Molar enthalpy of fusion and the degree of thermal dissociation of Na_3FSO_4

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The value of molar enthalpy of fusion of complex compound Na_3FSO_4, which is formed in the system $NaF—Na_2SO_4$, was determined by the method of molten salt cryometry. The result is compared with the Sutra's rule. Calculation of the degree of thermal dissociation b_0 of pure compound Na_3FSO_4 showed that $b_0=0.65—0.70$ if the cryometric value $\Delta H^f(Na_3FSO_4) = 62.3$ kJ mol^{-1} is used. If the value $\Delta H^f(Na_3FSO_4)=53$ kJ mol^{-1} (obtained by means of the Sutra's rule) is applied then b_0 equals 0.80—0.85.

Мольная энтальпия плавления комплексного соединения Na_3FSO_4, которое образуется в системе $NaF—Na_2SO_4$, была определена методом криометрии расплавов и сравнена со значением, полученным по правилу Сутра. Расчет степени термической диссоциации b_0 чистого соединения Na_3FSO_4 показал, что $b_0 = 0{,}65—0{,}70$, если используется криометрическое значение $\Delta H^f(Na_3FSO_4) = 62{,}3$ кДж моль$^{-1}$. При использовании значения $\Delta H^f(Na_3FSO_4)=53$ кДж моль$^{-1}$ (полученного при помощи правила Сутра) было рассчитано значение $b_0=0{,}80—0{,}85$.

The degree of thermal dissociation b_0 of complex compound $Z=A_xB_y$ can be obtained on the basis of knowledge of the course of liquidus curve of this compound in the system with the substance A or B. The most simple application of the method, (for the case that $x=y=1$) is described by *Glasstone* [1]. This method assumes

a) nonexistence of solid solutions of the substance A (resp. B) on the base of the compound Z;

b) knowledge of the enthalpy of fusion of the compound Z.

Investigation of the phase diagram of the system $NaF—Na_2SO_4$, in which the compound $Z=Na_3FSO_4=NaF\cdot Na_2SO_4$ is formed, has shown [2] that the condition a) is fulfilled. In order to make possible to apply the Glasstone's method for determination of b_0 it was necessary to determine the value of molar enthalpy of fusion ΔH^f_Z.

Cryometric determination of the molar enthalpy of fusion of the compound Na_3FSO_4

Application of the cryometric method for determination of enthalpy of fusion of components in true binary systems or in quasi-binary systems formed by thermally stable components has a good theoretical background [3]. However, the case of cryometry carried out on the base of complex compound which partially thermally dissociates has not been treated in literature yet. This stimulated theoretical analysis of this problem [4]. It has been proved that cryometric method is correct also in this case.

Success of cryometric determination of the enthalpy of fusion depends very much on the choice of the additive which will be used as admixture to the substance the enthalpy of which will be determined. The two main requirements on the additive are following: nonexistence of solid solutions formed on the base of investigated substance and binary (or quasi-binary) character of the system "investigated substance—additive".

In our case, the investigated compound is Na_3FSO_4 and as additives NaCl and LiF were chosen. The former additive has a noncommon anion with Na_3FSO_4 and the latter noncommon cation. It is known that sodium chloride forms with sodium fluoride and sodium sulfate simple eutectic systems [5, 6]. Therefore, it is reasonable to assume that it will form no solid solutions on the base of substance $Na_3FSO_4 = NaF \cdot Na_2SO_4$. One should take into account that a possibility of formation of compound Na_3ClSO_4 by a substitution reaction cannot be excluded. The second substance, LiF, forms with NaF a eutectic system with limited solid solution on the NaF side [7]. It does not form a quasi-binary system with Na_2SO_4. However, also in this case, substitution reactions may be present. In order to clear these questions we have investigated phase diagrams of the systems Na_3FSO_4—NaCl and Na_3FSO_4—LiF in a whole concentration range. It has been found that both additives NaCl and LiF allow to make correct cryometry on the base of Na_3FSO_4 [8].

Experimental

Chemicals of anal. grade were used. Their purity is characterized by melting point. NaF ($T' = 1266.5$ K $= 993.5$°C), Na_2SO_4 ($T' = 1157.8$ K $=$ 884.8°C), NaCl ($T' = 1073.8$ K $=$ 800.8°C), LiF ($T' = 1121.5$ K $=$ 848.5°C).

