Determination of the Dissociation Degree and Dissociation Enthalpy in a Melt of a Compound AB with the Dystectic Melting Point Application to the Compounds Na₃FSO₄ and K₃FSO₄

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The calculation procedures to determine the dissociation degree α and dissociation enthalpy $\Delta_{dis}H$ of a compound AB with the dystectic melting point are presented. These procedures are based on the generalized LeChatelier—Shreder equation without hypothetical equilibrium states being taken into account. All the calculations utilize the phase diagram of a system A—B and/or additional thermodynamic properties available, *e.g.* experimentally measured enthalpy of fusion of a compound AB at its temperature of fusion and composition and temperature dependences of the enthalpy of mixing. The way of calculation of characteristic quantities α and $\Delta_{dis}H$ depends on the condition that the melts of a system behave like ideal, quasi-athermal or real solutions.

Some procedures were applied to the compounds Na_3FSO_4 and K_3FSO_4 formed in the binary systems Na_2SO_4 —NaF and K_2SO_4 —KF. The most reliable values for dissociation degree appear to be 0.77 for Na_3FSO_4 at 1060 K and 0.42 for K_3FSO_4 at 1148 K and respective values of dissociation enthalpy are – 10.8 kJ mol⁻¹ and 4.5 kJ mol⁻¹ These quantities we obtained by the iterative method assuming real solutions. Phase diagram, heat of fusion, and enthalpy of mixing measured at 1203 K and 1187 K in the systems Na_2SO_4 —NaF and K_2SO_4 —KF, respectively, were used as input data.

When a binary compound AB with the dystectic melting point occurs in a system A—B, then the equilibrium coexistence of its crystalline phase AB(cr) with a melt at the fixed pressure p_c and temperature T_c is conditioned by equilibrium of two simultaneous reactions

$$AB(cr) = AB(I) \tag{(A)}$$

and

$$AB(I) = A(I) + B(I) \tag{B}$$

where AB(I) denotes the substance AB in liquid state which is in equilibrium with its dissociation products A(I) and B(I). As a consequence of reaction (B), a ternary system consisting of constituents A, B, and AB arises in the melt.

Equilibrium conditions of reactions (A) and (B) may be expressed by the equations

$$\mu$$
(AB, I, x_{eq} , T_c) – μ^{o} (AB, cr, T_c) = 0 (1)

and

$$\Delta_{\rm dis} G({\rm I}, \, x_{\rm eq}, \, T_{\rm c}) = 0 \tag{2}$$

where $\mu^{o}(AB, cr, T_{c})$ is the chemical potential of pure, crystalline substance AB at the temperature

 T_c , μ (AB, I, x_{eq} , T_c) is the chemical potential of liquid substance AB at the equilibrium composition x_{eq} and the same temperature, $\Delta_{dis}G(I, x_{eq}, T_c)$ is the dissociation Gibbs energy of the reaction (*B*) in the melt at composition x_{eq} and the same temperature, x_{eq} is the mole fraction of the substance AB in the system A(B)—AB (quantities related to phase equilibria are denoted by the subscript eq).

The generalized LeChatelier—Shreder equation which may be written in the form

$$\ln \frac{\nu(AB, I, x_{eq}, T_c)k_{H}(AB, I, x_{eq}, T_c)y(AB, I, x_{eq}, T_c)}{\nu_{+}(AB, I, T_c)k_{H,+}(AB, I, T_c)y_{+}(AB, I, T_c)} = \int_{T_{tus}(AB)}^{T_c} \frac{\Delta_{tus}H(AB, T)}{RT^2} dT$$
(3)

was presented in [1]. This equation was derived using eqns (1) and (2) and considering standard state of a pure, fused substance AB which is in equilibrium with its dissociation products A and B. Symbols ν (AB, I, x_{eq} , T_c), k_H (AB, I, x_{eq} , T_c), and y(AB, I, x_{eq} , T_c) stand for the fugacity coefficient, the Henry constant, and the true mole fraction of the constituent AB in the ternary system A—B—AB, respectively, T_{fus} (AB) and $\Delta_{fus}H$ (AB, T) are melting temperature and experimentally (*i.e.* calorimetrically and/or cryometrically) measurable enthalpy of fusion of the same constituent. Subscript + denotes the quantities related to the standard state mentioned above. The expressions

$$y(AB, I, x_{eq}, T_c) = \frac{[1 - \alpha(T_c)]x_{eq}}{1 + \alpha(T_c)x_{eq}}$$
(4)

$$y_{+}(AB, I, T_{c}) = \frac{1 - \alpha_{+}(T_{c})}{1 + \alpha_{+}(T_{c})}$$
 (5)

where $\alpha(T_c)$ and $\alpha_+(T_c)$ denote equilibrium degrees of dissociation of a substance AB in the molten mixture and of a pure substance AB, respectively, are substituted into eqn (3) [1].

