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Experimental determination of the heat of fusion and calculation of the dissociation degree and dissociation enthalpy of K_3FMoO_4

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Abstract

The molar enthalpy of fusion $\Delta_{fus}H_m$ of $KF \cdot K_2MoO_4$ at the temperature of fusion, 1025 K, was measured in the high-temperature Setaram HTC 1800 K calorimeter as 58 ± 2 kJ mol^{-1}. This quantity, together with the known phase diagram of the system $KF-K_2MoO_4$ and the composition dependence of the enthalpy of mixing at 1273 K, enabled both the dissociation enthalpy $\Delta_{dis}H$ and the dissociation degree α of the compound $KF \cdot K_2MoO_4$ to be calculated at the temperature of its fusion. The Le Chatelier–Shreder equation, derived without taking hypothetical equilibrium states into account, was also used. The most reliable values of the quantities are those obtained by an iterative procedure using a "quasi-athermal" solution model. Their values are $\Delta_{dis,+}H(1, 1025\,K) = -1.2$ kJ mol^{-1} and $\alpha_+(KF \cdot K_2MoO_4, 1025\,K) = 0.51$.

Keywords: Degree of dissociation; Heat of dissociation; Heat of fusion; Heat of mixing; Mixed oxide; Model

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1. Introduction

Electrolytes applied in the electrolytic deposition of molybdenum from fused salts also contain melts of the system $KF-K_2MoO_4$ [1]. The binary compound $KF \cdot K_2MoO_4$, which has a dystectic melting point at 752°C, occurs in this system

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[2, 3]. Daněk and Chrenková [4] calculated its dissociation degree using a phase diagram as well as volume properties. They calculated the dissociation enthalpy from density values, assuming ideal behaviour of the constituents.

Kleppa and Julsrud [2, 5] studied thermodynamic properties of liquid mixtures of the system $MF-M_2YO_4$ (M is Li, Na, K; Y is S, Mo, W) with asymmetrically charged anions but with common cations, using calorimeric and cryometric methods. They found significant deviations in the partial molar mixing entropies of the constituents from ideal Temkin solutions. They suggested this difference may be due to either the charge asymmetry of the anions or the differences in their sizes.

The known enthalpy of fusion of this binary compound at the dystectic temperature of its fusion increases the reliability of the calculated dissociation degree α and dissociation enthalpy $\Delta_{\rm dis}H$. The experimental determination of the heat of fusion of $KF \cdot K_2MoO_4$ [$\Delta_{\rm fus}H(KF \cdot K_2MoO_4)$] and the estimations of α and $\Delta_{\rm dis}H$ at the temperature of fusion of $KF \cdot K_2MoO_4$ are reported in this paper.

2. Theoretical

Henceforth, the constituents KF and K_2MoO_4 will be denoted A and B, respectively.

When a binary compound AB with a dystectic melting point occurs in a system A–B, the equilibrium coexistence of its crystalline phase with a melt at fixed pressure p_c and temperature T_c is conditioned by the equilibrium of the reaction

$$\mathrm{AB(cry)} \rightleftharpoons \mathrm{AB(l,dis)} \qquad (1)$$

where AB(l,dis) denotes the substance AB in liquid state which is in equilibrium with its dissociation products A(l) and B(l) according to the reaction

$$\mathrm{AB(l)} \rightleftharpoons \mathrm{A(l)} + \mathrm{B(l)} \qquad (2)$$

As a consequence of reaction (2), a ternary system consisting of constituents A, B and AB is present in the melt.