For the purpose of cryometry part of liquidus curve of Na_3FSO_4 in the systems with NaCl and LiF was measured in the concentration range 90—100 mole % Na_3FSO_4. Experimental arrangement has been described in detail previously [2].

Results of cryometric measurements and their discussion

By the treatment of experimental data the dependence $\Delta T_{Z}\ \mathrm{K}^{-1}/x(\mathrm{NaCl}$, resp. LiF) = f[$x$(NaCl, resp. LiF)] was obtained (Table 1). Limit of this function at x(NaCl, resp. LiF) → 0 equals the slope of tangent to the liquidus curve of Na_3FSO_4 in the system Na_3FSO_4—NaCl or in the system Na_3FSO_4—LiF for $x_Z \rightarrow 1$. In both systems the same result, *viz.* $k^0_Z = 150$ K, was obtained. Putting this value in eqn (*1*) we obtain the sought molar enthalpy of fusion of the compound Na_3FSO_4

Table 1

Cryometric treatment of a part of liquidus curve of Na_3FSO_4 in the systems with NaCl and LiF

x_i	$T^f(Na_3FSO_4)/K$		$\Delta T(Na_3FSO_4)\ K^{-1}/\Delta x_i$	
	i = NaCl	i = LiF	i = NaCl	i = LiF
0.00	1060.0	1060.0	150	150
0.01	1058.5	1058.5	150	150
0.02	1057.0	1057.5	150	175
0.03	1055.5	1055.5	150	150
0.04	1054.0	1054.5	150	137.5
0.05	1052.5	1052.5	150	150
0.10	1045.0	1045.0	150	150

$$\Delta H^{f}_{Z} = \frac{R(T^{f}_{Z})^2}{k^0_Z}\, k^{St}_{i/Z} \doteq 62\,280\ \mathrm{J\ mol^{-1}} \qquad (1)$$

($Z = Na_3FSO_4$; i = NaCl resp. LiF; $k^{St}_{i/Z} = 1$).

Determination of the enthalpy of fusion by the cryometric method can be deteriorated by the existence of limited solid solutions which are formed on the base of the substance the enthalpy of fusion of which is to be found. When a complex compound is dealt with it should be taken into account that the substance can thermally dissociate into "original" components and therefore, also enthalpy of dissociation and enthalpy of mixing of resulting molten mixture should be considered. We shall estimate how the above-mentioned phenomena can influence correctness of determination of cryometric value of ΔH^{f}_{Z}.

Experimental study of phase diagrams of the systems Na_3FSO_4—NaCl and Na_3FSO_4—LiF showed that the eutectic temperature can be registered from 3 mole

% NaCl and 4 mole % LiF, respectively. It has been proved [9] that we can formally write

$$\ln x_Z^s = \frac{\Delta H_Z^+}{R} \frac{T^E - T_Z^f}{T^E T_Z^f} \qquad (2)$$

where x_Z^s is the mole fraction of component Z in a limited solid solution which exists on the base of the compound Z at eutectic temperature T^E, ΔH_Z^+ is the parameter characterizing limited solid solution formed on the base of Z, T^E is the eutectic temperature in the system "Z—*i*", and T_Z^f is the temperature of fusion of substance Z. In our case, $T_Z^f = 1060$ K.

In case of the system Na_3FSO_4—NaCl, $x_Z^s = 0.97$, $T^E = 900$ K. Then from eqn *(2)* it follows that $\Delta H_Z^+ = 1510$ J mol^{-1}, which is 2.4% from the cryometric value of enthalpy of fusion $\Delta H_Z^f = 62\,280$ J mol^{-1}.

Similarly, for the system Na_3FSO_4—LiF it holds $x_Z^s = 0.96$, $T^E = 890$ K and $\Delta H_Z^+ = 1884$ J mol^{-1}, which is 3% from ΔH_Z^f.

Therefore it may be stated that eventual presence of a narrow region of limited solid solutions formed on the base of complex compound Z cannot influence substantially the accuracy of the cryometric determination of the quantity ΔH_Z^f.

