

Thermodynamics of Charge-unsymmetrical Anion Mixtures.

I. The Liquid Systems $AF - A_2SO_4$

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The thermodynamic properties of the liquid mixtures $AF - A_2SO_4$ ($A = Li, Na, K$) have been studied by calorimetric and cryoscopic measurements. The enthalpies of mixing are small and mostly negative. When partial Gibbs energies calculated from the liquidus data are compared with corresponding enthalpies from calorimetry, it is found that the partial entropies are significantly larger than calculated from the Temkin model. It is suggested that these excess entropies may be due either to the charge asymmetry or to the large difference in size between the small F^- and the large SO_4^{2-} anion.

During the post-war years there has been a great increase in our knowledge and understanding of fused salt mixtures. In these developments Førlund has played a major role; his doctoral thesis published in 1957 remains a milestone publication.¹ This provided the first detailed analysis of the thermodynamics of simple fused salt solutions from the viewpoint of quasi-lattice theory.

In the early years thermodynamic studies of fused salt mixtures were based exclusively on the equilibrium approach, *i.e.* on applications of EMF, vapor pressure and/or cryoscopic methods of investigation. During the last two decades new insight has been gained also from calorimetric studies, particularly from measurements of the enthalpy of mixing. On the whole, it is now found that the most reliable thermodynamic information on fused salt solutions consists of Gibbs energies from equilibrium work, enthalpies from calorimetry and entropies from a combination of these two methods. Perhaps the most successful

examples of this combined approach have been provided by Østvold,² who has considered a wide range of mixed cation-common anion systems. At the present time there are no comparable data for mixed anion-common cation mixtures. The present series of investigations was initiated in order to remedy this situation.

It is well-known that mixed anion-common cation fused salt mixtures often form very nearly ideal solutions. This was shown already by Flood *et al.*³ in their pioneering EMF study of $Na_2CO_3 - Na_2SO_4$ carried out about 30 years ago. For many other binaries of this type nearly ideal solution behavior can be inferred from the published phase diagrams. During recent years some of these observations have been confirmed by precise calorimetric measurements. Thus Melnichak and Kleppa,⁴ in their study of the binary alkali chloride–bromide, chloride–iodide and bromide–iodide systems, found only small, positive and nearly symmetrical enthalpies of mixing. The corresponding alkali fluoride mixtures, on the other hand, show much more complex behavior.⁵ For these systems the enthalpies are considerably larger, and may have either positive or negative values; energetic asymmetry often is strong, so that some systems show both positive and negative mixing enthalpies within the same binary. In the present work we are extending these calorimetric studies to charge-unsymmetrical mixed anion-common cation systems, and are presenting new enthalpy data for three alkali fluoride–sulfate mixtures. Work is in progress on other systems.

When the present investigation was initiated, it was our plan to compare the new enthalpy data

with Gibbs energies derived from published phase diagrams.⁶⁻⁹ It was expected that this would provide reliable entropy data, so that it would throw light on the applicability of the Temkin model¹⁰ to this type of solution system. We had also taken note of the fact that Schmitz-Dumont and Heckmann⁶ had found that the phase diagrams of four of the five alkali fluoride-sulfate systems show equimolar solid compounds $AF \cdot A_2SO_4$ which give rise to local liquidus maxima. Even so, Schmitz-Dumont and Heckmann had concluded that electrostatic considerations do not favor complex formation according to the reaction $SO_4^{2-} + F^- \rightarrow SO_4F^{3-}$.

Unfortunately, we found that the cryoscopic data which could be read from the published phase diagrams were not precise enough to provide reliable partial Gibbs energies and entropies. This prompted us to undertake a reinvestigation of the liquidus curves of the considered systems. The results of this thermal analysis study are also reported in the present communication.

EXPERIMENTAL

Calorimetric measurements. The calorimetric measurements were performed in a Calvet-type twin microcalorimeter for work at temperatures up to 1300–1400 °C. The apparatus used and the mixing setup adopted were similar to those of Kleppa and Hong.¹¹ However, in order to further protect the fused silica liner from the fluoride vapors, we used a longer nickel protection tube (abt 28 cm). In a few experiments we used a protection tube made from platinum-20% rhodium rather than from nickel.

The radiation shield assembly was constructed from a series of ceramic rings cemented to a central mullite tube which enclosed a 7 mm O.D. mullite manipulation tube. To the lower end of this was attached a small platinum crucible, "the dipper". Inside the manipulation tube there was a 3 mm diameter alumina rod which was used to move a platinum plunger up and down.