The equilibrium conditions of reactions (1) and (2) may be expressed by the equations

$$\mu(\mathrm{AB, l, dis}, x_{\rm w,eq}, T_c) - \mu^{\ominus}(\mathrm{AB, cry}, T_c) = 0 \qquad (3)$$

and

$$\Delta_{\rm dis(2)}G(\mathrm{l}, x_{\rm w,\,eq}, T_c) = 0 \qquad (4)$$

where $\mu^{\ominus}(\mathrm{AB, cry}, T_c)$ is the chemical potential of pure, crystalline AB at T_c, $\mu(\mathrm{AB, l, dis}, x_{\rm w,eq}, T_c)$ is the chemical potential of liquid AB at composition $x_{\rm w,eq}$ and temperature T_c, $\Delta_{\rm dis(2)}G(l, x_{\rm w,eq}, T_c)$ is the dissociation Gibbs energy of reaction (2) in the melt at composition $x_{\rm w,eq}$ and temperature T_c, $x_{\rm w,eq}$ is the mole fraction of AB in the melt which is in phase equilibrium with crystalline AB at the temperature T_c in the system A(B)–AB.

The generalized Le Chatelier–Shreder equation which may be written in the form

$$\ln\frac{\nu(\mathrm{AB},\mathrm{l},x_{\mathrm{w,eq}},T_{\mathrm{c}})k_{\mathrm{H}}(\mathrm{AB},\mathrm{l},x_{\mathrm{w,eq}},T_{\mathrm{c}})x(\mathrm{AB},\mathrm{l},x_{\mathrm{w,eq}},T_{\mathrm{c}})}{\nu_{+}(\mathrm{AB},\mathrm{l},T_{\mathrm{c}})k_{\mathrm{H},+}(\mathrm{AB},\mathrm{l},T_{\mathrm{c}})x_{+}(\mathrm{AB},\mathrm{l},T_{\mathrm{c}})} = \int_{T_{\mathrm{fus}}(\mathrm{AB})}^{T_{\mathrm{c}}}\frac{\Delta_{\mathrm{fus,exp}}H(\mathrm{AB},T)}{RT^{2}}\,\mathrm{d}T \tag{5}$$

was given in ref. 6. This equation was derived using Eqs. (3) and (4), and by considering the standard state of a pure, fused substance AB which is in equilibrium with its dissociation products A and B. The symbols $\nu(\mathrm{AB},\mathrm{l},x_{\mathrm{w,eq}},T_{\mathrm{c}})$, $k_{\mathrm{H}}(\mathrm{AB},\mathrm{l},x_{\mathrm{w,eq}},T_{\mathrm{c}})$ and $x(\mathrm{AB},\mathrm{l},x_{\mathrm{w,eq}},T_{\mathrm{c}})$ represent the fugacity coefficient, Henry's constant and a mole fraction of the constituent AB in the ternary system A–B–AB, respectively. $T_{\mathrm{fus}}(\mathrm{AB})$ and $\Delta_{\mathrm{fus,exp}}H(\mathrm{AB},T)$ are the melting temperature and the experimentally, i.e. calorimetrically and/or cryometrically, measurable enthalpy of fusion of the constituent AB. The subscript + denotes the quantities related to the standard state mentioned above.

Rearranging the left-hand side of Eq. (5), according to ref. 7, to the form

$$\ln\frac{\nu(\mathrm{AB},\mathrm{l},x_{\mathrm{w,eq}},T_{\mathrm{c}})k_{\mathrm{H}}(\mathrm{AB},\mathrm{l},x_{\mathrm{w,eq}},T_{\mathrm{c}})x(\mathrm{AB},\mathrm{l},x_{\mathrm{w,eq}},T_{\mathrm{c}})}{\nu_{+}(\mathrm{AB},\mathrm{l},T_{\mathrm{c}})k_{\mathrm{H},+}(\mathrm{AB},\mathrm{l},T_{\mathrm{c}})x_{+}(\mathrm{AB},\mathrm{l},T_{\mathrm{c}})} = \ln\frac{a(\mathrm{AB},\mathrm{l},x_{\mathrm{w,eq}},T_{\mathrm{c}})}{a_{+}(\mathrm{AB},\mathrm{l},T_{\mathrm{c}})} \tag{6}$$

