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Thermodynamics of Charge-unsymmetrical Anion Mixtures. II. The Liquid Systems $AF-A_2MoO_4$ and $AF-A_2WO_4$

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The thermodynamic properties of the liquid mixtures $AF-A_2MoO_4$ and $AF-A_2WO_4$ (A = Li, Na, K) have been studied by calorimetric and cryoscopic measurements. When the partial Gibbs energies, derived from the phase diagrams, are compared with partial enthalpies from calorimetry, we obtain precise information on the partial entropies of mixing. These entropies generally are larger than calculated from the Temkin model. The results are discussed in terms of a Flory-type model for monovalent–divalent mixtures, and of the size parameters of the salts. The heat of fusion of K_2MoO_4 was not known and has been measured. It was found to be 34.7 ± 0.7 kJ/mol.

In a recent communication[1] we have discussed the thermodynamic properties of alkali fluoride-alkali sulfate mixtures. In that study the partial entropies of the two components derived from cryoscopic and calorimetric data were compared with configurational entropies calculated from several quasilattice models proposed by Førland.[2] It was found that these mixed anion–common cation systems have entropies of mixing which are predicted quite well by a Flory-type model, in which the divalent sulfate ion occupies two anion positions in a quasi-lattice of the Temkin type. However, the calorimetric measurements on the fluoride–sulfates did not provide a clear answer to the question of whether the enthalpies of mixing in these charge-unsymmetrical systems can be represented better by an equation based on equivalent fractions than on mol fractions.

In order to investigate such charge-unsymmetrical mixtures in greater detail we have extended our study to the fluoride–molybdate and fluoride–tungstate systems. Since the MoO_4^{2-} and WO_4^{2-} anions are considerably larger than SO_4^{2-}, it was hoped that this would throw light on the influence of the size of the divalent anion on the thermodynamic properties.

The phase diagrams of the alkali fluoride–molybdate and fluoride–tungstate systems are available.[3-7] However, as for fluoride–sulfate, we found that the cryoscopic data were not sufficiently accurate to provide reliable Gibbs energy information. For this reason the phase diagrams were reinvestigated.

EXPERIMENTAL

Cryoscopic measurements. These measurements were carried out by monitoring the cooling curves of the mixtures in the manner described previously.[1] The composition of the melts was changed by adding weighed amounts of crystals (fluorides) or pellets (molybdates and tungstates) through a feeding tube. The maximum absolute error in the measured liquidus temperatures was esitmated to be ± 2 °C. However, the freezing point depressions, relative to the melting point of the pure salts, in most cases, could be measured to about ± 0.3 °C.

Calorimetric measurements. The calorimetric measurements were performed in a Calvet-type twin microcalorimeter which has been described elsewhere.[8] The mixing experiments were of the liquid–liquid type and were carried out in an argon atmosphere at 1273 K. The procedures were similar to those used previously.[1]

We found enthalpy of fusion data in the literature for all salts studied except for potassium molybdate. In order to secure this information we carried out a series of calorimetric measurements in which solid potassium molybdate was dissolved in a liquid

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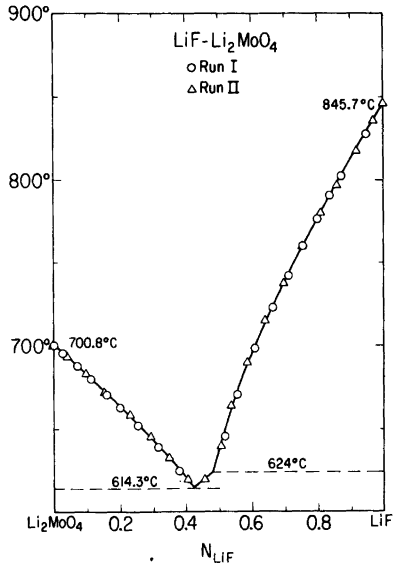

Fig. 1. Liquidus curves for the phase diagram LiF – Li_2MoO_4.

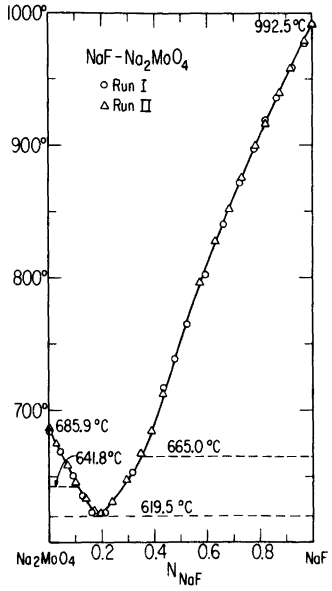

Fig. 3. Liquidus curves for the phase diagram NaF – Na_2MoO_4.

mixture of potassium molybdate (~85 %) and potassium fluoride (~15 %) at 1180 K, *i.e.*, about 20 °C below the melting point of potassium molybdate. The enthalpy of fusion was then obtained by correcting for the small liquid – liquid heat of mixing. In other ways the experimental procedures were similar to those used in the liquid – liquid

