

The Enthalpy of Fusion of Samarium Trifluoride

JAN LÜTZOW HOLM^a and
FREDRIK GRØNVOLD^b

^a*Institute of Inorganic Chemistry, The Technical University of Norway, N-7034 Trondheim-NTH, Norway, and* ^b*Institute of Chemistry, The University of Oslo, Blindern, Oslo 3, Norway*

Thermodynamic data for the fusion of lanthanoide trifluorides are scarce in the literature, due to the high melting temperatures of these salts, which range from 1413 K for erbium trifluoride to 1766 K for lanthanum trifluoride.¹

The first enthalpy of fusion measurements for a lanthanoide fluoride were presented by King and Christensen² in 1959. They reported a value $\Delta H_f = 13.2$ kcal mol⁻¹ for the enthalpy of fusion of cerium trifluoride at 1743 K, corresponding to an entropy of fusion of $\Delta S_f = 7.6$ cal K⁻¹ mol⁻¹.

Brewer³ earlier had estimated values around 8 kcal mol⁻¹ for the enthalpies of fusion of the lanthanoide trifluorides. The enthalpies of fusion of DyF₃, HoF₃, and ErF₃, given by Besenbruch *et al.*⁴ as differences between the enthalpies of sublimation and vaporization, were, however, in the range 18–22 kcal mol⁻¹. It may also be mentioned that Phipps *et al.*⁵ estimated the entropy of fusion of plutonium trifluoride from vapor pressure measurements of solid and liquid PuF₃ to be $\Delta S_f = 5.5$ cal K⁻¹ mol⁻¹ at 1698 K, corresponding to $\Delta H_f = 9.3$ kcal mol⁻¹.

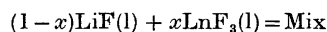
Here we report a new value for the enthalpy of fusion of samarium trifluoride. SmF₃ crystallizes with an orthorhombic structure, which transforms to the hexagonal thymonite structure at 929 K.¹ The technique used is based on high precision drop calorimetry in the temperature range 850–1050 K. The lanthanoide trifluoride is dissolved in lithium fluoride in a proportion corresponding to the eutectic composition in the LiF–LnF₃ system. The enthalpy of fusion of the lanthanoide trifluoride can be determined from the following relation:

$$(1-x)\Delta H_f(\text{LiF}) + x\Delta H_f(\text{LnF}_3) = \Delta H_f(\text{Mix})$$

$$\Delta H_f(\text{LnF}_3) = \Delta H_f(\text{Mix}) - (1-x)\Delta H_f(\text{LiF})/x$$

where x is the mol fraction of lanthanoide

trifluoride at the eutectic temperature. Here it is assumed that the enthalpy of mixing ΔH^M for the process



is zero.

Experimental. The drop experiments were carried out by using the same method and technique and also the same adiabatic shield calorimeter as described by Grønvold⁶ and used for enthalpy of fusion determinations on alkali cryolites by Jenssen Holm and Grønvold.⁷

The following chemicals were used: LiF, Fisher Certified Reagent, USA; SmF₃, 99.9 %, Westo Industrial Products Ltd., London.

Before use the lithium fluoride was melted in a platinum crucible in an atmosphere of pure, dry nitrogen. After solidification, clear crystals were picked from the sample. Samarium trifluoride and lithium fluoride were mixed in the molar proportions 0.35 SmF₃ + 0.65 LiF, corresponding to the eutectic composition in the system as given by Thoma.⁸

In the calorimetric experiments steady state conditions were usually obtained after about 25 min. The calorimeter temperature during the experiments ranged from 300 to 330 K, with a mean of 315 K. The heat capacities of the mixture at 315 K was taken to be:

$$C_{p, 315} = 0.35 C_p(\text{SmF}_3) + 0.65 C_p(\text{LiF}) = 0.35 \times 22.0 + 0.65 \times 10.2 = 14.5 \text{ cal K}^{-1} \text{ mol}^{-1}$$

Here the C_p value of CeF₃ given by Westrum and Beale⁹ and the C_p value of LiF given by JANAF¹⁰ were used.

Table 1. Enthalpy increments $H_T - H_{298.15}$ for 0.35 SmF₃ + 0.65 LiF.