Eq. (5) takes the form

$$\ln\frac{\gamma(\mathrm{AB},\mathrm{l},x_{\mathrm{w,eq}},T_{\mathrm{c}})x(\mathrm{AB},\mathrm{l},x_{\mathrm{w,eq}},T_{\mathrm{c}})}{\gamma_{+}(\mathrm{AB},\mathrm{l},T_{\mathrm{c}})x_{+}(\mathrm{AB},\mathrm{l},T_{\mathrm{c}})} = \int_{T_{\mathrm{fus}}(\mathrm{AB})}^{T_{\mathrm{c}}}\frac{\Delta_{\mathrm{fus,exp}}H(\mathrm{AB},T)}{RT^{2}}\,\mathrm{d}T \tag{7}$$

In Eqs. (6) and (7), $a(\mathrm{AB},\mathrm{l},x_{\mathrm{w,eq}},T_{\mathrm{c}})$ and $a_{+}(\mathrm{AB},\mathrm{l},T_{\mathrm{c}})$ denote the activities of the constituents AB related to a standard state of a liquid consisting of only undissociated particles of AB, and $\gamma(\mathrm{AB},\mathrm{l},x_{\mathrm{w,eq}},T_{\mathrm{c}})$ and $\gamma_{+}(\mathrm{AB},\mathrm{l},T_{\mathrm{c}})$ are the corresponding activity coefficients. Assuming the validity of these relations, and with X being A, B or AB

$$\nu(\mathrm{X},\mathrm{l},x_{\mathrm{w,eq}},T_{\mathrm{c}}) \approx \nu_{+}(\mathrm{X},\mathrm{l},T_{\mathrm{c}}) \tag{8}$$

$$k_{\mathrm{H}}(\mathrm{X},\mathrm{l},x_{\mathrm{w,eq}},T_{\mathrm{c}}) \approx k_{\mathrm{H},+}(\mathrm{X},\mathrm{l},T_{\mathrm{c}}) \tag{9}$$

$$\gamma(\mathrm{X},\mathrm{l},x_{\mathrm{w,eq}},T_{\mathrm{c}}) \approx \gamma_{+}(\mathrm{X},\mathrm{l},T_{\mathrm{c}}) \tag{10}$$

$$\Delta_{\mathrm{dis}}H(\mathrm{l},x_{\mathrm{w,eq}},T_{\mathrm{c}}) \approx \Delta_{\mathrm{dis},+}H(\mathrm{l},T_{\mathrm{c}}) \approx \Delta_{\mathrm{dis}}H^{\ominus}(\mathrm{l},T_{\mathrm{c}}) \tag{11}$$

$$\Delta_{\mathrm{dis,inc}}S(\mathrm{l},x_{\mathrm{w,eq}},T_{\mathrm{c}}) \approx \Delta_{\mathrm{dis},+,\mathrm{inc}}S(\mathrm{l},T_{\mathrm{c}}) \approx \Delta_{\mathrm{dis,inc}}S^{\ominus}(\mathrm{l},T_{\mathrm{c}}) \tag{12}$$

where $\Delta_{\mathrm{dis,inc}}S$ is a change in inconfigurational entropy of reaction (2), a transcendental equation may be derived, as in refs. 6 and 8

$$\Phi\{x_{\mathrm{w,eq}},T_{\mathrm{c}},\alpha_{+}[T_{\mathrm{fus}}(\mathrm{AB})],\Delta_{\mathrm{dis},+}H[\mathrm{l},T_{\mathrm{fus}}(\mathrm{AB})],\Delta_{\mathrm{fus,exp}}H[\mathrm{AB},T_{\mathrm{fus}}(\mathrm{AB})]\} = 0 \tag{13}$$

Note that configurational entropy is related to the particle distribution in the volume under consideration, whereas inconfigurational entropy is related to the energies of all parts of the single particle. The transcendental equation cannot be directly transformed into the algebraic form.

Using the phase diagram and Eq. (13), the quantities $\alpha_{+}[T_{\mathrm{fus}}(\mathrm{AB})]$, $\Delta_{\mathrm{dis},+}H[1, T_{\mathrm{fus}}(\mathrm{AB})]$ and $\Delta_{\mathrm{fus,exp}}H[\mathrm{AB}, T_{\mathrm{fus}}(\mathrm{AB})]$ which characterize the system may be calculated for ideal solutions. When dealing with real solutions, only their estimates can be obtained.