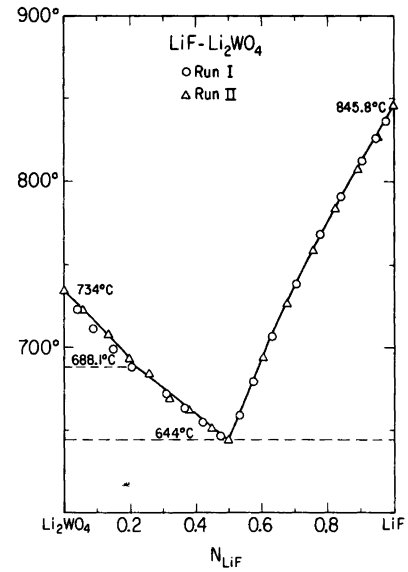

Fig. 2. Liquidus curves for the phase diagram LiF – Li_2WO_4.

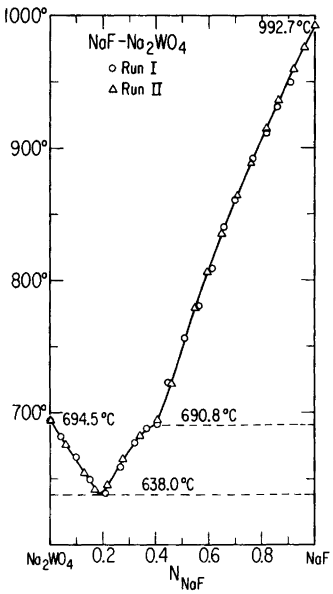

Fig. 4. Liquidus curves for the phase diagram NaF – Na_2WO_4.

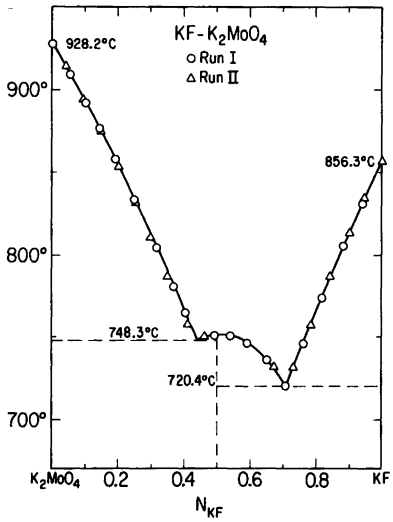

Fig. 5. Liquidus curves for the phase diagram KF – K_2MoO_4.

mixing experiments. A preliminary survey of the data for the Na_2MoO_4 – NaF and Li_2WO_4 – LiF mixtures indicated that the partial entropies of the molybdate and tungstate in these two systems differed from all the other entropy data. For this reason the enthalpies of fusion of Na_2MoO_4 and of Li_2WO_4 were redetermined using the same procedure as for K_2MoO_4.

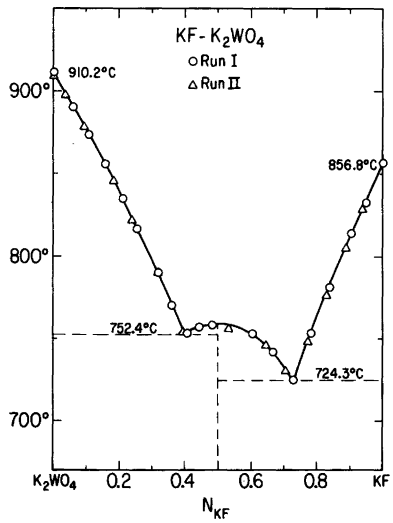

Fig. 6. Liquidus curves for the phase diagram KF – K_2WO_4.

In our calorimetric measurements as 1253 K the calorimeter was calibrated electrically as described previously,[1] with a precision of about ±0.6 %. In the other calorimetric measurements we used a drop calibration based on the heat content equation for platinum recommended by Kelley.[15]

Chemicals. The chemicals used were: LiF, Fisher Certified Reagent (min. 99.5 %); $LiMoO_4$, Research Inorganic/Organic Chemicals (99.5 %); Li_2WO_4, for calorimetric work: Research Inorganic/Organic Chemicals (99 %), for cryoscopy: Research Inorganic/Organic Chemicals (99.9 %); NaF, Baker Analyzed Reagent (min. 99 %); Na_2MoO_4, Baker Analyzed Reagent ($Na_2MoO_4 \cdot 2H_2O$, 101 %); Na_2WO_4, Apache Chemicals, Inc. ($Na_2WO_4 \cdot 2H_2O$, Folin grade); KF, Baker and Adamson, Anhydrous Granular Reagent (min. 99 %); K_2MoO_4, Research Inorganic/Organic Chemicals (99.9 %). The chemicals were dried overnight in vacuum at 150 °C. The fluorides used in the cryoscopic work were melted in an inert, dry atmosphere, after which clear crystals were picked from the solidified melts.

RESULTS AND DISCUSSION

Cryoscopic data. The experimental results are presented graphically in Figs. 1 – 6; liquidus temperatures for round figure and eutectic compositions are summarized in Tables 1 – 6.