The quantities ν and $k_{\rm H}$ cancel on the left-hand side of eqn (3) at the compositions close to the pure substance AB because their values are the same. $\alpha(T_{\rm c})$ as a function of $\alpha_{+}(T_{\rm c})$ and $x_{\rm eq}$ can be obtained from eqn (2) if it is written in the form [1]

$$K_{y}(x_{eq}, \alpha, T_{c}) = \frac{y(A, I, x_{eq}, \alpha, T_{c})y(B, I, x_{eq}, \alpha, T_{c})}{y(AB, I, x_{eq}, \alpha, T_{c})} =$$
$$= \exp \frac{\Delta_{dis}S_{inconf}(I, x_{eq}, T_{c})}{R} \exp \left[-\frac{\Delta_{dis}H(I, x_{eq}, T_{c})}{RT_{c}}\right]$$
(6)

where $\Delta_{dis} S_{inconf}(l, x_{eq}, T_c)$ and $\Delta_{dis} H(l, x_{eq}, T_c)$ are inconfigurational entropy of dissociation and enthalpy of dissociation of reaction (*B*), respectively. In this limiting case the changes in inconfigurational entropy of dissociation and enthalpy of dissociation are practically independent of composition (because $x_{eq} \rightarrow 1$) and of temperature (because the tangent line to the liquidus curve is parallel to the composition axis and therefore the difference between $T_{fus}(AB)$ and T_c is very small [2]), which implies that the following relations are valid

$$\Delta_{\rm dis}S_{\rm inconf}(I, x_{\rm eq}, T_{\rm c}) \cong \Delta_{\rm dis}S_{\rm +,inconf}(I, T_{\rm fus}({\rm AB}))$$
(7)

and

$$\Delta_{\rm dis} H(\mathsf{I}, x_{\rm eq}, T_{\rm c}) \cong \Delta_{\rm dis} H_+(\mathsf{I}, T_{\rm fus}(\mathsf{AB})) \tag{8}$$

Combining eqns (6), (7), and (8) we obtain

$$\begin{aligned} & \mathcal{K}_{y}(x_{\mathsf{eq}}, \alpha, T_{\mathsf{c}}) \cong \mathcal{K}_{y, +}(\alpha_{+}, T_{\mathsf{c}}) \cong \\ & \cong \exp \frac{\Delta_{\mathsf{dis}} \mathcal{S}_{\mathsf{+},\mathsf{inconf}}(\mathsf{I}, T_{\mathsf{fus}}(\mathsf{AB}))}{R}. \end{aligned}$$

$$\cdot \exp\left[-\frac{\Delta_{\rm dis}H_{+}({\rm I},T_{\rm fus}({\rm AB}))}{RT_{\rm c}}\right] \tag{9}$$

Eqn (9) is also the condition for ν and $k_{\rm H}$ to be independent of composition both for reactant and products of the reaction (*B*).

The expressions

$$y(A, I, x_{eq}, T_c) = \frac{1 - [1 - \alpha(T_c)] x_{eq}}{1 + \alpha(T_c) x_{eq}}$$
(10)

$$y_{+}(A, I, T_{c}) = \frac{\alpha_{+}(T_{c})}{1 + \alpha_{+}(T_{c})}$$
 (11)

$$y(\mathsf{B},\mathsf{I},x_{\mathsf{eq}},T_{\mathsf{c}}) = \frac{\alpha(T_{\mathsf{c}})x_{\mathsf{eq}}}{1 + \alpha(T_{\mathsf{c}})x_{\mathsf{eq}}} \tag{12}$$

$$y_{+}(B,I,T_{c}) = \frac{\alpha_{+}(T_{c})}{1 + \alpha_{+}(T_{c})}$$
 (13)

for true mole fractions of the constituents A, B, derived for the subsystem A—AB, as well as those for the constituent AB (eqns (3) and (4)) are substituted into eqn (9) to get $\alpha(T_c)$ as a function of $\alpha_+(T_c)$ and x_{eq}

$$\alpha(T_{\rm c}) \approx \frac{-(1-x_{\rm eq}) \pm \sqrt{(1-x_{\rm eq})^2 + 4x_{\rm eq}} \frac{K_{y,+}}{1+K_{y,+}}}{2x_{\rm eq}}$$
(14)

where

$$K_{y,+} \equiv K_{y,+}(\alpha_{+}, T_{c}) = \frac{\left[\alpha_{+}(T_{c})\right]^{2}}{1 - \left[\alpha_{+}(T_{c})\right]^{2}}$$
(15)