If a reliable phase diagram over the entire compositional range is available, the values of these unknown quantities can be obtained, being the limiting values of their estimates. The estimates are calculated numerically using the figurative points lying on the liquidus curves. The limiting values are obtained when the length of the liquidus curve goes to zero.

Additional information connected with the behaviour of the system is the composition dependence of the measured heat of mixing $[\Delta_{\mathrm{mix,exp}}H(\mathrm{A{-}B}, x_{\mathrm{B}}, T_{\mathrm{exp},i})]$, where x_{B} denotes the mole fraction of component B in a system A–B and $T_{\mathrm{exp},i}$ is the ith experimental temperature. Unknown quantities characterizing an ideal solution can, in this case, be calculated using both this dependence and Eq. (13). If, in addition, the temperature function of $\Delta_{\mathrm{fus,exp}}H(\mathrm{AB}, T)$ is known, liquidus curves of AB in the phase diagram can also be calculated.

It is necessary to decide whether the investigated system is ideal or not for the described procedure to be used. The following are conditions of ideal behaviour [8]:

(i) The liquidus curve of the compound AB is symmetrical with respect to the isopleth AB.

(ii) The volume of the solution is an additive function of substantial amounts of constituents and of their constant molar volumes.

(iii) The isothermal molar enthalpies of mixing in the system A–B are symmetrical functions of x_{B} with respect to the isopleth $x_{\mathrm{B}} = 0.5$.

(iv) The enthalpy of mixing is given by the relations

$$\Delta_{\mathrm{mix,exp}}H(\mathrm{A{-}AB}, x_{\mathrm{w,I}}, T_{\mathrm{exp},i}) = \frac{x_{\mathrm{w,I}}}{1 + x_{\mathrm{w,I}}}[1 - \alpha(x_{\mathrm{w,I}})][-\Delta_{\mathrm{dis}}H^{\ominus}(1, T_{\mathrm{exp},i})] \tag{14}$$

for $x_{\mathrm{B}} \leqslant 0.5$; $(x_{\mathrm{w,I}})$

and

$$\Delta_{\mathrm{mix,exp}}H(\mathrm{B{-}AB}, x_{\mathrm{w,II}}, T_{\mathrm{exp},i}) = \frac{x_{\mathrm{w,II}}}{1 + x_{\mathrm{w,II}}}[1 - \alpha(x_{\mathrm{w,II}})][-\Delta_{\mathrm{dis}}H^{\ominus}(1, T_{\mathrm{exp},i})] \tag{15}$$

for $x_{\mathrm{B}} \geqslant 0.5$; $(x_{\mathrm{w,II}})$

in which α is calculated from the equilibrium condition of reaction (2)

$$K_a = K_\gamma K_x = K_x \tag{16}$$

A suitable model, considering an activity coefficient different from 1, has to be used to calculate the characteristic quantities of a system, if some of the conditions for ideal behaviour solutions are not fulfilled. We considered a model performing under the following conditions.

(i) Equation (11) is perfectly valid for reaction (2).

(ii) Only reaction (2) takes place in the melt. There is no heat effect on mixing when pure constituents A(l), B(l) and a fictive, pure constituent AB(l) are mixed together in the ratio of the number of moles corresponding to the ratio of their equilibrium mole fractions.

(iii) The activity coefficients of A(l) and B(l) $[\gamma(\mathrm{A(B)}, 1, x_{\mathrm{w}}, \alpha)]$ depend on how the particles are arranged in a melt. In other words, they are a function of both mole fraction and degree of dissociation.

(iv) The activity coefficient of AB(l) is independent of composition within the temperature range $T_{\mathrm{fus}} - T_{\mathrm{eut}}$ (eutectic temperature). This condition is fulfilled in the limiting case $x_{\mathrm{w,eq}} \rightarrow 1$.