Our liquidus curves show general agreement with the previously published phase diagrams; even so, numerical discrepancies in some cases are quite substantial. Note that the two potassium systems have congruently melting 50 – 50 interstitial compounds, while the two sodium systems have compounds of the same composition which melt incongruently. In LiF – Li_2MoO_4 we found indication of an incongruently melting compound of a somewhat different composition. This compound was not reported by Schmitz-Dumont and Weeg.[3] However, Karov and Bilokov[7] found evidence for its existence and suggested that its composition is $Li_2MoO_4 \cdot 2LiF$. Unfortunately, our cryoscopic data do not allow us to draw firm conclusions regarding its stoichiometry.

In contrast to this, the corresponding LiF – Li_2WO_4 binary is of the simple eutectic types. Note, however, that the tungstate-rich part of this diagram may be less accurate than the other cryoscopic data. As discussed below, the phase transition in Li_2WO_4 at 688 °C is very slow. Therefore, it is very difficult to obtain equilibrium cryscopic data by the thermal analysis procedure which was used.

Table 1. Partial thermodynamic data for the liquid system $LiF-Li_2MoO_4$.

N_{LiF}	T_{liq} K	$\Delta\bar{G}_{LiF}$ J mol^{-1}	$\Delta\bar{H}_{LiF}$ J mol^{-1}	$\Delta\bar{S}_{LiF}$ J mol^{-1} K^{-1}	$\Delta\bar{S}^{E}_{LiF}$ J mol^{-1} K^{-1}
1.0	1118.9	–	–	–	–
0.90	1084.4	−821.7	250.4	0.99	0.11
0.80	1049.0	−1662.5	842.6	2.39	0.53
0.70	1011.6	−2570.6	1571.6	4.07	1.11
0.60	968.4	−3570.6	2277.1	6.04	1.79
0.50	909.4	−4964.6	2843.4	8.59	2.83
0.48_2	897.2 Peritect.				
		$\Delta\bar{G}_{Li_2MoO_4}$	$\Delta\bar{H}_{Li_2MoO_4}$	$\Delta\bar{S}_{Li_2MoO_4}$	$\Delta\bar{S}^{E}_{Li_2MoO_4}$
0.43_5	887.5 Eut.	−4277.8	50.9	4.88	0.13
0.40	894.0	−3962.2	−19.8	4.41	0.16
0.30	916.2	−2876.6	−89.5	3.04	0.08
0.20	936.4	−1878.9	−59.7	1.94	0.09
0.10	955.7	−917.7	−16.2	0.94	0.07
0.0	974.0	–	–	–	–

Table 2. Partial thermodynamic data of LiF in the liquid system $LiF-Li_2WO_4$.

N_{LiF}	T_{liq} K	$\Delta\bar{G}_{LiF}$ J mol^{-1}	$\Delta\bar{H}_{LiF}$ J mol^{-1}	$\Delta\bar{S}_{LiF}$ J mol^{-1} K^{-1}	$\Delta\bar{S}_{LiF}$ J mol^{-1} K^{-1}
1.00	1119.0	–	–	–	–
0.90	1084.2	−828.7	224.9	0.97	0.10
0.80	1048.0	−1688.4	758.3	2.33	0.48
0.70	1009.8	−2593.5	1419.0	3.97	1.01
0.60	965.0	−3653.0	2066.5	5.93	1.68
0.50	918.2	−4758.6	2600.9	8.02	2.26
0.49_8	917.4 Eut.	−4777.5	2610.0	8.05	2.26

Table 3. Partial thermodynamic data for the liquid system $NaF-Na_2MoO_4$.

N_{NaF}	T_{liq} K	$\Delta\bar{G}_{NaF}$ J mol^{-1}	$\Delta\bar{H}_{NaF}$ J mol^{-1}	$\Delta\bar{S}_{NaF}$ J mol^{-1} K^{-1}	$\Delta\bar{S}^{E}_{NaF}$ J mol^{-1} K^{-1}
1.0	1265.7	–	–	–	–
0.90	1224.5	−866.0	167.1	0.84	−0.03
0.80	1179.6	−1803.8	542.5	1.99	+0.13
0.70	1133.2	−2767.1	974.1	3.30	0.34
0.60	1082.8	−3807.8	1358.5	4.77	0.53
0.50	1024.7	−5001.6	1641.7	6.48	0.72
0.40	963.2	−6260.8	1818.2	8.39	0.77
0.35_3	938.2 Peritect.	−6772.0	1875.0	9.22	0.56
		$\Delta\bar{G}_{Na_2MoO_4}$	$\Delta\bar{H}_{Na_2MoO_4}$	$\Delta\bar{S}_{Na_2MoO_4}$	$\Delta\bar{S}^{E}_{Na_2MoO_4}$
0.19_0	892.7 Eut.	−2029.8	79.8	2.36	0.61
0.10	919.2	−882.9	31.9	1.00	0.13
0.00	959.1	–	–	–	–

Table 4. Partial thermodynamic data for the liquid system $NaF-Na_2WO_4$.

