Fusion Properties and Heat Capacities of the Eutectic LiF–NaF–KF Melt

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The fusion properties (melting point, enthalpy and entropy of fusion) of the eutectic LiF–NaF–KF and the heat capacity of this system in the polycrystalline state and in the molten state have been investigated by the technique of high-temperature differential scanning calorimetry. The fusion properties and heat capacities may be summarized as follows: mp 462 ± 2 °C; ΔH_{fus} = 3.98 kcal mol^{-1}; ΔS_{fus} = 5.42 eu; C_p(solid) = 12.8218 − (9.651 × 10^{-3})T + (1.513 × 10^{-5})T^2 and C_p(melt) = 9.6360 + (10.487 × 10^{-3})T, both in cal mol^{-1} K^{-1}, respectively. The heat capacity temperature ranges are 57–450 °C (solid) and 475–590 °C (melt), and the accuracy limits for both the enthalpy and the heat capacities are ±2.0%. For conversion to SI units, 1 cal = 4.184 J.

High-temperature thermodynamic data have been reported previously for LiF, NaF, and KF but not for the ternary eutectic, LiF–NaF–KF (FLINAK). As part of our investigations of energy-related candidate salt systems using the technique of high-temperature differential scanning calorimetry (DSC), it was decided to extend the fluoride data to the ternary eutectic. Measurements were undertaken also on a series of eutectics that had been subjected to various melt pretreatments. These results, and a redetermination of the melting point of this eutectic, are reported herewith.

Experimental Section

Our high-temperature differential scanning calorimetry facility has been described in detail elsewhere (*1*). The facility centers around a Perkin-Elmer DSC-Model 2 calorimeter, with ancillary microprocesser components and software for computer-assisted data acquisition, base-line corrections, and data analysis in enthalpy and heat capacity measurements (*2*). A quantitative and accurate small mass measurement capability completes the assembly. The latter, together with the sample capsules, and seal-press, was housed in a dry N_2 atmosphere glovebag so that the final sample transfer and encapsulation could be completed in an inert environment.

Cross-check measurements for energy calibration were made with three metals, indium, tin, and lead, and two salt systems, KNO_3 and the LiCl–KCl eutectic (*3–5*). The accuracy limits of the measurements thus established were as follows: temperatures, ±0.5 °C; heats of fusion, ±2%; heat capacities, ±2%.

Both reagent-grade (Baker Chemicals) and highest purity spectroscopic grade (SPEX Industries Inc.) alkali fluorides were used for preparation of the eutectic mixture. The composition of the latter was accepted as that reported from phase-diagram studies (*6–12*), i.e. (mol %): LiF, 46.5; NaF, 11.5; KF, 42.0. The melting point generally reported is 454 °C (with the exception of Hoffman (*9*), who reported 457 °C).

Before being used, the individual components were oven-dried under dynamic vacuum, the temperature being increased stepwise after the equilibrium pressures registered ~10^{-4} mmHg. The maximum oven temperature in this pretreatment was ~180 °C.

For the enthalpy and heat capacity measurements, the eutectic composition was prepared by the "in-capsule" DSC technique of this laboratory (*1*). In this method, the reactant materials are weighed in milligram amounts in the exact stoichiometries required for the eutectic, and the DSC sample pans are hermetically sealed. All transfers are performed in a rigorously dry inert atmosphere. Possible contamination through trace impurities is minimized, if not completely bypassed, in this preparative method. The samples thus prepared were conditioned, before measurements, by repeated thermal cycling through the melting–crystallization range using the calorimetric facility.

Table I. Fusion Properties for the Eutectic LiF-NaF-KF (FLINAK)[a]

thermal cycle in DSC calorimeter	melting process		crystallization process	
	t_m, °C	ΔH_{fus}, kcal mol^{-1}	t_m, °C	ΔH_{fus}, kcal mol^{-1}
1	463.6	3.88 (6)	450.2	3.88 (5)
2	461.4	3.99 (6)	451.6	3.92 (7)
3	461.5	3.96 (3)	436.1	3.64 (2)
7	460.5	3.99 (9)	426.8	*b*
14	461.1	3.96 (8)	437.7	3.72 (2)

[a] Sample composition (mol %): LiF, 46.6; NaF, 11.4; KF, 42.0. Apparent mol wt: 41.29. Sample weight: 5.021 mg. Preparative method: direct weighing using the "in-capsule" DSC technique; highest purity fluorides as reactants. Recommended values: t_m, 462 ± 2 °C; ΔH_{fus} = 3.98 kcal mol^{-1}; ΔS_{fus} = 5.42 eu; cryoscopic constant, k_f = 11.21 deg mol^{-1} kg^{-1}. For conversion to SI units, 1 cal = 4.184 J. [b] For this cooling cycle 426.8 °C (700 K) was the lower limit of the scan. Crystallization was observed isothermally (about 10 s after standing at 700 K); thus, no heat of crystallization is given.

Further eutectics were prepared (in ~100-g amounts) from the reagent-grade chemicals. In this series the following pretreatments were undertaken before sample encapsulation for DSC measurements: (i) fusion and crystallization in pyrolytic graphite crucibles under argon atmosphere; (ii) the prefused eutectics thus prepared were filtered by using either glass frits or platinum frits in the filtration assembly; and (iii) the samples were further submitted to preelectrolysis, and the residual currents were noted. These procedures were based on FLINAK pretreatments in the open scientific literature. Atomic absorption spectroscopy was used for composition analysis.