(v) The value of α can be calculated from the equilibrium condition for reaction (2) in Eqs. (14) and (15)

$$K_x = \frac{K_a}{K_\gamma} = \frac{K_{\gamma,+}}{K_\gamma} K_{x,+} = \Gamma K_{x,+} \tag{17}$$

Binary mixtures satisfying all these conditions are termed “quasi-athermal” solutions.

Conditions (iii) and (iv) imply that the activity coefficients of all the constituents are dependent only on the arrangement of particles in the melt. We have shown in ref. 8 that the quantity Γ_r is important to calculate characteristic quantities

$$\Gamma_r = \frac{K_{\gamma,+,r}}{K_\gamma} = \psi(x_{\mathrm{w}}, \alpha) \tag{18}$$

where $K_{\gamma,+,r}$ is always referred to the same experimental temperature $T_{\mathrm{exp},i}$. The function $\psi(x_{\mathrm{w}}, \alpha)$ is expressed by a polynomial

$$\Gamma_r = a_1 + a_2 x_{\mathrm{w}} + a_3 \alpha + a_4 x_{\mathrm{w}} \alpha + a_5 x_{\mathrm{w}}^2 + a_6 \alpha^2 \tag{19}$$

The coefficients a_j are obtained by fitting the data of x_{w}, $\alpha(x_{\mathrm{w}})$ and $\Gamma_r(x_{\mathrm{w}}, \alpha)$ calculated from Eqs. (14), (15) and (17). Using Eqs. (7), (19) and van't Hoff's equation of reaction isobars, it is possible to obtain estimates of the characteristic quantities $\alpha_+(T_{\mathrm{fus}}(\mathrm{AB}))$, $\Delta_{\mathrm{dis},+}H(1, T_{\mathrm{fus}}(\mathrm{AB}))$ and $\Delta_{\mathrm{fus,exp}}H(\mathrm{AB}, T_{\mathrm{fus}}(\mathrm{AB}))$.

These quantities are for real solutions calculated using the iterative procedure described above (see Eq. (13)).

3. Experimental

The K_3FMoO_4 sample was prepared by melting equimolar amounts of potassium fluoride and potassium molybdate in a Pt crucible. The melting point of the prepared K_3FMoO_4 was checked by thermal analysis. Before its use, the potassium fluoride was dehydrated by first keeping $KF \cdot 2H_2O$ (Lachema, Czech Republic) under vacuum at room temperature for one week in the presence of P_2O_5, and then gradually heating it to 200°C for one more week. The potassium molybdate (Fluka, Switzerland) was dried at 600°C. Both chemicals were of p.a. purity.

The enthalpy of fusion of K_3FMoO_4 was measured with a high-temperature Setaram HTC 1800 K heat-flow calorimeter working in a DSC mode with a rate of temperature change of 1 K min^{-1}. The measuring procedure was described in detail in ref. 9. KCl was used as the calibration standard. Both the investigated sample of K_3FMoO_4 (250.09 mg) and the calibration standard KCl (250.90 mg) were sealed in the platinum crucibles and put into the upper sintered alumina crucible of the calorimetric cell. The platinum crucible containing the reference standard (small pieces of sintered alumina) was placed in the lower sintered alumina crucible of the calorimetric cell. During the experiment, the temperature and the difference in temperature between the upper and lower crucibles, which is proportional to the heat-flow, was recorded.

The experimental data-processing was discussed in ref. 9. The measured quantities at melting (Q_{fus}/λ_{fus}) and crystallization ($Q_{cryst}/\lambda_{cryst}$) were not adjusted to the equilibrium temperature because the heat contribution from the difference in heat capacity between the solid and liquid phase to the transformation heat is less than the experimental error. Q_{fus} and Q_{cryst} are the heat effects of fusion and crystallization, respectively, and λ_{fus} and λ_{cryst} are constants proportional to the heat-transfer coefficient.