N_{NaF}	T_{liq} K	$\Delta\bar{G}_{NaF}$ J mol^{-1}	$\Delta\bar{H}_{NaF}$ J mol^{-1}	$\Delta\bar{S}_{NaF}$ J mol^{-1} K^{-1}	$\Delta\bar{S}^{E}_{NaF}$ J mol^{-1} K^{-1}
1.0	1265.9	–	–	–	–
0.90	1224.1	−878.4	157.6	0.85	−0.03
0.80	1179.7	−1805.6	518.1	1.97	+0.12
0.70	1133.0	−2774.9	943.0	3.28	0.32
0.60	1081.7	−3833.9	1333.8	4.78	0.53
0.50	1021.0	−5080.7	1631.9	6.57	0.81
0.40	964.0 Peritect.	−6247.5	1818.7	8.37	0.75
		$\Delta\bar{G}_{Na_2WO_4}$	$\Delta\bar{H}_{Na_2WO_4}$	$\Delta\bar{S}_{Na_2WO_4}$	$\Delta\bar{S}^{E}_{Na_2WO_4}$
0.18_5	911.2 Eut.	−1622.0	37.8	1.82	0.12
0.10	937.4	−872.2	16.4	0.95	0.07
0.00	967.7	–	–	–	–

Table 5. Partial thermodynamic data for the liquid system $KF-K_2MoO_4$.

N_{KF}	T_{liq} K	$\Delta\bar{G}_{LiF}$ J mol^{-1}	$\Delta\bar{H}_{KF}$ J mol^{-1}	$\Delta\bar{S}_{KF}$ J mol^{-1} K^{-1}	$\Delta\bar{S}^{E}_{KF}$ J mol^{-1} K^{-1}
1.00	1129.5	–	–	–	–
0.90	1085.7	−1144.0	9.1	1.06	0.19
0.80	1038.7	−2371.8	36.3	2.32	0.46
0.708	993.6 Eut. I	−3550.2	77.3	3.65	0.78
0.70	995.7	–	–	–	–
0.60	1018.7	–	–	–	–
0.50	1025.0	–	–	–	–
		$\Delta\bar{G}_{K_2MoO_4}$	$\Delta\bar{H}_{K_2MoO_4}$	$\Delta\bar{S}_{K_2MoO_4}$	$\Delta\bar{S}^{E}_{K_2MoO_4}$
0.44	1021.6 Eut. II	−5003.9	279.9	5.17	0.35
0.40	1039.7	−4537.2	142.7	4.50	0.26
0.30	1084.7	−3326.9	80.1	3.14	0.18
0.20	1127.7	−2121.9	35.5	1.91	0.06
0.10	1166.0	−1024.8	8.9	0.89	0.01
0.00	1201.5	–	–	–	–

Enthalpy data. The results of the calorimetric mixing measurements are presented in Fig. 7, which shows plots against composition of the enthalpy interaction parameters, λ_m, defined as $\lambda_m = \Delta H_{mix}/N_1N_2$; N_1 and N_2 are the mol fractions of the two components. We found that λ_m could be fitted to simple polynomials, eqn. (1). Values of the coefficients a, b, and c determined by a least squares

$$\lambda_m = a + bN_1 + cN_1^2 \quad (1)$$

treatment of the experimental data are listed in Table 7. Note that the relative partial enthalpies of the two components can be calculated from eqns. (2a) and (2b), where a, b, and c are the parameters in eqn. (1).

$$\Delta\bar{H}_1 = (a + 2bN_1 + 3cN_1^2)(1 - N_1)^2 \quad (2a)$$

$$\Delta\bar{H}_2 = (a - b + 2(b - c)N_1 + 3cN_1^2)N_1^2 \quad (2b)$$

According to simple quasi-lattice theory the enthalpy interaction parameter should be independent of composition. This seems to hold well for the potassium fluoride – molybdate and fluoride – tungstate mixtures. However, it clearly does not

Table 6. Partial thermodynamic data for the liquid system $KF-K_2WO_4$.

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}	$\Delta\bar{S}^{E}_{KF}$ J mol^{-1} K^{-1}
1.00	1129.9		–	–	–	–
0.90	1084.2		−1193.2	11.1	1.11	0.24
0.80	1036.2		−2446.7	42.5	2.40	0.55
0.72_8	997.5	Eut. I	−3457.5	77.0	3.54	0.91
0.70	1005.7		–	–	–	–
0.60	1026.4		–	–	–	–
0.50	1031.7		–	–	–	–
			$\Delta\bar{G}_{K_2WO_4}$	$\Delta\bar{H}_{K_2WO_4}$	$\Delta\bar{S}_{K_2WO_4}$	$\Delta\bar{S}^{E}_{K_2WO_4}$
0.40	1025.6	Eut. II	−4547.7	97.6	4.53	0.28
0.30	1069.2		−3340.7	50.4	3.17	0.21
0.20	1111.6		−2119.7	20.4	1.93	+0.07
0.10	1150.0		−990.1	4.6	0.86	−0.01
0.00	1183.4		–	–	–	–

apply for the corresponding lithium and sodium systems, which show much larger positive interaction parameters in the fluoride-rich than in the molybdate and tungstate-rich regions.