The same equations we obtain using analogous relations to eqns (10–13) for true mole fractions derived for the subsystem B–AB. Eqns (9) and (15) imply also the dependence $\alpha_+(T_c)$

$$\frac{[\alpha_{+}(T_{c})]^{2}}{1-[\alpha_{+}(T_{c})]^{2}} \cong$$
$$\cong \frac{[\alpha_{+}(T_{fus}(AB))]^{2}}{1-[\alpha_{+}(T_{fus}(AB))]^{2}} \exp\left[-\frac{\Delta_{dis}H_{+}(I, T_{fus}(AB))}{R} \cdot \frac{(\frac{1}{T_{c}} - \frac{1}{T_{fus}(AB)})}{R}\right]$$
(16)

Assuming that

$$\Delta_{\rm fus} C_{\rho} (\rm AB) \approx 0 \tag{17}$$

is valid within the experimental errors of $\Delta_{tus} H(AB)$, a transcendental equation

$$\Phi[x_{eq}, T_c, \alpha_+(T_{fus}(AB)), \Delta_{dis}H_+(I, T_{fus}(AB)), \Delta_{fus}H(AB, T_{fus}(AB))] \cong 0$$
(18)

is obtained substituting eqns (4), (5), (14), (15), and (16) into eqn (3) which is valid for real solutions at compositions close to pure substance AB.

If a reliable phase diagram is available, the three unknown quantities $\alpha_{+}(T_{fus}(AB))$, $\Delta_{dis}H_{+}(I, T_{fus}(AB))$, and $\Delta_{fus}H(AB, T_{fus}(AB))$ can be obtained solving this equation numerically assuming different parts of the liquidus curve adjacent to the pure compound AB. The final values of unknown quantities can be then obtained extrapolating in this way calculated values to the zero length of liquidus curve. The validity of relations (7–9) and (14) is assumed.

Because the liquidus curve, especially around the melting point of the substance AB, is not sufficiently precisely measured ($\delta T = \pm 2 \text{ K}$) in many high-temperature binary systems with partly dissociated compound, only approximate values of the mentioned quantities can be obtained. It is therefore necessary to involve additional information about the investigated system into calculations (*e.g.* experimentally determined enthalpy of fusion and/or enthalpy of mixing in the system A—B as a function of temperature and composition). The calculated unknown quantities are more reliable if investigated melts behave like ideal or quasi-athermal solutions.

The method for calculation of the dissociation degree of binary compounds, especially for complicated dissociation schemes without considering hypothetical equilibrium state, was proposed by *Brynestad* [3]. However, the liquid system was proposed to be an ideal mixture and the enthalpy of dissociation was proposed to be zero.

In the present paper we show how to calculate the degree of dissociation and dissociation enthalpy in a melt of binary compound AB. The calculations have been applied to the compounds Na_3FSO_4 and K_3FSO_4 contained in the systems Na_2SO_4 —NaF and K_2SO_4 —KF.

THEORETICAL

The calculations of the unknown quantities characterizing a system are based on various combining information available: phase diagram, $\Delta_{fus}H(AB, T)$, $\Delta_{mix}H(z, T_i)$ (*z* is the mole fraction of the constituent B in the system A—B and T_i is the *i*-th experimental temperature). There are various calculation procedures depending on the condition that the solutions are ideal, quasi-athermal or real ones.

1. Ideal Solutions

The melts are considered to be ideal solutions of constituents if, except the equations

$$\Delta_{dis}H(I, x_{eq}, T_c) = \Delta_{dis}H_+(I, T_c) = \Delta_{dis}H^o(I, T_c) \quad (19)$$
$$\Delta_{dis}S_{inconf}(I, x_{eq}, T_c) = \Delta_{dis}S_{+,inconf}(I, T_c) =$$
$$= \Delta_{dis}S_{inconf}^o(I, T_c) \quad (20)$$

the following criteria are fulfilled:

- a) The AB liquidus curve is symmetrical with respect to the isopleth AB;
- b) the volume is an additive function of the products of numbers of moles and of constant molar volumes of constituents;
- c) isothermal molar enthalpies of mixing in the system A—B are symmetrical with respect to the ordinate z = 0.5;
- d) the enthalpy of mixing is given by

$$\Delta_{\text{mix}} H(\text{A}-\text{AB}, x, T_i) = -\Delta_{\text{dis}} H^{\circ}(\mathbf{I}, T_i) \frac{x}{1+x} [1-\alpha(x)]$$
(21)

Analogous expression is also valid for the system B—AB. The method of computation of unknown thermodynamic quantities varies depending on the information available.

