Heat of Fusion of 3LiF·ThF$_4$

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EQUILIBRIUM phase relationships in many fused salt systems have been studied during the last several years (3). These investigations reflect the increasing significance of fundamental and applied chemistry of molten salts. Many congruently melting compounds are formed within the binary systems AX-MX_4 [A = alkali metal, M = heavy metal (Th, U, Zr, Hf), X = halogen]. While the melting points and some information concerning the crystal structure of these complex salt compounds are usually available, thermodynamic properties, such as the heat of fusion, have not been determined calorimetrically. This information would be of value in calculating ideal phase diagrams for comparison with experimental results.

The measurements were made using a Bunsen ice calorimeter similar to that used at the National Bureau of Standards (1), except that nickel cylinders are used instead of silver in the furnace. The accuracy of the calorimetric system was checked by measuring the enthalpy of α-aluminum oxide. Smoothed enthalpy values from these measurements are compared in Table I with similar values calculated from the work of Furukawa, Douglas, McCoskey and Ginnings (1).

Table I. Comparison of Enthalpy Values of α-Al$_2$O$_3$ Obtained Using This Calorimeter With Values From NBS

Temp., °C.	$H_t - H_{0°C.}$, Cal./Mole		Deviation	% Deviation
	NBS	This Work		
100	19.64	19.73	+0.09	0.46
200	42.77	42.74	−0.03	0.07
300	68.00	68.01	+0.01	0.01
400	94.64	94.77	+0.13	0.14
500	122.26	122.48	+0.22	0.18
600	150.61	150.79	+0.18	0.12
700	179.50	179.55	+0.05	0.03
800	208.83	208.83	0.00	0.00
900	238.49	238.87	+0.36	0.15

Temperatures up to 550° C. were measured using a platinum resistance thermometer calibrated by comparison with a Leeds and Northrup platinum resistance thermometer which had been standardized on the International Temperature Scale of 1948 at the ice, steam, and sulfur points by the NBS. Above 550° C., a platinum vs. platinum-10% rhodium thermocouple was used. The latter was calibrated by comparing it at the melting points of tin, zinc, aluminum, and silver with a similar couple standardized at NBS.

The heat of fusion reported here for 3LiF·ThF$_4$ is the first such value for a complex salt compound. This compound was chosen for study because of its relatively low melting point (approx. 570° C.) and because no solid state transitions occur below the melting point (2, 5). The sample was prepared from previously purified LiF and ThF$_4$ by mixing the stoichiometric amounts of these materials and fusing them together with NH$_4$HF$_2$ to remove traces of oxygen and water. All steps in the purification processes were carried out under a protective blanket of purified argon. The best crystals from the final melt were transferred in an inert atmosphere box to a Nichrome V capsule which was sealed by Heliarc welding in a high purity helium atmosphere. The weight of 3LiF·ThF$_4$ was 13.4624 grams.

Examination of the material with the polarizing light microscope showed no detectable amounts of oxide present either before or after the determinations.

The total heat content of the capsule plus sample is shown as a function of the temperature in Figure 1. The equations for the solid and liquid lines were determined from the data by the method of least squares. The data used in the least squares treatment and values calculated from the equations are compared in Table II. Over the relatively short temperature ranges shown, the heat capacities of the solid and liquid are constant within the experimental precision.
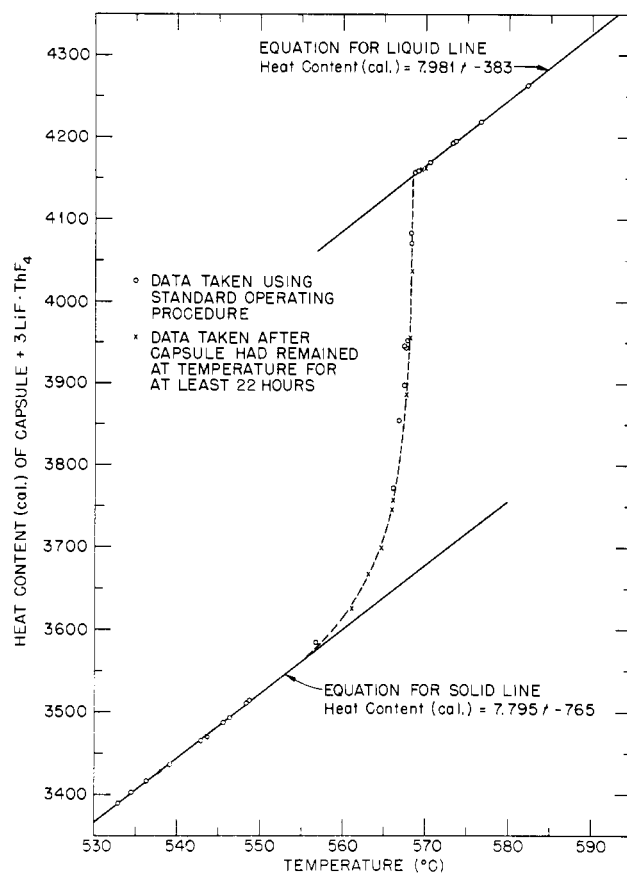