The mixing experiments, all of the liquid-liquid type, were initiated by lowering the dipper into the melt contained in the main platinum crucible. The plunger was then moved up and down 5 times in order to mix the two liquids. Following this, all movable parts were returned to their original positions. The mixing operation was repeated three or four times, and then finally a last time towards the end of the experiment, in order to make sure that mixing was complete. The

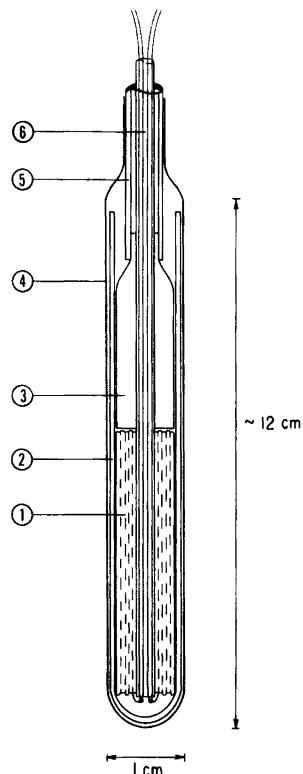


Fig. 1. Electrical calibration heater. 1. Heater, vertically wound 0.254 mm Pt20Rh wire in shallow grooves in alumina tube; 2. Alumina crucible; 3. Alumina tube; 4. Platinum protection sleeve; 5. Mullite tube; 6. Four-bore alumina tube with four Pt20Rh leads of 0.254 mm diameter.

measurements were carried out in an argon atmosphere at 1253 K (Li,Na) and 1345 K (K).

The calorimeter was calibrated electrically, using a constant current source coupled with an electronic timer and a digital voltmeter. A schematic diagram of the heater assembly is shown in Fig. 1. The heating coil and leads were made from Pt20Rh wire of 0.254 mm diameter. At each end of the main heating coil (room temperature resistance $\sim 1.1 \Omega$) were welded a pair of wires to connect with current source and voltmeter through a four-bore alumina tube. During calibrations the heater assembly replaced the manipulation tube and plunger unit.

In a typical calibration experiment a constant current of about 0.4 A was passed through the assembly for about 60 s. In this time the voltage drop through the heating coil was measured so that

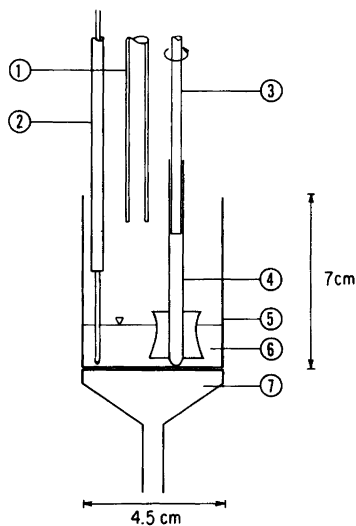


Fig. 2. Experimental setup for cryoscopic measurements. 1. Alumina tube for adding salt; 2. Two-bore alumina tube with thermocouple; 3. Alumina rod for stirring; 4. Platinum stirrer; 5. Platinum crucible; 6. Salts melt; 7. Support.

the total heat released could be calculated. In order to correct for heat detected in the calorimeter but actually generated in the long leads, a 0.4 A current was passed in two subsequent experiments for the same period of time through the pairs of leads on each side of the heating coil. The average of these two measurements was subtracted from the effect observed in the first experiment. We found that this correction represented about 50 % of the total heat actually observed in the calorimeter. By this procedure we could calibrate the calorimeter with a precision of about $\pm 0.6\%$.

Cryoscopic measurements. The furnace used in these experiments has been described by Motzfeldt.¹² Other parts of the thermal analysis setup are shown in Fig. 2.

All temperature measurements were carried out by a Pt13Rh-Pt thermocouple checked against a Pt10Rh-Pt couple certified by N.B.S. The EMF was measured by a Hewlett-Packard 3645 digital voltmeter which could be read to the nearest microvolt. The hot junction of the thermocouple dipped directly into the melt; the cold junction was maintained in distilled water and ice in a Dewar flask.

During the cryoscopic measurements, the fused salt mixture was first heated to a temperature somewhat above the liquidus and then allowed to cool at a rate of about $0.1\text{ }^\circ\text{C/s}$. When a solid started

to precipitate, an abrupt change in the cooling rate was observed. For most compositions there was a definite tendency toward super-cooling. This problem was solved by dropping small pieces of platinum wire, about 10 mg in size, into the melt when the crystallization temperature was reached. This nucleated crystallization without otherwise influencing the cooling rate.

A typical run was started with about 15 g of pure salt in the crucible. The composition of the melt was then gradually changed by adding weighed amounts of the second component as crystals (fluorides) or as pellets (sulfates) through the feeding tube.

The maximum absolute error in the liquidus determinations was estimated to be of the order of $\pm 2\text{ }^\circ\text{C}$. However, the freezing point depressions, relative to the melting point of the pure salt, could be measured to about $\pm 0.3\text{ }^\circ\text{C}$.