1.1. $\Delta_{mix}H(z, T_i)$ at several temperatures together with either $\Delta_{fus}H(AB, T)$ or the phase diagram are known, or all the three characteristics are available

1.1.1. The conditions a—d are perfectly fulfilled and very reliable measurements are available

An initial value of $\Delta_{dis}H^{\circ}(I, T_i)$ gives through eqn (21) the values of $\alpha_+(T_i)$ and $K_{y,+}(T_i)$. Substituting α from eqn (14) into eqn (21) the values of $\Delta_{mix}H(A(B)$ —AB, $x, T_i)$ are calculated. There are no differences between experimental and calculated enthalpy of mixing if the initial value of $\Delta_{dis}H^{\circ}(I, T_i)$ was successfully chosen. The temperature dependences of $\Delta_{dis}C_{\rho}^{\circ}(I,T)$, $\alpha_+(T)$, and $K_{y,+}(T)$ can be determined using $\Delta_{dis}H^{\circ}(I, T_i)$ and van't Hoff's reac-

tion isobar. The $\Delta_{dis} H^{\circ}(I, T_{fus}(AB))$ and $\alpha_{+}(T_{fus}(AB))$ are thus given.

- a) When the temperature dependence of $\Delta_{\text{fus}}H(AB, T)$ is known, it is possible to calculate the liquidus curve of the compound AB using eqns (4), (5), (14) and the generalized Le-Chatelier—Shreder equation (3).
- b) When the phase diagram is known, it is possible to determine the temperature dependence of $\Delta_{\text{fus}} H(AB, T)$ using the same equations.
- c) When all three characteristics of the system A— B are known, the values of $\Delta_{dis}H^{\circ}(I, T_{c}), \alpha_{+}(T_{c}),$ and $\Delta_{fus}H(AB, T_{c})$ must correspond with the AB liquidus curve (T_{c} corresponds to x_{eq}).

1.1.2. The conditions a-d are only approximately fulfilled and not reliable measurements are available

It is usually possible to assume eqn (17) is valid because of experimental errors.

- a) When the temperature dependences $\Delta_{mix}H(z, T_i)$ are measured more reliably than the phase diagram and the enthalpy of fusion of AB is also known, the AB liquidus curve can be optimized using the procedure indicated in 1.1.1*a*.
- b) When the phase diagram is more reliable, using eqn (18) and assuming the relation

$$\Delta_{\rm dis} C_{\rm p}^{\rm o}({\rm I},T) \approx 0 \tag{22}$$

the value of $\Delta_{dis}H^{o}(I)$ and the dependence $\alpha_{+}(T)$ can be calculated. In addition, the dependences $\Delta_{mix}H(z, T_i)$ are obtained with higher precision.

1.2. $\Delta_{mix}H(z, T_i)$ at the only temperature is known together with either $\Delta_{fus}H(AB, T)$ or the phase diagram, or all the three characteristics are available

1.2.1. The conditions a-d are perfectly fulfilled and very reliable measurements are available

Eqn (21) is for the temperature T_i unambiguously determined by the single value of $\Delta_{dis} H^0(I, T_i)$ and thus also of $\alpha_+(T_i)$ and of $K_{\gamma,+}(T_i)$.

- a) In the case the temperature dependence of $\Delta_{\text{fus}} H(AB, T)$ is known, it is possible using eqns (4), (5), (14), the general LeChatelier—Shreder equation, van't Hoff's reaction isobar and simplifying assumption (22) to calculate the AB liquidus curves.
- b) When the phase diagram is known, it is possible using eqn (18), van't Hoff's reaction isobar and the corresponding pairs of figurative points on the

AB liquidus curve to determine the temperature dependences $\Delta_{dis}H^{\circ}(I, T)$ and $\Delta_{fus}H(AB, T)$ as well as to estimate the value of $\alpha_{+}(T_{fus}(AB))$. In this case the number of unknowns in eqn (18) is increased by $\Delta_{dis}C_{p}^{\circ}(I)$ and $\Delta_{fus}C_{p}(AB)$ provided these two quantities are temperature-independent. The value of $\Delta_{dis}H^{\circ}(I, T_{i})$ allows to decrease the number of figurative points on the AB liquidus curve the coordinates of which are used for calculations.

c) When all three characteristics of the system A— B are known, it is possible to determine in addition to $\alpha_+(T_{fus}(AB))$ also the temperature dependence of $\Delta_{dis}H^o(I, T)$ using less number of figurative points on the AB liquidus curve than in the above section.

1.2.2. The conditions a-d are only approximately fulfilled and not reliable measurements are available

Regarding the errors of measurement, it is usually possible to assume the conditions (17) and (22) to be valid.

- a) When the dependence $\Delta_{mix}H(z, T_i)$ is measured more reliably than the phase diagram and the value of $\Delta_{fus}H(AB, T_{fus}(AB))$ is known, the AB liquidus curve can be made more accurate. The value of $\Delta_{dis}H^{\circ}(I, T_{fus}(AB))$ is equal to $\Delta_{dis}H^{\circ}(I, T_i)$ and the value of $\alpha_+(T_{fus}(AB))$ is obtained by eqn (16).
- b) When the phase diagram and the dependence $\Delta_{\text{mix}}H(z, T_i)$ are measured more reliably than that of $\Delta_{\text{fus}}H(AB, T_{\text{fus}}(AB))$, it is possible to estimate $\Delta_{\text{fus}}H(AB, T_{\text{fus}}(AB))$ and $\alpha_+(T_{\text{fus}}(AB))$ applying the procedure 1.2.1.*b*.
- c) When all three characteristics of the system are known, the reliable estimate of $\Delta_{dis}H^{\circ}(I)$ must be in accord with the least deviations between experimental and calculated enthalpies of mixing and AB liquidus curves over the whole composition range.