The question of estimation of enthalpy of dissociation and/or enthalpy of mixing which originate at melting of the complex compound Na_3FSO_4 is more complicated. It cannot be directly determined even by a calorimetric measurements. Importance of neglection of these quantities can be estimated so that we compare the value of enthalpy of fusion obtained by the cryometric method with enthalpy of fusion calculated by application of Sutra's rule [10]. According to this rule molar entropy of fusion of each particle (*e.g.* of an ion) of given substance equals 12.6 J mol^{-1} K^{-1}. This rule is valid satisfactorily for substances of type (1,1) the behaviour of which is close to ideality. If we apply this rule to NaF, then for total dissociation to Na^+ and F^- we obtain ΔH^f(NaF) = 32 900 J mol^{-1}, which is only about 4% lower than the experimental value [11]. For Na_2SO_4, if we assume that it dissociates into Na^+ and $NaSO_4^-$, we get $\Delta H^f(Na_2SO_4)$ = 29 200 J mol^{-1}, which is about 27% higher than the experimental value [11]. It can be assumed that dissociation of Na_2SO_4 will be higher in equivalent mixture of $NaF + Na_2SO_4$ than in pure Na_2SO_4. We estimate that the calculated value can be about 10% higher than the measured one. If we take $b_0 = 0.75$, one formula molecule of Na_3FSO_4 yields 4 particles: 2.25 Na^+, 0.25 FSO_4^{3-}, 0.75 F^-, and 0.75 $NaSO_4^-$. Using Sutra's rule the molar enthalpy of fusion can be estimated to be 53 000 J mol^{-1}, which is about 85% of the value determined by cryometry. It is probable that a correct value of ΔH_Z^f lies between these two limit values.

Thermodynamic determination of the degree of thermal dissociation of compound Na_3FSO_4

Let the degree of thermal dissociation of pure compound be denoted b_0. After melting of 1 mole of Na_3FSO_4 the molten mixture contains $(1-b_0)$ moles of thermally undissociated compound which is in equilibrium with b_0 moles of NaF and b_0 moles of Na_2SO_4. If we assume an ideal behaviour of solution, $a(Na_3FSO_4) = (1-b_0)/(1+b_0)$, $a(NaF) = a(Na_2SO_4) = b_0/(1+b_0)$. The equilibrium constant of thermal dissociation of pure substance equals

$$K_{\mathrm{dis}}^0 = \frac{b_0^2}{1-b_0^2} \tag{3}$$

It follows that assuming ideal behaviour the liquidus of Na_3FSO_4 should have the same course in both subsystems, *viz.* Na_3FSO_4—NaF and Na_3FSO_4—Na_2SO_4. In the first subsystem $T^{\mathrm{f}}(Na_3FSO_4) - T(E_1) \doteq 6$ K, in the second $T^{\mathrm{f}}(Na_3FSO_4) - T(E_2) = 36$ K. The calculation will be carried out for the subsystem Na_3FSO_4—Na_2SO_4 because here is the difference $T^{\mathrm{f}}(Na_3FSO_4) - T(E_2)$ greater and therefore greater is also the part of liquidus curve which can be compared with calculation.

In a mixture of the system Na_3FSO_4—Na_2SO_4 the degree of thermal dissociation of Na_3FSO_4 will change from b_0 to b which is a function of composition. From x weight-in moles of Na_3FSO_4 it results bx moles of NaF, bx moles of Na_2SO_4 and it remains $x(1-b)$ moles of Na_3FSO_4. Together with x moles of Na_3FSO_4 also $(1-x)$ moles of Na_2SO_4 was weight-in and the total sum of the amount of substance is $(1+bx)$ moles. Then for activities of each component (assuming ideal behaviour) it holds: $a(NaF) = bx/(1+bx)$, $a(Na_2SO_4) = (1-x+bx)/(1+bx)$, $a(Na_3FSO_4) = x(1-b)/(1+bx)$. The equilibrium constant of dissociation of compound Na_3FSO_4 in mixture with Na_2SO_4 equals

$$K_{\mathrm{dis}} = \frac{(1-x+bx)\,b}{(1-b)\,(1+bx)} \tag{4}$$

If temperature of fusion of Na_3FSO_4 ($T_{\mathrm{z}}^{\mathrm{f}}$) is not very far from the temperature of liquidus T which we are interested in (this assumption is fulfilled in our case very good) it holds $K_{\mathrm{dis}}^0 \doteq K_{\mathrm{dis}}$. Solving eqns (*3*) and (*4*) we found dependence $b = \mathrm{f}(x; b_0)$

$$b = -\frac{1-x}{2x} + \left[\left(\frac{1-x}{2x}\right)^2 + \frac{b_0^2}{x}\right]^{1/2} \tag{5}$$