Chemicals. The chemicals used were: LiF, Fisher Certified Reagent; Li_2SO_4 , Fisher Certified Reagent; NaF, Baker Analyzed Reagent; Na_2SO_4 , Anhydrous, Mallinckrodt Analytical Reagent; KF,

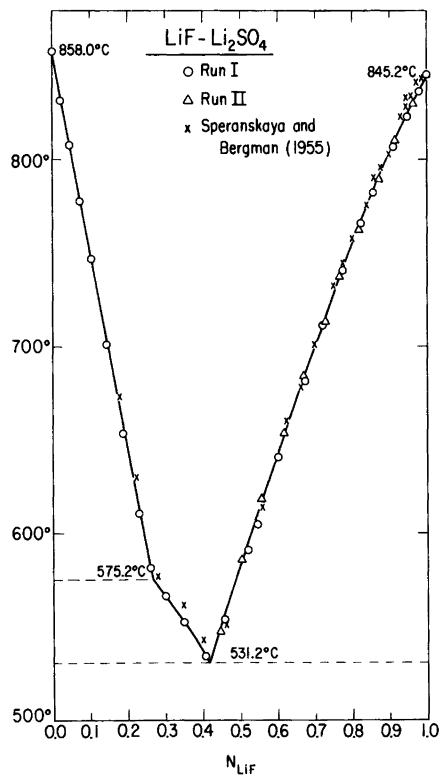


Fig. 3. Liquidus curves for the phase diagram $\text{LiF} - \text{Li}_2\text{SO}_4$.

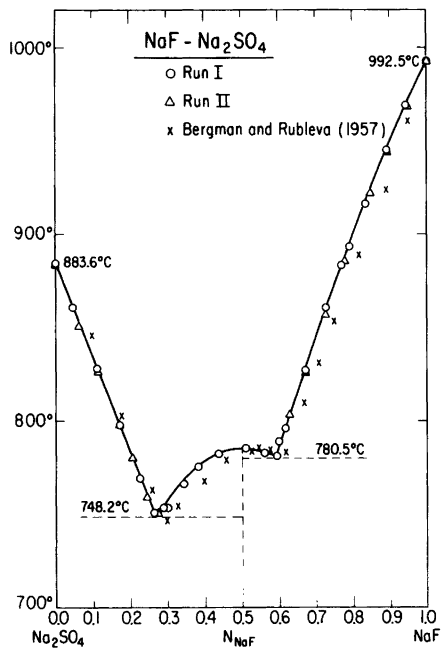


Fig. 4. Liquidus curves for the phase diagram NaF - Na₂SO₄.

Baker and Adamson, Anhydrous Granular Reagent; and K₂SO₄, Mallinckrodt Analytical Reagent.

All chemicals were dried overnight under vacuum at 150 °C. The fluorides used in the cryoscopic measurements were melted in an inert, dry atmosphere, and clear crystals were handpicked from the solidified melt.

RESULTS AND DISCUSSION

Cryoscopic measurements. All experimental results are presented graphically in Figs. 3–5; liquidus data for round figure and eutectic compositions are summarized in Tables 1–3. For comparison we have for each system included in Figs. 3–5 data points taken from the latest published phase diagram study. All earlier data are normalized to our own melting points for the pure components so that cryoscopic effects can be compared directly. Our liquidus curves, as might be expected, are in general agreement with the earlier results; in some cases, however, there are very considerable numerical discrepancies.

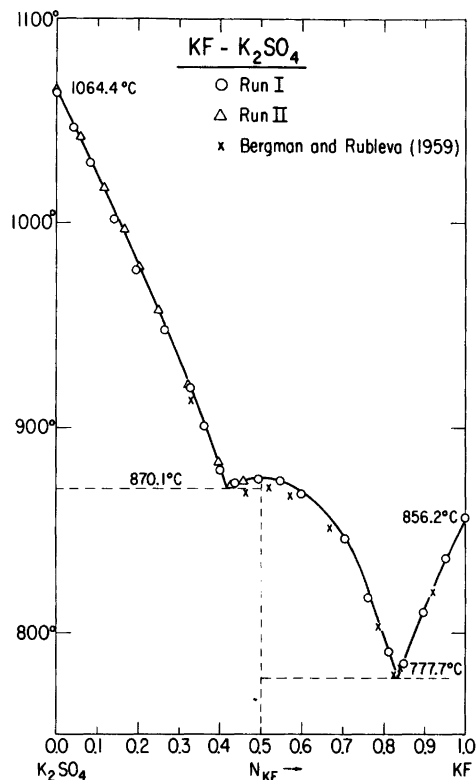


Fig. 5. Liquidus curves for the phase diagram KF - K₂SO₄.

Calorimetric measurements. The results of these measurements are given in Fig. 6. This figure shows the enthalpy interaction parameter, $\lambda_m = \Delta H_{\text{mix}}/N_{\text{AF}}N_{\text{A}_2\text{SO}_4}$, plotted against composition: N_{AF} is the mol fraction of fluoride [$n_{\text{AF}}/(n_{\text{AF}} + n_{\text{A}_2\text{SO}_4})$] while $N_{\text{A}_2\text{SO}_4}$ is that of sulfate [$n_{\text{A}_2\text{SO}_4}/(n_{\text{AF}} + n_{\text{A}_2\text{SO}_4})$]. We found that the experimental values of the interaction parameters could be fitted to straight lines, eqn. (1). The coefficients a and b ,

$$\lambda_m = \Delta H_{\text{mix}}/N_{\text{AF}}N_{\text{A}_2\text{SO}_4} = a + bN_{\text{AF}} \quad (1)$$

determined by least squares treatment of the data, are listed in Table 4.