Førland[2] developed a quasi-lattice theory for charge-unsymmetrical fused salt mixtures based on equivalent fractions rather than on mol fractions. In this theory the enthalpy interaction parameter has the form (3), where N_1 is the mol fraction of the

$$\lambda'_m = \Delta H_{mix}/(N_1+2N_2)(N'_1N'_2) \quad (3)$$

monovalent salt, N_2 the mol fraction of the divalent salt, while N'_1 and N'_2 are the respective equivalent fractions (4a) and (4b). The results are plotted according to eqn. (3) in Fig. 8.

$$N'_1 = N'_{AF} = n_{AF}/(n_{AF}+2n_{A_2XO_4}) \quad (4a)$$

$$N'_2 = N'_{A_2XO_4} = 2n_{A_2XO_4}/(n_{AF}+2n_{A_2XO_4}) \quad (4b)$$

In our earlier paper we presented the enthalpy of mixing data for the $AF-A_2SO_4$ system in the same

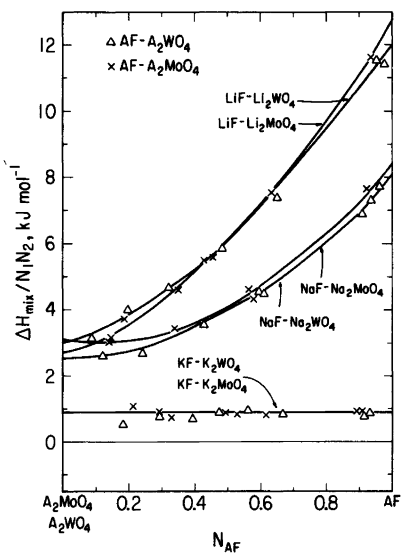

Fig. 7. Plots of enthalpy interaction parameters, λ_m, for $AF-A_2MoO_4$ and $AF-A_2WO_4$.

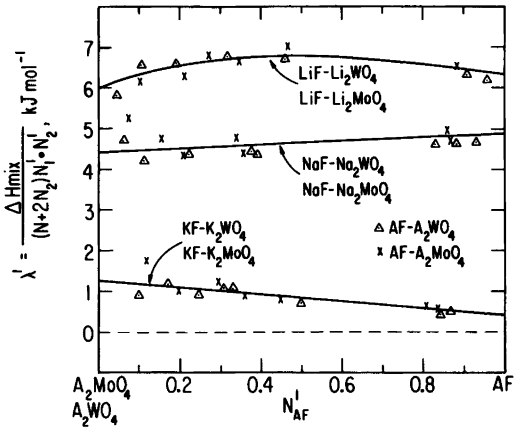

Fig. 8. Plots of enthalpy interaction parameters, λ'_m, for $AF-A_2MoO_4$ and $AF-A_2WO_4$.

Table 7. Summary of experimentally determined coefficients according to Eqn. (1).

System	a, J mol^{-1}	b, J mol^{-1}	c, J mol^{-1}
$LiF-Li_2MoO_4$	2672	4044	6210
$LiF-Li_2WO_4$	2936	3225	5657
$NaF-Na_2MoO_4$	3067	−1601	6801
$NaF-Na_2WO_4$	2483	−121	5554
$KF-K_2MoO_4$	894	9	–
$KF-K_2WO_4$	660	251	–

manner. However, for those systems it was not evident that the equivalent fraction representation (eqn. (3)) was preferable to the mol fraction representation. Fig. 8 shows that this situation is different for the molybdate – fluoride and tungstate – fluoride mixtures; we see that the plots of λ_m' against N' are much more symmetrical than plots of λ_m against N.

From our measurements on K_2MoO_4 we found that the enthalpy of fusion of this salt at the melting point, $\Delta H_m(K_2MoO_4)$ is 34.7 kJ mol^{-1} with an estimated uncertainty of 0.7 kJ mol^{-1} (± 2 %).

We also measured the heats of fusion of Na_2MoO_4 and $LiWO_4$ a few degrees below their respective melting points; this yielded the values 20.4 ± 0.4 kJ mol^{-1} and 40.3 ± 0.8 kJ mol^{-1}, respectively. In order to obtain information on the enthalpy change associated with the solid state phase transformations in these salts we measured also the heats of fusion below the phase transformation temperature. We found for Na_2MoO_4 at 641.0 °C 28.7 ± 0.4 kJ mol^{-1}, and for $LiWO_4$ at 687.0 °C 50.8 ± 1.0 kJ mol^{-1}. If heat capacity terms are neglected, we find for the phase transformation in Na_2MoO_4 28.7 − 20.4 = 8.3 kJ mol^{-1} and in Li_2WO_4 50.8 − 40.3 = 10.5 kJ mol^{-1}. For Na_2MoO_4 our results are in good agreement with the literature,[11] which gives 21.42 kJ mol^{-1} and 8.28 kJ mol^{-1} for the heat of fusion and phase transformation, respectively. For Li_2WO_4, on the other hand, we find good agreement for the heat of fusion near the melting point (41.0 kJ mol^{-1} from Ref. 10), but a wide discrepancy for the heat of transformation (2.0 kJ mol^{-1}, compared to our calculated result of 10.5 kJ mol^{-1}). However, if we take the heat capacity difference between solid and liquid into account (Ref. 10), this latter discrepancy is largely eliminated.