1.3. The enthalpy of mixing as a function of composition is not known in a system A—B

1.3.1. The conditions a and b are perfectly fulfilled for ideal solutions and the phase diagram and/or heat of fusion of AB were very reliably measured

a) It is possible to estimate the dependences $\Delta_{dis}H^{\circ}(I, T)$, $\Delta_{fus}H(AB, T)$ and the value of $\alpha_{+}(T_{fus}(AB))$ from eqn (18) and van't Hoff's reaction isobar using sufficient number of figurative points on the AB liquidus curve. Even in this case

the number of unknowns is increased by $\Delta_{dis} C_{\rho}^{\circ}(I)$ and $\Delta_{fus} C_{\rho}(AB)$ provided both these quantities are temperature-independent.

b) When the temperature dependence of the heat of fusion of AB is known, the number of figurative points, from which the estimates of $\alpha_{+}(T_{\text{fus}}(AB))$ and $\Delta_{\text{dis}}H^{\circ}(I, T)$ are obtained, is decreased. In addition, using eqns (14), (21) and van't Hoff's reaction isobar also the dependence of $\Delta_{\text{mix}}H(A(B))$ —AB, x, T_{c}) can be calculated.

1.3.2. The conditions a—d are only approximately fulfilled, the phase diagram and Δ_{fus} H are known

During calculations the simplifying assumptions (17) and (22) are taken into consideration. The way of calculations is analogous to that in paragraphs 1.3.1.*a* and 1.3.1.*b*. The true estimates of $\Delta_{dis}H^{\circ}(I)$, $\Delta_{fus}H(AB, T_{fus}(AB))$, and $\alpha_{+}(T_{fus}(AB))$ are gained on the basis of the least deviation between experimental and calculated AB liquidus curves.

2. Quasi-Athermal Solutions

Quasi-athermal solutions are considered to be the melts that do not satisfy some of the conditions to be the ideal ones. On the other hand, they satisfy the following conditions:

- a) Eqn (19) is again valid for reaction (B).
- b) The reaction (B) is the only running in the melt. The enthalpies of mixing are zero when pure constituents A(I), B(I) and a fictive one AB(I) are mixed in the ratio of their equilibrium mole fractions.
- c) The values of ν and k_H (thus also activity coefficients γ) of constituents A(I) and B(I) are functions of particle ordering in the melt.
- d) The values of ν and $k_{\rm H}$ (thus also activity coefficient γ) of constituent AB(I) are compositionindependent within the temperature range from $T_{\rm fus}$ to the eutectic temperature $T_{\rm eut}$.

It is convenient to rewrite the left-hand side of the LeChatelier—Shreder equation (3) when dealing with the quasi-athermal solution model. It can be written in the form [4]

$$\ln \frac{\nu(AB, I, x_{eq}, T_c) k_{H}(AB, I, x_{eq}, T_c) y(AB, I, x_{eq}, T_c)}{\nu_{+}(AB, I, T_c) k_{H,+}(AB, I, T_c) y_{+}(AB, I, T_c)} = \\ = \ln \frac{\operatorname{const} \gamma(AB, I, x_{eq}, T_c) y(AB, I, x_{eq}, T_c)}{\operatorname{const} \gamma_{+}(AB, I, T_c) y_{+}(AB, I, T_c)}$$
(23)

so the generalized LeChatelier—Shreder equation is of the form

$$\ln \frac{\gamma(AB, I, x_{eq}, T_c) \gamma(AB, I, x_{eq}, T_c)}{\gamma_+(AB, I, T_c) \gamma_+(AB, I, T_c)} = \int_{T_{fus}(AB)}^{T_c} \frac{\Delta_{fus} H(AB, T)}{RT^2} dT$$
(24)

Temperature dependences will be neglected (eqns (17) and (22)) to estimate the unknown quantities because the studied melts are quasi-athermal only approximately.

2.1. The dependences $\Delta_{mix}H(z, T_i)$, phase diagram and $\Delta_{fus}H(AB, T_{fus}(AB))$ are known

A regression polynomial follows from eqn (21) at the fixed value of $\Delta_{dis} H^{\circ}(I)$ and at any temperature T_i

$$\alpha(T_i) = \varphi(x) = \sum_{j=0}^k a_j x^j$$
(25)

It is possible to determine temperature dependences of the coefficients a_j on the right-hand side of this equation. Substituting them into the equation we get

$$\alpha = \psi(\mathbf{X}, T) \tag{26}$$

For the chosen temperatures T_c the corresponding values of x_{eq} are read off the AB liquidus and the ordered couples are substituted into eqn (26). For $x = 1 \ \alpha_+$ is also determined from the same equation. Using eqns (4) and (5) the left-hand side of the Le-Chatelier—Shreder equation (24) is obtained. The temperature function, in which $\Delta_{fus}H(AB, T_{fus}(AB))$ is involved, is then substituted into the right-hand side. The most reliable is the estimate of $\Delta_{dis}H^{\circ}(I)$ to which the least deviation between both sides of eqn (24) corresponds.