If eqn. (1) is valid, the partial enthalpies of the two components can be calculated from eqns. (2a) and (2b). Note that for all three systems the

$$\overline{\Delta H}_{\text{AF}} = (a + 2bN_{\text{AF}})(1 - N_{\text{AF}})^2 \quad (2a)$$

$$\overline{\Delta H}_{\text{A}_2\text{SO}_4} = ((a - b) + 2bN_{\text{AF}})N_{\text{AF}}^3 \quad (2b)$$

Table 1. Partial thermodynamic data for the liquid system LiF – Li₂SO₄ at liquidus temperatures.

N_{LiF}	T_{Liq} K	$\Delta\bar{G}_{\text{LiF}}$ J mol ⁻¹	$\Delta\bar{H}_{\text{LiF}}$ J mol ⁻¹	$\Delta\bar{S}_{\text{LiF}}$ J mol ⁻¹ K ⁻¹	$\Delta\bar{S}_{\text{LiF}}^{\text{E}}$ J mol ⁻¹ K ⁻¹
1.0	1118.4	0.0	0.0	0.0	0.0
0.90	1076.3	-1002.1	-13.2	0.92	0.04
0.80	1027.8	-2150.5	-53.6	2.04	0.19
0.70	972.5	-3453.1	-122.1	3.43	0.46
0.60	915.2	-4796.7	-219.6	5.00	0.76
0.50	855.2	-6198.7	-347.3	6.84	1.08
0.41 ₆	804.4 Eut	-7383.5	-478.4	8.58	1.30
N_{LiF}	T_{Liq} , K	$\Delta\bar{G}_{\text{Li}_2\text{SO}_4}$	$\Delta\bar{H}_{\text{Li}_2\text{SO}_4}$	$\Delta\bar{S}_{\text{Li}_2\text{SO}_4}$	$\Delta\bar{S}_{\text{Li}_2\text{SO}_4}^{\text{E}}$
0.41 ₆	804.4 Eut	-4151.4	-256.9	4.84	0.38
0.40	809.7	-3935.6	-238.0	4.57	0.33
0.30	839.4	-2725.1	-135.3	3.09	0.13
0.20	913.1	-1733.7	-60.4	1.83	-0.02
0.10	1023.2	-844.0	-15.4	0.81	-0.07
0.00	1131.2	0.0	0.0	0.0	0.0

enthalpies of mixing are numerically small. Note also that the interaction parameters show no evidence of any special stability at the 50–50 composition for the sodium and potassium systems which both have stable compounds AF·A₂SO₄.

In a very recent paper Hatem *et al.*¹³ have reported excess enthalpies of mixing for the reciprocal ternary system Na⁺, K⁺/F⁻, SO₄²⁻. Without providing experimental detail this paper gives analytical equations which represent their enthalpies of mixing for the two binary systems NaF–Na₂SO₄ and KF–K₂SO₄. From these

equations we have calculated the interaction parameters; in the insert of Fig. 3 these are compared with our own experimental results.

It will be seen that the agreement with our data is less than satisfactory. It was particularly surprising to us that the equations of Hatem *et al.* indicated widely different mixing enthalpies for the sodium and potassium systems. We can think of no physical reason why this should be the case. In fact, to a first approximation one often finds that the enthalpy of mixing in simple fused salt mixtures does not vary a great deal when the common ion is

Table 2. Partial thermodynamic data for the liquid system NaF – Na₂SO₄ at liquidus temperatures.

N_{NaF}	T_{Liq} K	$\Delta\bar{G}_{\text{NaF}}$ J mol ⁻¹	$\Delta\bar{H}_{\text{NaF}}$ J mol ⁻¹	$\Delta\bar{S}_{\text{NaF}}$ J mol ⁻¹ K ⁻¹	$\Delta\bar{S}_{\text{NaF}}^{\text{E}}$ J mol ⁻¹ K ⁻¹
1.0	1265.7	0.0	0.0	0.0	0.0
0.90	1220.2	-1203.3	8.8	0.99	0.12
0.80	1171.2	-2499.2	30.1	2.16	0.31
0.70	1116.5	-3960.8	56.7	3.60	0.63
0.60	1058.0	-5493.2	80.9	5.27	1.02
0.59 ₂₅	1053.7 Eut I	-5606.9	82.5	5.40	1.05
0.50	1058.4				
0.40	1051.4				
0.30	1030.5	$\Delta\bar{G}_{\text{Na}_2\text{SO}_4}$	$\Delta\bar{H}_{\text{Na}_2\text{SO}_4}$	$\Delta\bar{S}_{\text{Na}_2\text{SO}_4}$	$\Delta\bar{S}_{\text{Na}_2\text{SO}_4}^{\text{E}}$
0.26 ₆	1021.4 Eut II	-2872.8	-37.3	2.78	0.21
0.20	1055.2	-2133.4	-24.4	2.00	0.14
0.10	1105.2	-1064.2	-7.3	0.96	0.08
0.00	1156.8	0.0	0.0	0.0	0.0

Table 3. Partial thermodynamic data for the liquid system KF–K₂SO₄ at liquidus temperature.

