(ABu,eq,T)}{f_o(ABu,eq,T)}}{\dfrac{f_*(ABu,eq,T)}{f_o(ABu,eq,T)}} = \\ = \mu^*(ABu,eq,T) + RT\ln\frac{a(ABu,eq,T)}{a_*(ABu,eq,T)} = \\ = \mu^*(ABu,eq,T) + RT\ln a_{rel}(ABu,eq,T) \qquad (6)$$

With "o" we denoted the hypothetical "PURE UNDIS-SOCIATED MOLTEN CONSTITUENT AB AT THE TEMPERATURE T". Analogous equations we get for $\mu(A,T)$ and $\mu(B,T)$

$$\mu(A,T) = \mu^*(A,T) + RT\ln a_{rel}(A,T) \qquad (7)$$

and

$$\mu(B,T) = \mu^*(B,T) + RT\ln a_{rel}(B,T) \qquad (8)$$

Assuming the mixtures behave ideally $a(i,eq,T) = x(i,eq,T)$ and $a_*(i,eq,T) = x_*(i,eq,T)$ and for the equilibrium activities of the constituents ABu, A, B in the mixture the following relations are valid

$$a_{rel}(ABu,eq,T) = \frac{x(ABu,eq,T)}{x_*(ABu,eq,T)} = \\ = \frac{\dfrac{y(ABw,T)\cdot(1-\alpha(T))}{1+\alpha(T)\cdot y(Bw,T)}}{\dfrac{1-\alpha_*(T)}{1+\alpha_*(T)}} \qquad (9)$$

$$a_{rel}(A,eq,T) = \frac{x(A,eq,T)}{x_*(A,eq,T)} = \\ = \frac{\dfrac{1-y(ABw,T)\cdot(1-\alpha(T))}{1+\alpha(T)\cdot y(ABw,T)}}{\dfrac{\alpha_*(T)}{1+\alpha_*(T)}} \qquad (10)$$

$$a_{rel}(B,eq,T) = \frac{x(B,eq,T)}{x_*(B,eq,T)} = \\ = \frac{\dfrac{\alpha(T)\cdot y(ABw,T)}{1+\alpha(T)\cdot y(ABw,T)}}{\dfrac{\alpha_*(T)}{1+\alpha_*(T)}} \qquad (11)$$

where $x_*(i,eq,T)$ are the equilibrium mole fractions of constituents A, B, and ABu in the pure molten undercooled component ABw and $\alpha_*(T)$ is the dissociation degree of the pure component ABw at the temperature T.

For the chemical potential of the to chemical equilibrium dissociated component ABw in the mixture (denotation "dis"), which is at the temperature T in equilibrium with the crystalline compound AB, the following relation may be written

$$\mu(ABw,dis,l,T) = \mu^*(ABw,dis,l,T) + \\ + RT\ln a_{rel}(ABw,dis,l,T) \qquad (12)$$
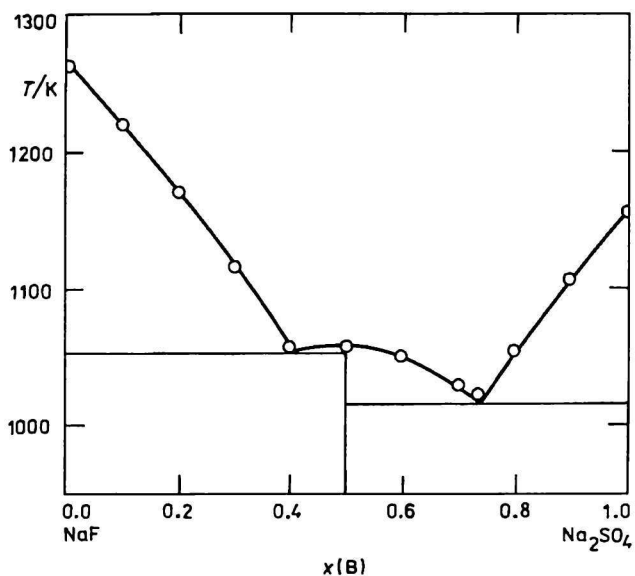
Introducing eqns (6—8) and (12) into eqn (5) we get