2.2. The dependence $\Delta_{mix}H(z, T_i)$ at the only temperature, phase diagram, and $\Delta_{fus}H(AB, T_{fus}(AB))$ are known

To calculate the quantities characterizing the system, the quantities K_{γ} and Γ are necessary to be introduced; they are defined by the relations

$$K_{\gamma} = \frac{\gamma(A, I, x, \alpha)\gamma(B, I, x, \alpha)}{\gamma(AB, I)}$$
(27)

and

$$\Gamma = \frac{K_{\gamma,+}}{K_{\gamma}} \tag{28}$$

Regarding the condition c of this section, eqns (27) and (28) yield an equation

$$\Gamma = \Phi(x, \alpha, \alpha_{+}) \tag{29}$$

If the quantity in the numerator of eqn (28) is referred to the same reference state, the quantity Γ will be identified by the subscript *r* and eqn (29) will be of the form

$$\Gamma_r = \Psi(x, \alpha) \tag{30}$$

The reference state is always a state at the temperature T_i and x = 1 ($K_{\gamma,+}(x = 1, T_i)$, $\alpha_+(x = 1, T_i)$). It is assumed the function Ψ is unambiguous over the whole range of x and α no matter what is the temperature. We express this function in the polynomial form

$$\Gamma_{r} = a_{1} + a_{2}x + a_{3}\alpha + a_{4}x\alpha + a_{5}x^{2} + a_{6}\alpha^{2} \quad (31)$$

The quantities characterizing the system are calculated in the following steps:

1. A value of $\Delta_{dis} H^{\circ}(I)$ is chosen. The coefficients a_j are calculated for this value using a sufficient number of ordered three values x, $\alpha(x)$, $\Gamma_i(x, \alpha)$ determined from eqns (21) and (32)

$$K_{a}(T_{i}) = K_{\gamma}(T_{i})K_{\gamma}(T_{i}) = K_{\gamma,+}(T_{i})K_{\gamma,+}(T_{i})$$
(32)

the last equation being rewritten substituting from eqn (28) to the form

$$\alpha(T_i) = \frac{-(1-x) \pm \sqrt{(1-x)^2 + 4x \frac{\Gamma_r K_{y,+}(T_i)}{1 + \Gamma_r K_{y,+}(T_i)}}}{2x} \quad (33)$$

2. The value of $K_{y,+}(T_c)$ (thus also the value of $\alpha_+(T_c)$) is, for the above $\Delta_{dis}H^{\circ}(I)$ and the selected temperature T_c , given by the integrated van't Hoff's reaction isobar (using also eqn (15))

$$\frac{\Delta_{\rm dis} H^{\circ}(l)}{R} \left(\frac{1}{T_i} - \frac{1}{T_c} \right) = \ln K_a(T_c) - \ln K_a(T_i) =$$
$$= -\ln \Gamma_{r,+}(\alpha_+(T_c)) + \ln \frac{[\alpha_+(T_c)]^2}{1 - [\alpha_+(T_c)]^2} - \ln \frac{[\alpha_+(T_i)]^2}{1 - [\alpha_+(T_i)]^2}$$
(34)

Because $\alpha_{+}(T_i)$ is known for $\Delta_{dis}H^{\circ}(I)$, eqn (34)

becomes an equation of the only unknown $\alpha_+(T_c)$ after substituting from eqn (31).

3. Relations analogous to that of (32) are valid for the selected temperatures T_c from which the equations analogous to that of (33) are derived

$$\alpha(T_{c}) = \frac{-(1 - x_{eq})}{2x_{eq}} \pm \frac{\sqrt{(1 - x_{eq})^{2} + 4x_{eq}} \frac{\Gamma(T_{c})K_{y,+}(T_{c})}{1 + \Gamma(T_{c})K_{y,+}(T_{c})}}{2x_{eq}}$$
(33a)

$$\Gamma(T_{\rm c}) = \frac{K_{\gamma,+}(T_{\rm c})}{K_{\gamma}(T_{\rm c})} = \frac{\Gamma_r(x_{\rm eq}, \alpha(T_{\rm c}))}{\Gamma_{r,+}(x_{\rm eq}, \alpha_+(T_{\rm c}))}$$
(35)

and so eqn (33a) becomes an equation of the only unknown $\alpha(T_c)$ after substituting from eqns (15) and (34).