N_{KF}	T_{Liq} K	$\Delta\bar{G}_{KF}$ J mol ⁻¹	$\Delta\bar{H}_{KF}$ J mol ⁻¹	$\Delta\bar{S}_{KF}$ J mol ⁻¹ K ⁻¹	$\Delta\bar{S}_{KF}^E$ J mol ⁻¹ K ⁻¹
1.0	1129.4	0.0	0.0	0.0	0.0
0.90	1085.0	-1159.7	-52.1	1.02	0.15
0.83 ₄	1050.9 Eut I	-2050.5	-152.1	1.81	0.30
0.80	1070.3				
0.70	1120.9				
0.60	1142.0				
0.50	1148.4				
0.41 ₈	1143.3 Eut II				
0.40	1153.4				
0.30	1205.7				
0.20	1253.1				
0.10	1295.9				
0.00	1337.6				

	$\Delta\bar{G}_{K_2SO_4}$	$\Delta\bar{H}_{K_2SO_4}$	$\Delta\bar{S}_{K_2SO_4}$	$\Delta\bar{S}_{K_2SO_4}^E$
	-5518.7	11.2	4.84	0.34
	-5226.5	24.1	4.55	0.31
	-3718.7	61.8	3.14	0.17
	-2364.7	49.0	1.93	0.07
	-1157.6	17.6	0.91	0.03
	0.0	0.0	0.0	0.0

changed. Generally speaking, our own data are consistent with this.

In quasi-lattice theories of charge-symmetrical fused salt mixtures the enthalpy of mixing in the main is derived from second nearest neighbor interactions. For a random mixture of the two components such theories predict that the enthalpy interaction parameter should have a constant value for a given binary system.¹ If one attempts to treat charge-unsymmetrical mixtures by quasi-lattice models complications arise. These are related to the fact that the mixing of the two fused

Table 4. Summary of experimentally determined coefficients according to eqn. (1).

System	a , J mol ⁻¹	b , J mol ⁻¹
LiF–Li ₂ SO ₄	-1471	81.9
NaF–Na ₂ SO ₄	-237.5	619.4
KF–K ₂ SO ₄	-385.9	-2682.8

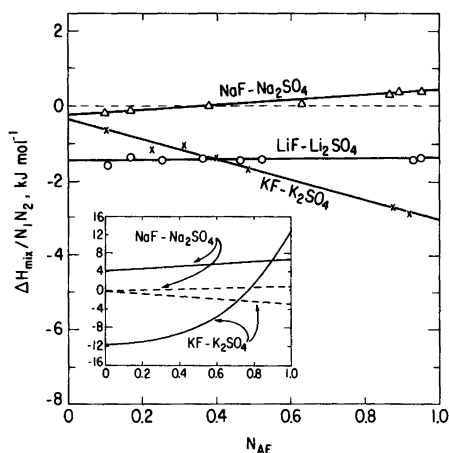


Fig. 6. Plots of enthalpy interaction parameters, λ_m , for AF–A₂SO₄ systems. Main figure presents experimental data; the insert compares our results (broken lines) with those of Hatem *et al.*¹³

salts of different charge structure must involve some changes in the mutual arrangements of the ions. One must consider, for example, changes with composition in the average numbers of second nearest neighbors surrounding a given ion. Only if this complication is neglected, one derives an enthalpy interaction parameter which is independent of composition. However, Førland¹⁴ has shown that if the difference in ionic charges is taken into account, it may be useful to express the enthalpy of mixing in terms of the equivalent fractions rather than the mol fractions. For the fluoride–sulfate mixtures considered in the present work we would then calculate a modified enthalpy interaction parameters, λ'_m , from the expression (3), where N_{AF} and $N_{A_2SO_4}$ are the mol

$$\lambda'_m = \Delta H_{mix} / (N_{AF} + 2N_{A_2SO_4}) N'_{AF} N'_{A_2SO_4} \quad (3)$$

fractions defined above, while N'_{AF} and $N'_{A_2SO_4}$ are the equivalent fractions $N'_{AF} = n_{AF} / (n_{AF} + 2n_{A_2SO_4})$ and $N'_{A_2SO_4} = 2n_{A_2SO_4} / (n_{AF} + 2n_{A_2SO_4})$.

If this treatment of the charge-asymmetry is valid, one might expect λ'_m for a given binary system to vary less with composition than λ_m .