The very strong temperature dependence of the heats of fusion and transformation in Li_2WO_4 suggests that the phase transformation in Li_2WO_4 at 688 °C is not a simple first order transformation, but extends over a range of temperatures, It is also possible that earlier measurements on this substance by drop calorimetry may not have yielded true equilibrium values.

Partial entropies. The partial Gibbs energy of component A in solution can be calculated from the liquidus by means of eqn. (5).[13]

$$-\Delta\bar{G}_A = \Delta G_{A,S-L}(T) = \Delta H_m\left(1-\frac{T}{T_m}\right) - a\left[(T_m - T) - T\ln\frac{T_m}{T}\right] - \frac{b}{2}(T_m - T)^2 - \tfrac{1}{2}cT\left(\frac{1}{T_m} - \frac{1}{T}\right)^2 \quad (5)$$

The standard state of component A here is the pure undercooled liquid; ΔH_m is the enthalpy of fusion of A at its melting point, T_m; T is the liquidus temperature. The coefficients a, b, and c are constants in the analytical expression for the heat capacity difference between solid and undercooled liquid, eqn. (6).

$$\Delta C_{p,s-l} = C_l - C_s = a + bT + c/T^2 \quad (6)$$

In applying eqn. (5) it is assumed that solid solubility is negligible; in view of the difference in the charge and size of the anions this is a very reasonable assumption. When the solid undergoes a phase transformation in the temperature range of interest, the calculation of $\Delta\bar{G}_A$ may still be performed if the enthalpy and entropy changes in the phase transformation are taken into account.[1]

If we make the further assumption that the enthalpy of mixing is independent of temperature in the considered temperature range, we can calculate the partial entropies of A along the liquidus curve from $\Delta\bar{G}_A$ and $\Delta\bar{H}_A$. Fig. 9 presents graphs of the calculated partial *excess* entropies with respect to the Temkin model.[1] Previously published values

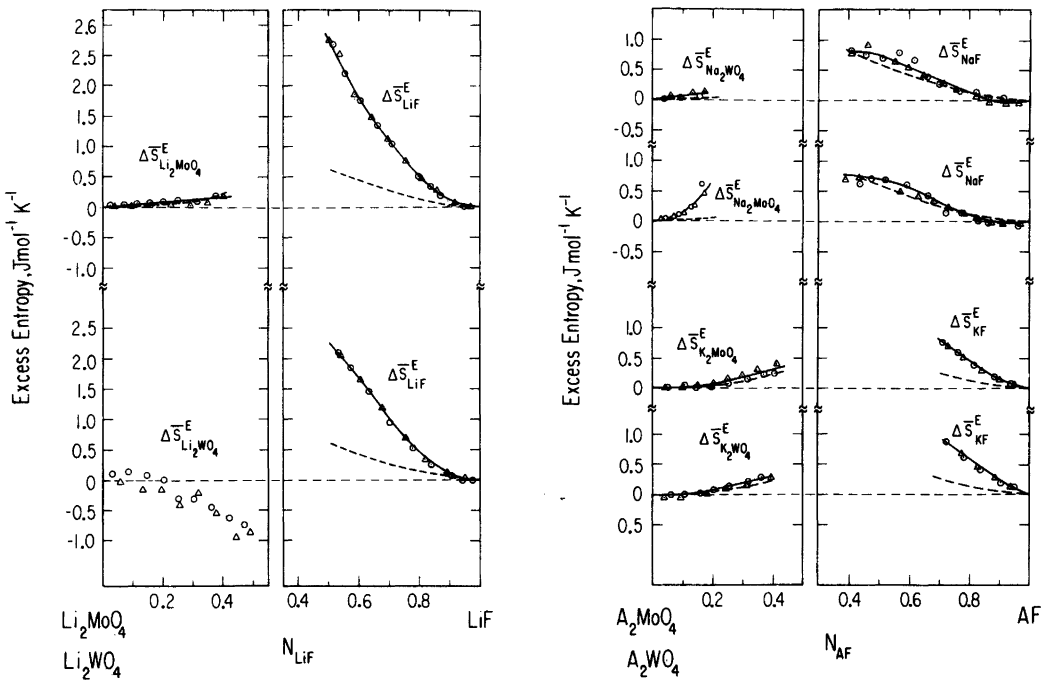

Fig. 9. Plots of partial excess and entropies for $AF-A_2MoO_4$ and $AF-A_2WO_4$ systems based on the Temkin model for the ideal entropy of mixing. The two symbols represent data based on runs I(0) and II(Δ) of the cryoscopic measurements. The broken lines represent excess partial entropies calculated from a Flory-type model (see text).