For the equilibrium between solid compound Na_3FSO_4 and the melt formed by melting of this compound the equation of liquidus yields the expression

$$\ln \frac{1-b_0}{1+b_0} = \frac{\Delta H_i^f}{R}\left[\frac{1}{T_{\mathrm{hyp}}^f} - \frac{1}{T_{\mathrm{exp}}^f}\right] \tag{6}$$

where T_{hyp}^f is the hypothetic temperature of fusion of undissociated compound Na_3FSO_4 and T_{exp}^f is the experimentally determined temperature of fusion of Na_3FSO_4, which equals 1060 K. For temperature of liquidus of Na_3FSO_4 in the subsystem Na_3FSO_4—Na_2SO_4 we readily obtain

$$T = \frac{\Delta H_i^f}{R\left[\dfrac{\Delta H_i^f}{RT_{\mathrm{hyp}}^f} - \ln \dfrac{x(1-b)}{(1+xb)}\right]} \tag{7}$$

We proceed so that we choose different values of b_0 ($0 < b_0 < 1$) and using eqn (*6*) we calculate corresponding values of T_{hyp}^f. Then from eqn (*5*) for each $x > E_2$ we calculate the value of b and from eqn (*7*) we obtain the calculated liquidus temperature of Na_3FSO_4. Agreement between the sets of calculated and experimental data is the criterion of correctness of the choice of b_0. Comparison of calculated liquidus curves of Na_3FSO_4 with experiment is presented in Fig. 1. It follows that the best agreement is achieved for $b_0 = 0.65$—0.70.

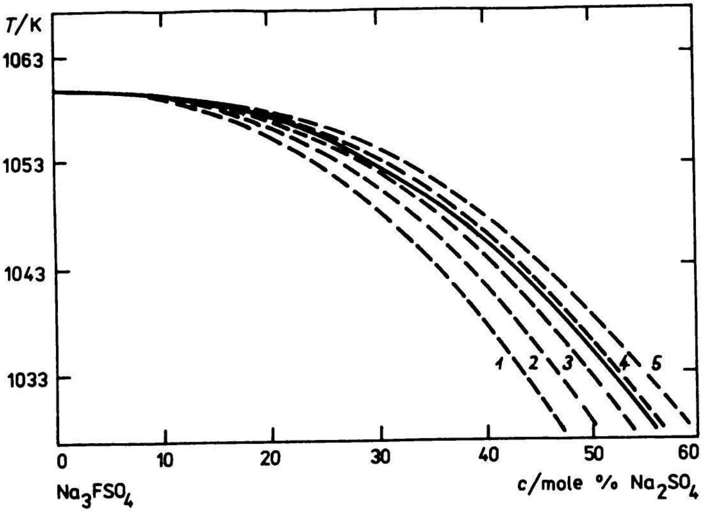

Fig. 1. Comparison of the experimental liquidus of Na_3FSO_4 in the system with Na_2SO_4 with the calculated one. The calculation is carried out for different degrees of thermal dissociation b_0 of pure compound Na_3FSO_4 assuming $\Delta H^f(Na_3FSO_4) = 62.280\ \mathrm{kJ\ mol^{-1}}$.
1. 0.4; *2.* 0.5; *3.* 0.6; *4.* 0.7; *5.* 0.8.

This calculation procedure was repeated taking ΔH_Z^f = 53 000 J mol^{-1}. In this case the best agreement between experimental and calculated data was obtained for $b_0 = 0.80—0.85$.

With respect to the former result it can be concluded that the most probable value of the quantity b_0 is 0.70—0.80. The value $b_0 = 0.70$ corresponds to the hypothetic temperature of fusion $T_{\mathrm{hyp}}^f = 1405$ K while $b_0 = 0.80$ gives $T_{\mathrm{hyp}}^f =$ 1670 K.

Comparison of the value of b_0 calculated in this work by a classical thermodynamic method with that obtained from the analysis of liquidus curve of NaF in the system NaF—Na_3FSO_4 [2] shows a good agreement between both results. It means that the course of liquidus of NaF in this system is very close to ideality.

In conclusion it can be stated that anions F^- and SO_4^{2-} form a complex anion FSO_4^{3-}. It can be assumed that formation of this complex anion influences current efficiency of aluminium electrolyses less negatively than SO_4^{2-} ion itself. However, taking into account a high degree of thermal dissociation b_0 it can be also concluded that this influence is not very manifest and the negative influence of SO_4^{2-} ion is not substantially eliminated. All these aspects are to be taken into account when the problem of recovery of fluoro salts from gas evolution from Hall—Héroult smelting cells is treated.

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