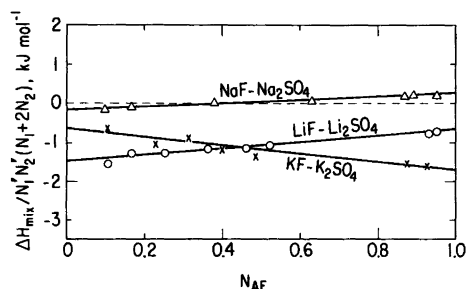


Fig. 7. Plots of enthalpy interaction parameters, λ'_m , for $AF - A_2SO_4$ systems.

We present in Fig. 7 plots of λ'_m for the fluoride-sulfate systems considered in the present work. A comparison between Figs. 6 and 7 indicates that there is not much difference between the two representations. Even so, it is evident that λ'_m varies less with composition than λ_m for the potassium system.

Partial entropies from cryoscopic and calorimetric data. If pure solid A is in equilibrium with a liquid solution, the relative partial Gibbs energy of A, referred to pure, supercooled liquid A as the standard state ($\Delta\bar{G}_A$) may be calculated from eqn. (4).¹⁵ Here ΔH_m is the enthalpy of fusion of pure A

$$\begin{aligned} -\Delta\bar{G}_A &= \Delta G_{A,S \rightarrow l}(T) = \Delta H_m \left(1 - \frac{T}{T_m}\right) \\ &- a \left((T_m - T) - T \ln \frac{T_m}{T} \right) - \frac{b}{2} (T_m - T)^2 \\ &- \frac{1}{2} c T \left(\frac{1}{T_m} - \frac{1}{T} \right)^2 \end{aligned} \quad (4)$$

at its melting point T_m ; T is the liquidus temperature. The coefficients a , b and c are constants in the expression for the difference in heat capacity between supercooled liquid and solid; eqn. (5).

$$\Delta C_{P,S \rightarrow l} = C_1 - C_S = a + bT + c/T^2 \quad (5)$$

If, as is the case for Li_2SO_4 , the solid undergoes a phase change from a low temperature form (I) to a high temperature form (II) in the temperature range of interest, the relative Gibbs energy of A below the transition temperature may be calculated from the relation (6).

$$-\Delta\bar{G}_A = \Delta\bar{G}_{A,I \rightarrow l} = \Delta\bar{G}_{A,I \rightarrow II} + \Delta\bar{G}_{A,II \rightarrow l} \quad (6)$$

In this expression the last term on the right-hand side, $\Delta\bar{G}_{A,II \rightarrow l}$, is derived from (4), while the first term, $\Delta\bar{G}_{A,I \rightarrow II}$, can be calculated from an expression analogous to (4) by substituting the enthalpy of transition for the enthalpy of fusion, the transition temperature for the melting point, and $\Delta C_{P,I \rightarrow II}$ for $\Delta C_{P,S \rightarrow l}$.

If we make the reasonable assumption that the enthalpy of mixing is independent of temperature in the considered temperature range, the partial entropies at the liquidus temperatures may be calculated from $\Delta\bar{G}_A$ and the corresponding partial enthalpies. We give the calculated partial entropies for round figure mol fractions and for the eutectic mixtures in Tables 1–3. The liquidus temperatures reported in these tables were read off large scale graphs; the partial enthalpies were calculated from eqns. (2a) and (2b). In the last column of these tables we give the partial excess entropies based on the model of Temkin.⁹ In these calculations we made use of ΔH_m and ΔC_P taken from Mcleod (fluorides)¹⁶ and from Danielou *et al.* (sulfates).^{17,18} In Table 5 we illustrate to what extent the choice of other enthalpy and heat capacity data might have influenced the calculated excess entropies at the eutectic compositions. Note that this table shows very satisfactory agreement for all calculated entropies except for Li_2SO_4 at the eutectic composition in $LiF - Li_2SO_4$. Even so, it should be noted that for lithium sulfate-rich compositions in this system both the adopted data of Danielou *et al.*¹⁸ and the earlier data of Voskresenskaya and Banashek¹⁹ yield small negative excess entropies for Li_2SO_4 .

In considering the Gibbs energy and entropy data in Tables 1–3 we believe that the adopted empirical equations for $\Delta C_{P,S \rightarrow l}$ should hold to a very good approximation for temperatures near T_m . Therefore the calculated values of $\Delta\bar{G}$ and $\Delta\bar{S}$ should be very reliable for modest freezing point depressions. On the other hand, the calculated values of these quantities may well be associated with larger errors for larger values of $T_m - T$. Due to the stronger temperature dependence of ΔH_m and $\Delta C_{P,S \rightarrow l}$ for the sulfates than for the fluorides, it seems likely that these errors will be larger for the sulfate-rich than for the fluoride-rich melts. In Fig. 8 we present a plot of all the partial excess entropies calculated in the present study. The broken lines in this figure were derived from Model III which is discussed below.

Table 5. Partial excess entropies at eutectic compositions using data from different sources.