Fig. 1. Phase diagram of the system NaF—Na$_2$SO$_4$ calculated for the dissociation degree $\alpha_*(Na_3FSO_4) = 0.71$. ○ Experimental [8] , —— calculated, $\sigma = 3$ K.

$$\mu^*(ABw,dis,l,T) + RT \ln a_{rel}(ABw,dis,l,T) =$$
$$= (1 - \alpha(T)) \cdot \mu^*(ABu,eq,T) + \alpha(T) \cdot$$
$$\cdot \mu^*(A,eq,T) + \alpha(T) \cdot \mu^*(B,eq,T) +$$
$$+ RT \cdot (1 - \alpha(T)) \cdot \ln a_{rel}(ABu,eq,T) +$$
$$+ \alpha(T) \cdot \ln a_{rel}(A,eq,T) + \alpha(T) \cdot$$
$$\cdot \ln a_{rel}(B,eq,T) \qquad (13)$$

and for the activity of the dissociated component AB in the mixture we obtain the final equation

$$a_{rel}(ABw,dis,l,T) = a_{rel}(ABu,eq,T)^{(1 - \alpha(T))} \cdot$$
$$\cdot a_{rel}(A,eq,T)^{\alpha(T)} \cdot a_{rel}(B,eq,T)^{\alpha(T)} \qquad (14)$$

where the equilibrium relative activity of the constituent ABu is given by eqn (9) and the equilibrium relative activities of the constituents A and B are similarly given by eqns (10) and (11). The dissociation degrees a and α_* are related to the equilibrium constant of the dissociation reaction

$$K(T) = \frac{x_*(A,eq,T) \cdot x_*(B,eq,T)}{x_*(ABu,eq,T)} =$$

$$= \frac{\alpha_*^2(T)}{1 - \alpha_*^2(T)} =$$

$$= \frac{x(A,eq,T) \cdot x(B,eq,T)}{x(ABu,eq,T)} =$$

$$= \frac{\alpha(T) \cdot (1 - y(ABw,T) + \alpha(T) \cdot y(ABw,T))}{(1 - \alpha(T))(1 + \alpha(T) \cdot y(ABw,T))} \qquad (15)$$

Using relation (14) we also simplify eqn (13) to the form

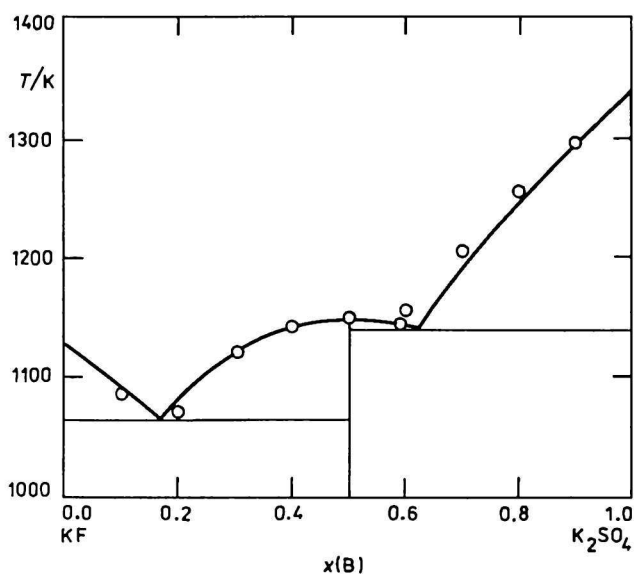Fig. 2. Phase diagram of the system KF—K_2SO_4 calculated for the dissociation degree $\alpha_*(K_3FSO_4) = 0.76$. $\bigcirc$ Experimental [8], —— calculated, $\sigma = 8$ K.

$$a_{rel}(ABw,dis,l,T) = a_{rel}(ABu,eq,T) \qquad (16)$$

The activity of the component A in the mixture, because its standard state is the pure liquid A, is given by the simple relation (see eqn (2))

$$a(A,l,T) = x(A,eq,T) \qquad (17)$$

For the activities of components A and ABw, defined in such a way, with respect to eqns (4—6), the LeChatelier—Shreder's equation may be derived

$$\left[\frac{d \ln a(i,l,T)}{dT} \right]_{p,eq} = \frac{\Delta H(fus,exp,i,T)}{RT^2} \qquad (18)$$

where $\Delta H(fus,exp,i,T)$ is the experimental enthalpy of fusion of components A and ABw, respectively.