4. Using eqns (4) and (5) with yet calculated $\alpha(T_c)$ and $\alpha_+(T_c)$ the validity of $\Delta_{dis}H^o(I)$ selection is verified through eqn (24) which can be, regarding the condition *d* and eqn (17), written in the form

$$\ln \frac{y(AB, I, x_{eq}, T_c)}{y_+(AB, I, T_c)} =$$
$$= \int_{T_{fus}(AB)}^{T_c} \frac{\Delta_{fus} H(AB, T_{fus}(AB))}{RT^2} dT \qquad (24a)$$

 α₊(T_{fus}(AB)) is then calculated for the right value of Δ_{dis}H^o(I) using the procedure 2. of this paragraph.

3. Real Solutions

If the constituents form a real solution, only the approximate values of the unknown quantities are obtained using the above procedures. The iterative methods which are discussed in the introduction are necessary to be used to obtain more reliable values. Depending on how large are the deviations of a considered system from the criteria 1. and 2., the model of ideal (or the general solution satisfying eqns (9) and (14)) or "quasi-athermal" solution of the constituents is used. The results may be inappropriate because of unreliably measured AB liquidus curves, especially close to its melting point.

4. Application to the System M_2SO_4 —MF (M = Na, K)

4.1. The System Na₂SO₄--NaF

The following quantities are available for this system: experimental heat of fusion (Afus H(Na2SO4 · \cdot NaF, 1060 K) = (69 ± 4) kJ mol⁻¹[5]), phase diagram [6], and experimentally determined dependence of $\Delta_{mix}H(z, 1203 \text{ K})$ [7]. From this information about this system it follows that it can be considered an ideal one only in the first approximation. Therefore the calculation procedure 1.2.2.a was not used to calculate Na₂SO₄ · NaF liquidus curves in the phase diagram. The calculation of the unknown guantities corresponds to the procedures 1.2. and 3. Regarding the experimental difficulties in obtaining this information and thus also the potential errors the procedures described in the sections 1.2.2.b, 1.2.2.c and the combinations with the procedure 3. were used to calculate $\Delta_{dis}H^{o}(I)$ or $\Delta_{dis}H_{+}(I, T_{fus}(Na_{2}SO_{4} \cdot NaF)),$ $\alpha_{+}(T_{\text{fus}}(\text{Na}_2\text{SO}_4 \cdot \text{NaF})), \Delta_{\text{fus}}H(\text{Na}_2\text{SO}_4 \cdot \text{NaF})$

 $T_{\text{fus}}(\text{Na}_2\text{SO}_4 \cdot \text{NaF}))$. The results including the section number of the procedure used are in Table 1.

4.2. The System K₂SO₄—KF

The following quantities are measured for this system: $\Delta_{\text{fus}} H(K_2 SO_4 \cdot KF, 1148 \text{ K}) = (86 \pm 3) \text{ kJ mol}^{-1}$ [8], phase diagram [6], and $\Delta_{\text{mix}} H(z, 1187 \text{ K})$ [7]. As follows from this information, the melts of this system cannot be considered ideal solutions. Similarly to the system Na₂SO₄—NaF the experimental errors must be taken into consideration. Therefore the procedures 2.2. and 3. combined with that of 2.2. were used to calculate the characteristics of the melts $\Delta_{\text{dis}} H_4(I, T_{\text{fus}}(K_2SO_4 \cdot KF)), \qquad \alpha_+(T_{\text{fus}}(K_2SO_4 \cdot KF)), \Delta_{\text{fus}} H(K_2SO_4 \cdot KF, T_{\text{fus}}(K_2SO_4 \cdot KF))$. The results of calculations including the section number of the procedure used are in Table 2.

DISCUSSION

The System Na₂SO₄—NaF

The values of the dissociation degree for $Na_2SO_4 \cdot NaF$ are within the limits from 60 % to 85 % depending on what calculation procedure and

Procedure	Known characteristics	$\frac{\Delta_{\rm dis}H_+(l,T_{\rm fus}(AB))}{\rm kJ\ mol^{-1}}$	$\alpha_+(T_{fus}(AB))$
1.2.2. <i>b</i>	Δ _{mix} H(z, T)) phase diagram	- 6.9	0.627
1.2.2. <i>c</i>	Δ _{mix} <i>H(z, T)</i>) phase diagram Δ _{fus} <i>H</i> (AB, <i>T</i> _{rus} (AB))	- 13.8	0.829
3 + 1.2.2. <i>b</i>	Δ_{mix} <i>H</i> (A—B, x_B , T_i) phase diagram	- 6.8	0.617
3 + 1.2.2. <i>c</i>	Δ _{mix,exp} <i>H</i> (<i>z, T</i>) phase diagram Δ _{fus} <i>H</i> (AB, <i>T</i> _{fus} (AB))	- 10.8	0.772