Because the temperatures of transformation (transformation means fusion and/or crystallization), Θ_{trans}, or K_3FMoO_4 (752°C) and of KCl (711°C) are close to each other, we can assume that λ_{fus} and λ_{cryst} are the same for the investigated and calibration substances. The specific enthalpy of transformation of K_3FMoO_4 can, therefore, be calculated using the relation

$$\frac{\left(\dfrac{Q_{trans}(K_3FMoO_4)}{\lambda_{trans}}\right)_{\Phi}\dfrac{1}{m(K_3FMoO_4)}}{\left(\dfrac{Q_{trans}(KCl)}{\lambda_{trans}}\right)_{\Phi}\dfrac{1}{m(KCl)}} = K_{trans} = \frac{\Delta_{trans}h(K_3FMoO_4)}{\Delta_{trans}h(KCl)} \qquad (20)$$

and the known value of this quantity for KCl. In Eq. (20), Φ and m denote the arithmetic mean and sample mass, respectively.

The experimental values of Q_{fus}/λ_{fus} and $Q_{cryst}/\lambda_{cryst}$, the arithmetic means and their errors, are given in Tables 1 and 2. The errors were calculated using the Student distribution at the confidence level of $(1-\alpha) = 0.95$.

Table 1
Experimental values of Q_{fus}/λ_{fus} and $(Q_{fus}/\lambda_{fus})_{\Phi}$ for K_3FMoO_4 and KCl

Sample	$(Q_{fus}/\lambda_{fus})/(K\ s)$					$(Q_{fus}/\lambda_{fus})_{\Phi}/(K\ s)$
K_3FMoO_4	269	266	283	279	261	(272 ± 11)
KCl	503	508	507	519	509	(509 ± 7)

Table 2
Experimental values of $Q_{\mathrm{cryst}}/\lambda_{\mathrm{cryst}}$ and $(Q_{\mathrm{cryst}}/\lambda_{\mathrm{cryst}})_{\Phi}$ for K_3FMoO_4 and KCl

Sample	$(Q_{\mathrm{cryst}}/\lambda_{\mathrm{cryst}})/(\mathrm{K\ s})$					$(Q_{\mathrm{cryst}}/\lambda_{\mathrm{cryst}})_{\Phi}/(\mathrm{K\ s})$
K_3FMoO_4	293	306	308	294	307	(302 ± 9)
KCl	538	536	524	532	523	(531 ± 9)

Substituting these experimental data and sample masses into Eq. (20), we get $\kappa_{\mathrm{fus}} = (0.536 \pm 0.023)$ and $\kappa_{\mathrm{cryst}} = (0.571 \pm 0.020)$. Their arithmetic mean is

$$\kappa_{\Phi} = (0.553 \pm 0.021) \tag{21}$$

Hence the specific enthalpy of fusion

$$\Delta_{\mathrm{fus}}h(\mathrm{K_3FMoO_4}) = \kappa_{\Phi}\Delta_{\mathrm{fus}}h(\mathrm{KCl}) = (195 \pm 8)\ \mathrm{kJ\ kg^{-1}} \tag{22}$$

The value of $\Delta_{\mathrm{fus}}h(\mathrm{KCl}) = 353\ \mathrm{kJ\ kg^{-1}}$ was taken from ref. 10. The error in $\Delta_{\mathrm{fus}}h(\mathrm{K_3FMoO_4})$ was determined from Gauss's law of error propagation. The molar enthalpy and entropy of fusion of K_3FMoO_4 at the temperature of fusion, 1025 K, are respectively

$$\Delta_{\mathrm{fus}}H_{\mathrm{m}}(\mathrm{K_3FMoO_4}) = (58 \pm 2)\ \mathrm{kJ\ mol^{-1}} \tag{23}$$

and

$$\Delta_{\mathrm{fus}}S_{\mathrm{m}}(\mathrm{K_3FMoO_4}) = (56 \pm 2)\ \mathrm{J\ mol^{-1}\ K^{-1}} \tag{24}$$

4. Calculation and discussion

The phase diagram of the system $KF-K_2MoO_4$ measured by Julsrud and Kleppa [2] and Patarák et al. [3], together with the composition dependence of the measured enthalpy of mixing in this system at 1273 K $[\Delta_{\mathrm{mix,exp}}H(\mathrm{KF-K_2MoO_4}, x(\mathrm{K_2MoO_4}), 1273\ \mathrm{K})]$ [2], were used to calculate the dissociation degree and dissociation enthalpy of K_3FMoO_4 at its melting temperature.