Figure 1. Heat content of capsule plus 3LiF·ThF$_4$ as a function of temperature

The melting point has been determined by the method described by Rossini (4) from heat content data obtained in the premelting region. The initial data in the region (indicated by circles in Figure 1) shows considerable scatter. This is certainly due to a lack of equilibrium between the solid and liquid phases since the capsule cannot be agitated in the furnace. For this reason, additional measurements were made (indicated by X in Figure 1) in which the capsule was maintained at temperature in the furnace at least 22 hours in order to ensure complete solubility of the impurity in the liquid phase. In Figure 2, $1/r$ (r = fraction melted for 3LiF·ThF$_4$) is plotted against the equilibrium temperature. The best straight line has been

Table II. Measurements of Heat Content of Sample Plus Capsule Compared with Those Calculated from the Least Squares Equations

Temp., °C.	ΔH, Cal. Measured	ΔH, Cal. Calcd.	Deviation, %
For Solid Points			
548.4	3511	3510	0.03
543.7	3470	3473	0.09
539.2	3436	3438	0.06
534.5	3402	3401	0.03
536.3	3416	3415	0.03
532.9	3389	3389	0.00
542.9	3465	3467	0.06
545.6	3487	3488	0.03
546.4	3493	3494	0.03
548.8	3514	3513	0.03
For Liquid Points			
569.2	4160	4160	0.00
570.6	4171	4171	0.00
573.3	4194	4193	0.02
568.9	4158	4157	0.02
573.7	4196	4196	0.00
576.7	4220	4220	0.00
582.3	4263	4264	0.02
570.1	4164	4167	0.07
569.5	4161	4162	0.02

Figure 2. Temperature of the liquid-solid equilibrium for $3LiF \cdot ThF_4$ as a function of the reciprocal of the fraction of sample melted

calculated for the points up to $1/r = 11.68$ (amount melted = 8.6%) by the method of least squares. From this line the melting point of the sample (temperature at $1/r = 1$) is found to be 568.4° C.

The heat contents were then calculated at the melting point from the equations for the solid and liquid lines. The difference between these values divided by the number of moles of sample yields a heat of fusion of $13,960 \pm 50$ cal. mole^{-1} for $3LiF \cdot ThF_4$.

The method (4) also gives a melting point for the pure material of 568.9° C. (temperature at $1/r = 0$). From this, the maximum impurity content was calculated to be 0.5 mole %. This impurity is due entirely to deviations from stoichiometry (5).
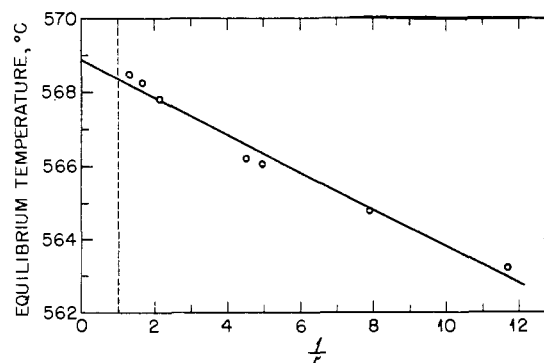
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Ideal Gas Thermodynamic Functions of Some Selected Elements

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SINCE THE APPEARANCE of previous tabulations of ideal gas thermodynamic properties of elements (3, 4) additional data for the heavier elements have become available (6). Because of the utility of the functions in the study of systems at high temperature, we have had occasion to calculate the free energy function, the enthalpy function, the entropy, and the constant pressure heat capacity of several neutral elements using equations derived in standard texts on statistical thermodynamics (7). The calculations were made on an electronic computer (2) at 100 degree intervals from 100° K. to 10,000° K. Presented here are the free-energy functions (Table I) and the enthalpy functions (Table II) for the elements Tc, Ru, Te, I, Hf, Tl, Pb, Bi, Po, Rn, Ra, Ac, and Th (1, 5) for a range