ΔH_m J mol ⁻¹	$\Delta C_{P,S \rightarrow 1}$ J mol ⁻¹ K ⁻¹	$\Delta \bar{S}^E$ J mol ⁻¹ K ⁻¹	Ref.
LiF - Li ₂ SO ₄ ; $N_{LiF} = 0.416$			
26 690	$-10.16 + 11.72 \times 10^{-3} T - 591913/T^2$	1.30 (LiF)	16
27 090	$21.41 - 17.42 \times 10^{-3} T - 530000/T^2$	1.31 (LiF)	25-27
25 564 (ΔH_{tr})	$291.59 - 31.35 \times 10^{-2} T (\Delta C_{P,I \rightarrow II})$		
9 330	$-157.5 + 15.19 \times 10^{-2} T$	0.38 (Li ₂ SO ₄)	18
27 324 (ΔH_{tr})	$79.3 - 65.44 \times 10^{-3} T + 3762.6/T^2 (\Delta C_{P,I \rightarrow II})$		
7 669	-16.3	0.76 (Li ₂ SO ₄)	19
NaF - Na ₂ SO ₄ ; $N_{NaF} = 0.5925$			
33 470	$0.51 - 0.43 \times 10^3 T + 31836/T^2$	1.05 (NaF)	16
33 600	$25.11 - 16.23 \times 10^3 T - 138000/T^2$	0.97 (NaF)	22
33 400	4.11	0.96 (NaF)	24
33 100	$35.37 - 26.07 \times 10^3 T + 821300/T^2$	0.92 (NaF)	23
NaF - Na ₂ SO ₄ ; $N_{NaF} = 0.264$			
23 346	$83.3 - 9.029 \times 10^{-2} T$	0.21 (Na ₂ SO ₄)	17
23 722	$75.8 - 8.09 \times 10^{-2} T$	0.23 (Na ₂ SO ₄)	28
KF - K ₂ SO ₄ ; $N_{KF} = 0.834$			
29 497	$-0.29 + 0.159 \times 10^{-3} T - 23059/T^2$	0.30 (KF)	16
KF - K ₂ SO ₄ ; $N_{KF} = 0.418$			
36 800	$87.9 - 7.832 \times 10^{-2} T$	0.34 (K ₂ SO ₄)	17
36 650	$85.7 - 8.4 \times 10^{-2} T$	0.44 (K ₂ SO ₄)	29

In quasi-lattice theories of solution it usually is assumed that the observed entropies of mixing are the result of two principal contributions: the configurational part, which arises from the distribution of the interchangeable particles among the available quasi-lattice sites, and the vibrational part, which is due to a possible modification of the vibrational spectrum in the mixing process. This latter term presumably is related to a possible excess volume.

For simple, charge-symmetrical fused salt mixtures with modest positive or negative enthalpies of mixing the vibrational entropy term usually is small. For the fluoride-sulfate systems, on the other hand, this term may well be of considerable importance due to the very significant difference in size between the large SO₄²⁻ ions and the small F⁻ ions. It would be very interesting to have excess volume data for these systems. However, to the best of our knowledge such data are not as yet available.

For charge-unsymmetrical fused salt mixtures, Førlund¹ has discussed four idealized quasi-lattice models for the configurational entropy. In these models, designated I-IV, it is assumed that the cations are distributed randomly over the cation sites, the anions over the anion sites; it is also assumed that there is no significant structural change on mixing. For the fluoride-sulfate mixtures considered in the present work these assumptions seem quite plausible in view of the small numerical values of the enthalpy interaction parameter.

Model I is the ideal Temkin model which assumes that the total number of anion sites is constant over the complete range of liquid compositions, *i.e.* the entropy is not influenced by the difference in charge between the two anions. We then get eqns. (I), (IA) and (IB).

$$\Delta S_{\text{mix}} = -R(n_{AF} \ln N_{AF} + n_{A_2SO_4} \ln N_{A_2SO_4}) \quad (\text{I})$$

$$\Delta \bar{S}_{AF} = -R \ln N_{AF} \quad (\text{IA})$$

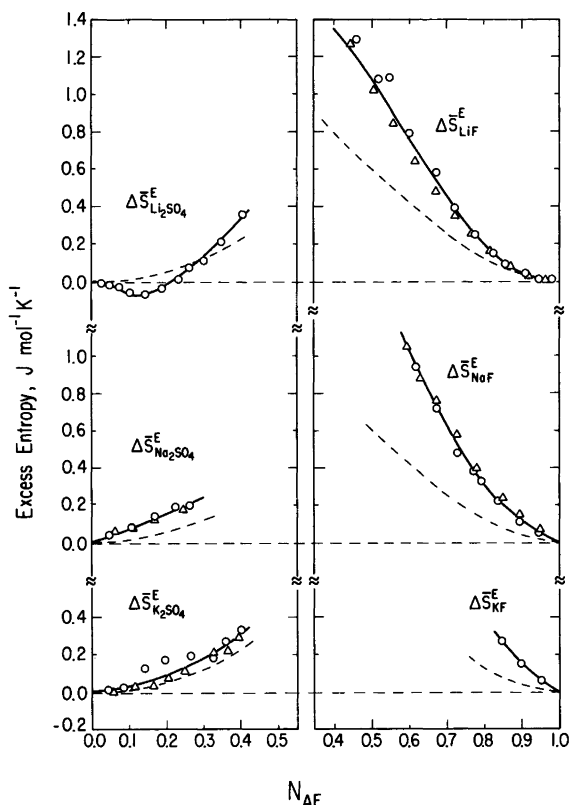


Fig. 8. Plots of partial excess entropies for AF–A₂SO₄ systems, based on the Temkin model for the ideal entropy of mixing. Data are calculated from calorimetric heats of mixing and cryoscopic results. The two different symbols represent data based on runs I and II of the cryoscopic measurements. The broken lines represent excess partial entropies calculated from Førland's Model III.