Table 8. Enthalpy and heat capacity data used in calculations of partial Gibbs energies.

Salt	ΔH_m J mol^{-1}	$\Delta C_{p_{s-l}}$ J mol^{-1} K^{-1}	Ref.
LiF	26,690	$-10.16+11.72\times10^{-3}T-\frac{591913}{T^2}$	9
Li_2MoO_4	49,000	$96.4-0.0823T$	10
Li_2WO_4	2,000 (ΔH_{tr})	$-5874+6.102T$ (ΔC_{pI-II})	10
	41,000	$5973-6.180T$	
NaF	33,470	$0.51-0.43\ 10^{-3}-\frac{31836}{T^2}$	9
Na_2MoO_4	8,280 (ΔH_{tr})	$405.17-184.5\ 10^{-2}T$ (ΔC_{pI-II})	11[a]
	21,420	$-892.4+95.4\ 10^{-2}T$	
Na_2WO_4	27,870	$245.6-25.58\ 10^{-2}T$	11
KF	29,500	$-0.29+0.159\ 10^{-3}T-\frac{23059}{T^2}$	9
K_2MoO_4	34,700	See text.	This work
K_2WO_4	35,100	$300.98-25.58\times10^{-2}T$	10

[a] C_p data in Ref. 11 have been used. Equations in this reference contain printing errors.

of ΔH_m and ΔC_p are summarized in Table 8. For Li_2WO_4 we adopted our own values of the heats of fusion and transformation, and did not take any ΔC_p contribution into account. Since the character of the solid state phase transformation is uncertain, any attempt to include heat capacity terms in the calculation would be of very doubtful value.

As no information is available on ΔC_p for K_2MoO_4, we adopted for this salt the known data for K_2WO_4. These salts have very similar melting points and heats of fusion. Furthermore, the ΔC_p term represents only a minor correction term.

From Fig. 9 we see that the partial excess entropies of the alkali fluorides in fluoride-rich mixtures are very nearly the same for molybdates and tungstates. However, among the molybdate- and tungstate-rich solutions we note that the data for Li_2WO_4 deviate significantly from the results for the other systems. We believe this is probably due to inaccuracies in the cryoscopic data, possibly caused by the sluggish character of the phase transformation in Li_2WO_4. Note also that it will be very difficult to reconcile the calculated partial entropies of LiF and Li_2WO_4 in this system with the Gibbs-Duhem relation.

In our earlier paper on fluoride-sulfate mixtures we discussed the various pseudo-lattice models for charge-unsymmetrical fused salt systems proposed by Førland.[2] The model which best predicted the observed entropies of mixing in these systems is based on the assumption that the divalent sulfate ion replaces two mono-valent fluoride ions in the anion "sub-lattice." In this model the entropy of mixing will be the same as for a mixture of monomers and dimers according to the theory of Flory:[14]

$$\Delta S_{mix} = -R(n_{AF} \ln N'_{AF} - n_{A_2XO_4} \ln N'_{A_2XO_4}) \quad (7a)$$

$$\Delta \bar{S}_{AF} = -R \ln N'_{AF} - \tfrac{1}{2} R N'_{A_2XO_4} \quad (7b)$$

$$\Delta \bar{S}_{A_2XO_4} = -R \ln N'_{A_2XO_4} + R N'_{AF} \cdot \quad (7c)$$

In Fig. 9 we have included graphs of the partial *excess* entropies calculated from this model for comparison with the experimental data. For solutions rich in molybdate and tungstate we see that the agreement generally is very good. For fluoride-rich solutions, on the other hand, a more detailed analysis will be attempted. For solutions of potassium tungstate and molybdate in potassium fluoride the observed excess entropies are considerably larger than calculated from the model; the entropies are also slightly larger than for sulfate in fluoride: at $N_{KF}=0.8$ we have $\Delta \bar{S}^E_{KF}$ (molybdate and tungstate) ≈ 0.5 J mol^{-1} K^{-1}, as compared to $\Delta \bar{S}_{KF}$ (sulfate) ≈ 0.4 J mol^{-1} K^{-1}.

The partial enthalpies of sodium fluoride in fluoride-rich mixtures with tungstate and molybdate agree very well with the model; in these cases, however, the observed excess entropies are significantly smaller than for sodium fluoride–sulfate: at $N_{NaF}=0.6$, we have $\Delta \bar{S}^E_{NaF}$ (molybdate and tungstate) ≈ 0.55 J mol^{-1} K^{-1}, as compared to $\Delta \bar{S}^E_{NaF}$ (sulfate) $\simeq 1.0$ J mol^{-1} K^{-1}.

For solutions rich in lithium fluoride the situation is reversed: at $N_{LiF}=0.6$, we have $\Delta \bar{S}^E_{LiF}$ (molybdate and tungstate) $\simeq 1.75$ J mol^{-1} K^{-1}, and $\Delta \bar{S}^E_{LiF}$ (sulfate) $\simeq 0.8$ J mol^{-1} K^{-1}.