Condition (i), which is valid for ideal solutions, is not satisfied because of the asymmetrical liquidus curve of K_3FMoO_4 in the phase diagram of the system $KF-K_2MoO_4$. The enthalpy of mixing calculated by Eqs. (14) and (15) (assuming the ideal solution model) fits the experimental curve only if the dissociation degree equals unity and the dissociation enthalpy reaches negative infinite values. In this case, Eqs. (14) and (15) become uncertain which implies that condition (iv) is invalid. The model of "quasi-athermal" solutions was therefore used.

Two methods of calculation were used. The first assumes "quasi-athermal" behaviour of solutions over the compositional range $x_{\mathrm{w,eq}}(T_{\mathrm{eut}}) < x_{\mathrm{w,eq}}(T_{\mathrm{c}}) < 1$. The second refers to an iterative calculation. The experimental value of the enthalpy of fusion given in Eq. (23) was used in both methods. The results are summarized in Table 3.

Table 3
Results of calculations of characteristic thermodynamic quantities obtained using the "quasi-athermal" solution model (I) and the real solution model (II) (KF is A, K_2MoO_4 is B)

Model	Known experimental data	$\Delta_{dis,+}H(1, T_{fus}(AB))$/kJ mol^{-1}	$\alpha_+(AB, T_{fus}(AB))$
I	Phase diagram $\Delta_{mix,exp}H(A-B, x_B, T_{exp})$ $\Delta_{fus,exp}H(AB, T_{fus}(AB))$	−1.4	0.59
II	Phase diagram $\Delta_{mix,exp}H(A-B, x_B, T_{exp})$ $\Delta_{fus,exp}H(AB, T_{fus}(AB))$	−1.2	0.51

Daněk and Chrenková [4] found that the dissociation degree of K_3FMoO_4 is 0.81 (from a thermodynamic analysis of the phase diagram of the system $KF-K_2MoO_4$) and 0.84 (from an analysis of the volume properties). They found the dissociation enthalpy to be 18.8 kJ mol^{-1} from the temperature dependence of the equilibrium dissociation constant. However, they used an ideal solution model. There may be two possible ways to explain the difference between the values of Daněk and Chrenková [4] and those found in this work:

(i) We incorporated the enthalpy of mixing to the calculations as additional information. In this case the calculated dissociation enthalpy has the opposite sign.

(ii) We used different models of solutions. The "quasi-athermal" solution model leads to a lower dissociation degree compared with the ideal solution model.

The values of $\Delta_{dis,+}H(1, T_{fus}(K_3FMoO_4)) = -2.9$ kJ mol^{-1} and $\alpha_+(K_3FMoO_4, T_{fus}(K_3FMoO_4)) = 0.80$ were also calculated assuming ideal solutions and taking into account the heat of mixing at the composition $x(K_2MoO_4) = 0.5$ and temperature 1273 K. The dissociation degree, calculated under these assumptions, is in good agreement with the values obtained by Daněk and Chrenková [4], whereas the dissociation enthalpy differs only slightly from that calculated by the previous method (Table 3).

We can see that including the enthalpy of mixing into the calculations strongly influences the dissociation enthalpy obtained. The dissociation degree primarily depends on the model used.

We suggest the most reliable values of the characteristic quantities for this system is to be $\Delta_{dis,+}H(1, T_{fus}(K_3FMoO_4)) = -1.2$ kJ mol^{-1} and $\alpha_+(K_3FMoO_4, T_{fus}(K_3FMoO_4)) = 0.51$.

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