

Short Communications

The Calorimetric Heat of Fusion
of Li_3AlF_6

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The heat content, $H_T - H_{298.15}^{\circ}\text{K}$, was determined by means of a calorimeter originally developed by Oelsen *et al.*¹ later modified by Tashiro.²

The heat content was measured by cooling the sample in a water calorimeter, while continuously recording both the sample and the water temperature. By this method the heat content can be determined as a function of temperature by one single experiment.

The temperature of the sample was measured by a Pt/Pt10Rh thermocouple. The water temperature was determined by a thermistor (Type F 22, Standard Telefon og Kabelfabrikk, Oslo, Norway). The thermistor was supplied with a stabilized voltage, and the temperature was determined by the voltage drop across a standard resistor in the thermistor circuit, the resistor forming part of a voltage divider. The output from the thermocouple was fed to another voltage divider (both made by Micro-Volt, Trondheim, Norway), and both were further connected to a two-point recorder (Multi-Point D. E. Recorder, Potentiometric Type, Cambridge Instrument Co., Cambridge, England). The recorder-range was 1 mV, corresponding to about 100° for the sample and 0.5° for the water. The temperature in the air near the calorimeter was kept constant within $\pm 0.3^\circ\text{C}$ by a water-cooling arrangement.

Lithium cryolite was made by fusing aluminium fluoride and lithium fluoride in

molar proportion 1:3. The aluminium fluoride was prepared by vacuum sublimation of anhydrous AlF_3 (A.D. Mackay Inc., USA). The lithium fluoride (LiF , Fisher Certified Reagent, Fisher, USA) was carefully dried in a vacuum furnace at 400–500°C before use.

The Pt-Rh-crucible and the sample were heated in a furnace constructed to eliminate temperature gradients. When a temperature of about 840°C was reached, the crucible was quickly transferred to the copper container in the calorimeter (transfer time about 4 sec). The sample and the calorimeter temperatures were registered alternately every 3 sec by the recorder. When the sample temperature was below 100°C, the crucible was transferred from the copper container to a brass screen basket to increase the cooling rate at low temperatures. The heat loss connected with this transfer was found to be negligible.

The heat capacity of the water calorimeter was determined by replacing the crucible with accessories with a copper cylinder having a bore for the thermocouple. Heat content data for Cu ($H_T - H_{298} = 5.41T + 0.75 \times 10^{-3} T^2 - 1680$) were taken from Kelley.³

The heat capacity of the empty crucible with accessories, determined by blank runs, amounted to about 25 % of the total heat capacity.

The calorimeter temperature showed a small drift due to the mechanical work of the stirrer and to the temperature difference between the calorimeter and the surroundings. All heat content measurements were corrected for this effect. The correction was less than 1 % of the total heat transfer.

The heat content of the sample is given by the relation:

$$H_T - H_{298.15} = \frac{W(\theta_{298.15} - \Delta\theta') - \theta}{P} \quad (1)$$

Table 1. Enthalpy of lithium cryolite above 298.15°K.

t_{sample}	$\theta_{\text{thermistor}}$ °C	$\Delta\theta_{\text{correction}}$	$H_T - H_{298.15^\circ\text{K}}$ cal·g ⁻¹
815	19.080	0.635	443.7
803	19.120	0.623	437.3
792	19.160	0.611	431.0
785	19.290	0.605	402.9
783	19.460	0.603	364.9
775	19.645	0.592	325.5
755	19.805	0.572	293.8
732	19.890	0.550	279.5
715	19.940	0.530	272.8
694	19.995	0.505	266.0
670	20.080	0.480	252.3
645	20.145	0.455	243.3
594	20.290	0.407	221.3
512	20.495	0.340	190.1
411	20.750	0.265	149.4
332	20.965	0.207	113.9

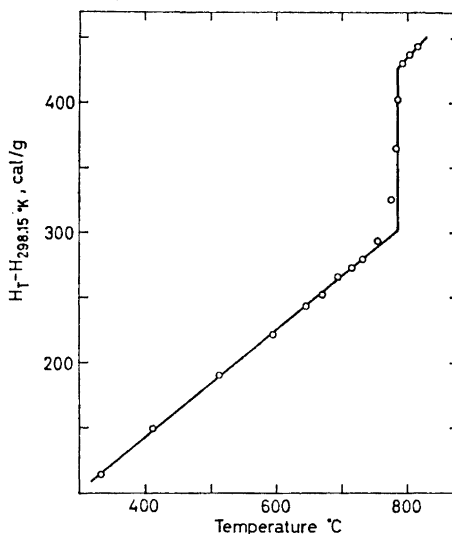


Fig. 1.

W = water value of calorimeter
 P = weight of sample
 θ = water temperature
 $\theta_{298.15}$ = water temperature when the sample is at 25°C.
 $\Delta\theta'$ = correction due to heat capacity of crucible.

In this case $W = 11.25$ kcal/degree,
 $P = 49.70$ g, $\theta = 21.675^\circ\text{C}$.

The measurements are given in Table 1 and the calculated heat content values plotted as a function of temperature in Fig. 1. The melting point was found to be 785°C. From Fig. 1 we obtain the heat of fusion of lithium cryolite, $\Delta H_f = 125$ cal/g, with an estimated limit of error of ± 5 cal/g.

$$\Delta H_f(\text{Li}_3\text{AlF}_6) = 20.2 \pm 1.0 \text{ kcal/mole}$$

An approximate value for the entropy of fusion of lithium cryolite can be calculated from the relation

$$\Delta S_f(\text{Li}_3\text{AlF}_6) = 3\Delta S_f(\text{LiF}) + \Delta S_f(\text{AlF}_3) \quad (2)$$

The hypothetical melting entropy of AlF_3 is obtained by using the relation:

$$\Delta S_f(\text{AlF}_3) = \Delta S_f(\text{Na}_3\text{AlF}_6) - 3\Delta S_f(\text{NaF}) \quad (3)$$

Data for NaF and LiF were taken from JANAF Thermochemical Tables⁴ and for

Na_3AlF_6 from Kelley.³ The following values were used at 785°C: $\Delta S_f(\text{Na}_3\text{AlF}_6) = 21.47$ cal/mole, $\Delta S_f(\text{LiF}) = 5.73$ cal/mole, and $\Delta S_f(\text{NaF}) = 6.05$ cal/mole.

Using these values in eqns. (2) and (3) we obtain

$$\Delta S_f(\text{Li}_3\text{AlF}_6) = 20.51 \text{ cal/mole}$$

or, for the heat of fusion at the melting point 785°C

$$\Delta H_f(\text{Li}_3\text{AlF}_6) = 21.70 \text{ kcal/mole}$$

This is in good agreement with the experimental value.

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