In order to rationalize these results let us consider in somewhat greater detail the size relations in the considered binary mixtures. For anion mixtures, in which a large divalent ion replaces two small singly charges ions, it is expected that the anion–anion separation in the salt with the smaller anion should be the size parameter of principal interest. Such information on the considered fluorides is available from the X-ray diffraction work of Zarzycki.[12] For the considered divalent anions the choice of an appropriate size parameter is more uncertain since we do not know to what extent the anions are free to rotate in the melts. Lacking such information, we arbitrarily adopt the radius of free rotation of the XO_4^{2-} ions; this is about 2.9 Å for sulfate, and about 3.3 Å for molybdate and tungstate. It we now compare the fluoride–fluoride distances in the salts with $r_{XO_4^{2-}}$, the following picture emerges:

For the potassium systems:

$$\frac{r_{SO_4^{2-}}}{d_{F^- - F^-}} = \frac{2.9 \text{ Å}}{3.86 \text{ Å}} = 0.75$$

$$\frac{r_{XO_4^{2-}}}{d_{F^- - F^-}} = \frac{3.3}{3.86} = 0.85$$

For the sodium systems:

$$\frac{r_{SO_4^{2-}}}{d_{F^- - F^-}} = \frac{2.9 \text{ Å}}{3.44 \text{ Å}} = 0.84$$

$$\frac{r_{XO_4^{2-}}}{d_{F^- - F^-}} = \frac{3.3}{3.94} = 0.96$$

For the lithium systems:

$$\frac{r_{SO_4^{2-}}}{d_{F^- - F^-}} = \frac{2.9\ \text{Å}}{2.9\ \text{Å}} = 1.0$$

$$\frac{r_{XO_4^{2-}}}{d_{F^- - F^-}} = \frac{3.3}{2.9} = 1.14$$

Of course, it is not possible to draw entirely firm conclusions from a comparison of these size ratios. Even so, our results indicate that when the ratio $r_{XO_4^{2-}}/d_{F^- - F^-}$ is close to 1, the partial entropies of fluoride in the fluoride-rich solutions agree reasonably well with the Flory model. This is the case, for example, for $NaF-Na_2WO_4$ and $NaF-Na_2MoO_4$, and also for $LiF-Li_2SO_4$.

On the other hand, when this ratio is either larger than 1 (*i.e.*, $LiF-Li_2WO_4$ and $LiF-Li_2MoO_4$) or significantly lower than 1 (*i.e.*, $KF-K_2SO_4$), the excess entropies tend to be larger than calculated from the Flory model. These additional entropy terms may be *either* configurational and/or vibrational in character; they may even to some extent be related to the freedom of rotation of the XO_4^{2-} anions. Since the model accounts fairly well for the general trend of the excess entropies, the differences from cation to cation probably are largely of a vibrational origin.

It seems to us highly probable that the model will break down when the considered size ratio differs very significantly from 1. In this context we believe it would be of considerable interest to obtain reliable entropy data for oxide–fluoride mixtures. It also would be of special interest to study fused salt mixtures in which the small, singly charged fluoride anion is mixed with anions of higher charge than 2, such as, *e.g.*, $F^- - PO_4^{3-}$ and $F^- - VO_4^{3-}$ mixtures.

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REFERENCES

1. Kleppa, O. J. and Julsrud, S. *Acta Chem. Scand. A 34* (1980) 655.
2. Førland, T. *On the Properties of Some Mixtures of Fused Salts*, Norges Tekn. Vitenskaps-akademi, Series 2, No. 4, 1957.
3. Schmitz-Dumont, O. and Weeg, A. *Z. Anorg. Chem. 265* (1951) 139.
4. Kislova, A. I., Posypaiko, V. I. and Bergman, A. G. *Zh. Fiz. Khim. 29* (1955) 359.
5. Mateiko, Z. A. and Bukhalova, G. A. *Zh. Neorg. Khim. II* [2] (1957) 407.
6. Mateiko, Z. A. and Bukhalova, G. A. *Zh. Obshch. Khim. 25* (1955) 1673.
7. Karov, Z. G. and Bilokov, V. T. *Uch. Zap. Kabard. Balkar. Gos. Univ. 41* (1969) 441.
8. Kleppa, O. J. and Hong, K. C. *J. Phys. Chem. 78* (1974) 1478.
9. Macleod, A. C. *J. Chem. Soc. Faraday Trans. 169* (1973) 2026.
10. Denielou, L., Petitet, J. P. and Tequi, C. *J. Chem. Thermodyn. 7* (1975) 901.
11. Denielou, L., Fournier, Y., Petitet, J. P. and Tequi, *C. R. Acad. Sci. Ser. C 272* (1971) 1855.
12. Zarzycki, G. *J. Phys. Radium 19* (1958) 13A; *18* (1957) 65A.
13. Blander, M. *Molten Salt Chemistry*, Interscience, New York 1964, p. 10.
14. Flory, J. P. *J. Chem. Phys. 10* (1942) 51.
15. Kelley, K. K. *U. S. Bur. Mines, Bull. 584* (1960).

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