$$\bar{\Delta S}_{A_2SO_4} = -R \ln N_{A_2SO_4} \quad (\text{IB})$$

In model II the considered fluoride-sulfate mixture is assumed to involve an exchange between SO₄²⁻ plus a vacant anion site, on the one hand, and pairs of F⁻ ions on adjacent sites, on the other. This model implies that occupied sites always occur in pairs, a structural arrangement which may possibly be found for dilute solutions of fluoride in a high sulfate environment. For this model we have eqns. (II), (IIA) and (IIB).

$$\Delta S_{\text{mix}} = -R \left[\frac{1}{2} n_{AF} \ln N'_{AF} + n_{A_2SO_4} \ln N'_{A_2SO_4} \right] \quad (\text{II})$$

$$\bar{\Delta S}_{AF} = -\frac{1}{2} R \ln N'_{AF} \quad (\text{IIA})$$

$$\bar{\Delta S}_{A_2SO_4} = -R \ln N'_{A_2SO_4} \quad (\text{IIB})$$

Note that for this model the molar entropy of mixing will be smaller than for the Temkin model, *i.e.* the excess entropies will be negative.

In model III it is assumed that there is no general pair formation among the anion sites; however, SO₄²⁻ may still replace two F⁻ ions on the anion sublattice. For this model the entropy of mixing will be equivalent to that which applies for mixtures of monomers with dimers; to a good approximation we may apply the theory of Flory²⁰ and write eqns. (III), (IIIA) and (IIIB).

$$\Delta S_{\text{mix}} = -R(n_{AF} \ln N'_{AF} + n_{A_2SO_4} \ln N'_{A_2SO_4}) \quad (\text{III})$$

$$\bar{\Delta S}_{AF} = -R \ln N'_{AF} - \frac{1}{2} R N'_{A_2SO_4} \quad (\text{IIIA})$$

$$\bar{\Delta S}_{A_2SO_4} = -R \ln N'_{A_2SO_4} + R N'_{AF} \quad (\text{IIIB})$$

In Model IV two singly charged anions exchange with one divalent anion + one separate independent vacant anion site. If one further assumes that the number of vacant anion sites is equal to the number of divalent anions, we find eqns. (IV), (IVA) and (IVB).

$$\Delta S_{\text{mix}} = -R(n_{\text{AF}} \ln N'_{\text{AF}} + 2n_{\text{A}_2\text{SO}_4} \ln N'_{\text{A}_2\text{SO}_4}) \quad (\text{IV})$$

$$\bar{\Delta S}_{\text{AF}} = -R \ln N'_{\text{AF}} \quad (\text{IVA})$$

$$\bar{\Delta S}_{\text{A}_2\text{SO}_4} = -2R \ln N'_{\text{A}_2\text{SO}_4} \quad (\text{IVB})$$

The concept of a vacant ion site, although very appropriate for solid ionic solutions, is of more doubtful value for fused salt mixtures. On the other hand, for the fluoride-sulfate mixtures considered in the present work, it is known that the ionic radius of the fluoride ion ($\sim 1.4 \text{ \AA}$) is roughly one-half that of the radius of free rotation of SO_4^{2-} ($\sim 2.9 \text{ \AA}$).²¹ Therefore, we have not only a difference in the charge of the two ions, but also a very large difference in size. Under these circumstances it seems possible that the sulfate ion may occupy a pair of neighboring sites in the anion "lattice", i.e. that SO_4^{2-} may be considered the "dimer", where F^- is the "monomer". This model would be associated with the same entropy of mixing as model III above.

The partial excess entropies of AF and A_2SO_4 (referred to the Temkin model) calculated from model III are shown as broken lines in Fig. 8. Among the considered models this is the only one which predicts the observed partial entropies better than the Temkin model. It should be noted, however, that our analysis does not allow us to establish whether this is the result of a charge effect (due to SO_4^{2-} having twice the charge of F^-) or a size effect (due to SO_4^{2-} having roughly twice the radius of F^-). In future work on charge-unsymmetrical anion mixtures we hope to throw more light on this problem.

Apart from this we take note of the fact that the observed small negative excess entropies of Li_2SO_4 for solutions low in LiF would be consistent with model II. Unfortunately, in view of the uncertainty in the enthalpy of fusion and in the heat capacities for Li_2SO_4 , it is difficult to assess the significance of this observation.

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