Results and Discussion

The fusion properties and the heat capacity results for highest purity FLINAK are summarized in Tables I and II, respectively. On the basis of the present measurements, the melting point is 462 ± 2 °C, with 3.98 kcal mol^{-1} and 5.42 eu as the best values for the enthalpy and entropy of fusion, respectively. The higher value for the melting temperature observed in the first thermal cycle (Table I) is attributed to inhomogeneity of the mechanical mixture; homogeneity is achieved after repeated thermal cycling. In general, in liquidus–solidus phase-diagram studies, the phase-transition temperatures are determined by cooling-curve techniques, i.e., freezing-point or crystallization-type measurements, whereas, in the present calorimetric technique, these are determined by melting of the samples. The lower melting points in the open scientific literature for this eutectic, 454 °C (*6–8*, *10–12*) and 457 °C (*9*)

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Table II. Heat Capacity Data for the Eutectic LiF-NaF-KF (FLINAK)[a]

FLINAK eutectic	C_p(cal mol^{-1} K^{-1}) = $a + bT + cT^2$			
	a	$10^3 b$	$10^5 c$	temp range, K
solid[b]	12.8218	−9.651	1.513	330–720
melt[b]	9.6360	10.487		750–860

Heat Capacity from above Equations

T, K	C_p, cal mol^{-1} K^{-1}	T, K	C_p, cal mol^{-1} K^{-1}
350	11.30	700	13.48
400	11.38	720	13.72
450	11.54	phase transition; t_m = 735 K	
500	11.78	750	17.50
550	12.09	800	18.03
600	12.48	850	18.55
650	12.94	860	18.60

[a] For sample specification, see Table I. The heat capacities were determined on samples conditioned by ~14 successive thermal cycles, and for which the integrity of the sample was cross-checked before and after the measurements, using t_m and ΔH_{fus} as criteria. Data base: solid, 65 data points; melt, 23 data points. The values of C_p increases from 11.3 to 13.7 cal mol^{-1} deg^{-1} as the polycrystalline solid is heated from 330 to 720 K, and from 17.5 to 18.7 cal mol^{-1} deg^{-1} as the melt is raised from 750 to 860 K. For the solid over the range 330–450 K the change in heat capacity is small. For conversion to SI units, 1 cal = 4.184 J.

are thus understood, i.e., as due to incomplete corrections for supercooling effects.

A limitation of the DSC technique for phase-transition enthalpy measurements is the relatively low capacity of the differential heat sink. For example, if the heat is released very suddenly as a "burst" (i.e., nucleation of a severely supercooled liquid), this capacity may be exceeded. The measured enthalpy will then be based on an incomplete record. Thus, if water is supercooled by ~25 °C, the DSC measured enthalpies of crystallization are ~25% lower than for the melting process (*13*). In the present measurements with FLINAK, a supercooling of 20–25 °C is observed in the 14th thermal cycle (Table I). The lower enthalpy effect (3.72) is undoubtedly, in part, due to the occurrence of an "overshoot" of the capacity of the differential heat sink.

Relative to the series of measurements directed at evaluation of additional pretreatments, such as filtration and melt preelectrolysis (when FLINAK is prepared from reagent-grade chemicals), the results are as summarized in Table III. Inspection shows that the melting points are in close accord with that of the reference standard (i.e., 462 ± 2 °C). The lower enthalpies of fusion for two of the samples are undoubtedly due to the off-eutectic compositions, i.e., due to a smaller amount of sample melting at the FLINAK eutectic composition, with the remainder dissolving in the off-eutectic liquidus range.

The in-capsule DSC technique, as already noted, minimizes the possibility of trace impurities that may be introduced in the various transfer steps of the more generally used macroscopic methods for melt preparation and pretreatments. The large supercooling effects for samples thus prepared attest to this (see Table I). While the beneficial effects of pretreatments, such as filtration and preelectrolysis, have been recognized (removing macroinsolubles and electroactive impurities, respectively), it appears that the resulting eutectics form melts that exhibit only very limited supercooling effects. Inspection of the results in Table III shows, for example, that the degree of supercooling decreases with the pretreatments and is the least after the preelectrolysis pretreatments. If the degree of supercooling is taken as a criterion of melt purity, then it is clear that both pretreatments may be contributing species that act as "nucleation impurities". This unexpected observation suggests an interesting prospect for further studies of nucleation in ionic melts, in which the DSC calorimetric technique and the electrochemical technique would be coupled in the experimental approach.

Table III. Evaluation of Additional Pretreatments for the Eutectic LiF-NaF-KF (FLINAK)[a]

additional pretreatments		fusion properties		
filtration frit	preelectrolysis i_r, mA	t_m, °C	ΔH_{fus}, kcal mol^{-1}	supercooling (max range), °C
		462.7	4.01; 4.06	4–8
glass	*b*	462.1	3.91; 3.96	1–6
glass	12	462.5	3.93	~4
Pt	2.8	461.7	3.40; 3.51	*c*
Pt	1.3	462.2	3.39; 3.55	~2[d]
Pt	4.5	461.2	2.88; 3.37	~<1[e]

[a] Component salts: reagent-grade quality. Preparative method: oven drying under vacuum and then fusion of the eutectic under argon and in vitreous graphite crucibles; then, additional pretreatments as noted. For conversion to SI units, 1 cal = 4.184 J. [b] Not measured. [c] Composition (mol %): LiF, 44.8_5; NaF, 9.9; KF, 45.1_7; nucleation due to phase-separation prior to eutectic temperatures was observed. [d] Composition (mol %): LiF, 43.9_8; NaF, 10.6_7; LiF, 45.3_5. [e] Preelectrolysis had been continued for ~3 days.

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