Table 1. The Calculation Results of the Characteristic Thermodynamic Quantities in the System Na₂SO₄---NaF (A = Na₂SO₄, B = NaF)

Table 2. The Calculation Results of the Characteristic Thermodynamic Quantities in the System K_2SO_4 —KF (A = K_2SO_4 , B = KF)

Procedure	Known characteristics	$\frac{\Delta_{\rm dis}H_+(l,T_{\rm fus}(AB))}{\rm kJ\ mol^{-1}}$	$\alpha_+(T_{fus}(AB))$
2.2.	phase diagram Δ _{mix} <i>Η</i> (<i>z</i> , <i>Τ</i>) Δ _{tus} <i>Η</i> (AB, <i>T</i> _{tus} (AB))	5.2	0.497
3 + 2.2.	phase diagram Δ _{mix} <i>H</i> (<i>z</i> , <i>Τ</i> _i) Δ _{tus} <i>H</i> (AB, <i>T</i> _{fus} (AB))	4.5	0.420

the information available have been used. The signs of the dissociation enthalpies in Table 1 are negative being in accordance with the positive signs of the measured enthalpy of mixing.

Comparison of the calculated enthalpy of fusion of $Na_2SO_4 \cdot NaF$ (using the methods 1.2.2.*b* and 3 + 1.2.2.*b* with its experimental value implies that the results are distorted mainly because of the unreliable experimental liquidus curves.

As the most probable values of the dissociation degree and dissociation enthalpy can be considered $\alpha_{+}(T_{fus}(Na_2SO_4 \cdot NaF)) = 77.2\%$ and $\Delta_{dis}H_{+}(I, T_{fus}(Na_2SO_4 \cdot NaF)) = -10.8$ kJ mol⁻¹ which were calculated assuming real solutions by the iterative procedure and on the basis of known $\Delta_{mix}H$, phase diagram, and $\Delta_{fus}H$.

Analyzing the cryoscopic data for the system Na_3FSO_4 —NaCl *Koštenská* and *Malinovský* [9] found out that about 70 % of Na_3FSO_4 dissociates under melting. They also estimated the enthalpy of fusion of Na_3FSO_4 to be 62.3 kJ mol⁻¹.

The System K₂SO₄—KF

The values of the dissociation degree for $K_2SO_4 \cdot KF$, calculated assuming the occurrence of real solutions by the iterative procedure as well as using the model of quasi-athermal solutions, are considerably lower than those for $Na_2SO_4 \cdot NaF$. This suggests that the complex anions are more stable in the system $K_2SO_4 \cdot KF$ than in Na_2SO_4 —NaF. It can be ascribed to the lower polarizing ability of the cation K⁺ than that of Na⁺.

The values of the dissociation enthalpy for $K_2SO_4 \cdot KF$, calculated by both calculation procedures, are positive being in accordance with the

negative values of the measured enthalpy of mixing. The iterative procedures give more reliable values for the searched quantities for both systems because at compositions close to that of a binary compound $M_2SO_4 \cdot MF$ the values of $\Delta_{dis}H$, $\Delta_{dis}S_{inconf}$ as well as of ν and $k_H(\gamma)$ are for all constituents practically independent of composition. The same conditions are also valid for the ideal and the quasi-athermal solutions the models of which were used for the calculations.

From the results shown in Tables 1 and 2 follows the importance of calorimetry for determination of $\Delta_{fus}H$ as well as $\Delta_{mix}H$ in order to calculate reliable values of $\Delta_{dis}H_{+}(I, T_{fus}(M_2SO_4 \cdot MF))$ and $\alpha_{+}(T_{fus}(M_2SO_4 \cdot MF))$.

REFERENCES

- 1. Proks, I., Daněk, V., Kosa, L., Nerád, I., Strečko, J., and Adamkovičová, K., to be published.
- Nerád, I., Strečko, J., Proks, I., Adamkovičová, K., and Kosa, L., *Chem. Papers 49*, 1 (1995).
- 3. Brynestad, I., *Z. Phys. Chem.* (Frankfurt) *30*, 123 (1961).
- 4. Daněk, V. and Proks, I., Chem. Papers 48, 7 (1994).
- Adamkovičová, K., Fellner, P., Kosa, L., Lazor, P., Nerád, I., and Proks, I., *Thermochim. Acta 191*, 57 (1991).
- 6. Kleppa, O. J. and Julsrud, S., Acta Chem. Scand., Ser. A 34, 655 (1980).
- Hatem, G., Gaune-Escard, M., and Pelton, A. D., J. Phys. Chem. 86, 3039 (1982).
- 8. Adamkovičová, K., Fellner, P., Kosa, L., Nerád, I., and Proks, I., *Thermochim. Acta 209*, 77 (1992).
- Koštenská, I. and Malinovský, M., Chem. Zvesti 36, 151 (1982).

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