The integrated relation (18) enables one to calculate the dissociation degree of the component ABw by fitting the calculated temperatures of primary crystallization T_{eq} for the chosen values of $\alpha_*(T)$ with those determined experimentally.

RESULTS AND DISCUSSION

The verification of the proposed thermodynamic approach was performed by the calculation of the phase diagrams of the systems NaF—Na_2SO_4 and KF—K_2SO_4. In these systems the additive compounds Me_3FSO_4 are formed. The degree of thermal dissociation of these compounds was calculated quite recently in two different ways [7]:

i) by fitting the phase diagrams using the Grjotheim's [3] approach,

ii) by fitting the density isotherms of these systems assuming the ideal behaviour in the volume properties.

In [7] it was found that the degrees of thermal dissociation, calculated from the phase diagrams, measured by Julsrud and Kleppa [8], attain the values $\alpha_*(Na_3FSO_4) = 0.71$ and $\alpha_*(K_3FSO_4) = 0.76$. The dependence of the dissociation constant on temperature was neglected.

The phase diagrams of the systems NaF—Na_2SO_4 and KF—K_2SO_4, calculated using the proposed thermodynamic approach, together with the published experimental temperatures of primary crystallization [8], are shown in Figs. 1 and 2, respectively. The values of the enthalpies of fusion of the pure components were taken from [8], while those for the additive compounds M_3FSO_4 were taken from [9, 10]. The enthalpy of mixing was not considered in the calculation.

As it is seen from the figures, a very good agreement between the calculated and experimental temperatures of primary crystallization was attained for

the values of thermal dissociation $\alpha_*(Na_3FSO_4) = 0.71$ and $\alpha_*(K_3FSO_4) = 0.76$, which are the same values as obtained in [7].

It may be therefore concluded that the proposed thermodynamic approach yields the same result as the formal approach applied by *Grjotheim* [3]. Moreover, introducing the temperature dependence of the dissociation constant into the calculation it is possible to obtain more information on the thermal stability of the additive compound, *e.g.* the enthalpy of dissociation. This information may be compared with the calorimetric data. This case will be discussed in detail in the next paper.

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Electrodeposition of Molybdenum from KF—K₂MoO₄—SiO₂ Melts

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Electrolytic preparation of molybdenum coatings has been investigated in the molten system KF—K$_2$MoO$_4$—SiO$_2$. It was found that from the above system coherent smooth and well adhesive Mo-layers on electrically conductive substrates can be prepared. The influence of composition, temperature, and cathodic current density j_c on the quality of Mo-coatings was studied. The best results were obtained with the electrolyte of the composition 85 mole % KF—10 mole % K$_2$MoO$_4$—5 mole % SiO$_2$, temperatures 1173 K up to 1273 K, and j_c in the range 73—450 A m^{-2}.

Molybdenum has from the practical point of view many significant properties, which promotes the effort for its effective preparation.

Electrodeposition from molten salts appears to be a very progressive method for preparation of compact surface layers of molybdenum on different materials. The importance of this method is emphasized by the fact that it is not possible to deposit molybdenum from aqueous solutions.

Recently there were published intensive studies concerning the deposition of molybdenum from the systems KF—M$_x$MoO$_4$, M = Na, K, Ca [1], KF—MoO$_3$ [2, 3], with addition of Li$_2$B$_4$O$_7$ [4], Na$_2$B$_4$O$_7$ [5], B$_2$O$_3$ [1, 6], and CaO [7].

In all the above listed literature the influence of the operational parameters of electrolysis (temperature, cathodic current density (j_c), electrolyte composition, *etc.*) on the character of the deposited product was studied. Most of the authors declared to obtain the best Mo coatings at temperatures 750—950 °C. The very important factor is j_c, the best results are reported for values 100—10000 A m^{-2}. It was found that the optimal value depends on both the temperature and concentration of the electroactive component in electrolyte.

In the present work, the electrodeposition of molybdenum from the molten ternary system KF—K$_2$MoO$_4$—SiO$_2$ was examined. In this work the limits