T K	$H_T - H_{298.15}$ kcal mol ⁻¹
858.7	10.211
874.6	10.490
894.9	10.829
924.5	11.475
963.4	12.709
974.2	15.647
992.2	19.169
1005.2	19.422
1015.6	19.708
1030.3	20.750
1047.6	20.574

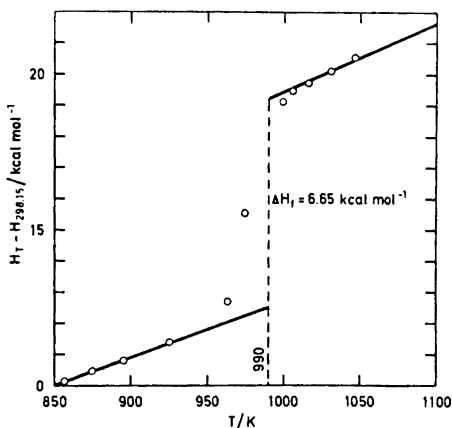


Fig. 1. The enthalpy increments, $H_T - H_{298.15}$, for the mixture $0.65\text{LiF} + 0.35\text{SmF}_3$.

Results and discussion. In the course of the present investigation eleven drops from different temperatures were carried out. The results are given in Table I and plotted in Fig. 1.

The slope of the $H_T - H_{298.15}$ curve for the solid $\text{SmF}_3 - \text{LiF}$ mixture corresponds to a heat capacity of $18.5 \text{ cal K}^{-1} \text{ mol}^{-1}$. This value is in good agreement with the heat capacity calculated from $C_p[\text{LiF}(s)] = 14.3 \text{ cal K}^{-1} \text{ mol}^{-1}$ (JANAF)¹⁰ and $C_p[\text{SmF}_3(s)] = 27.3 \text{ cal K}^{-1} \text{ mol}^{-1}$ (Charlu *et al.*¹¹) at 990 K.

$C_p(s) = 0.65 \times 14.3 + 0.35 \times 27.5 = 18.8 \text{ cal K}^{-1} \text{ mol}^{-1}$.

The slope of the $H_T - H_{298.15}$ curve for the liquid corresponds to $C_p(l) = 22.2 \text{ cal K}^{-1} \text{ mol}^{-1}$ as compared to a value of $21.7 \text{ cal K}^{-1} \text{ mol}^{-1}$ calculated from $C_p[\text{LiF}(l)] = 15.5 \text{ cal K}^{-1} \text{ mol}^{-1}$ (JANAF)¹⁰ and $C_p[\text{SmF}_3(l)] = 33.0 \text{ cal K}^{-1} \text{ mol}^{-1}$. The value for the heat capacity of liquid SmF_3 has been estimated, but is a reasonable value when compared with other liquid lanthanoide trifluorides.²

The obtained enthalpy increment at the melting point, 990 K, of the eutectic mixture, $0.35 \text{ mol SmF}_3 + 0.65 \text{ mol LiF}$, is $6.65 \text{ kcal mol}^{-1}$. The enthalpy of fusion of LiF at 990 K is, according to available

literature data,¹⁰ $6.1 \text{ kcal mol}^{-1}$. This gives the following relation

$$0.35 \Delta H_f(\text{SmF}_3) + 0.65 \times 6.1 = 6.65$$

or $\Delta H_f(\text{SmF}_3) = 7.7 \text{ kcal mol}^{-1}$ at 990 K.

Using the heat capacity equation for solid CeF_3 given by King and Christensen,² and the estimated value for the liquid, $33.0 \text{ cal K}^{-1} \text{ mol}^{-1}$, we arrive at a value for the enthalpy of fusion for samarium trifluoride at the melting point, 1579 K, of $\Delta H_f = 8.9 \pm 0.6 \text{ kcal mol}^{-1}$. The uncertainty $\pm 0.6 \text{ kcal mol}^{-1}$ in the enthalpy of fusion is due to the estimated uncertainty of $\pm 1 \text{ cal K}^{-1} \text{ mol}^{-1}$ in the C_p value for liquid samarium trifluoride.

Acknowledgement. Financial support to one of the authors (J.L.H.) from *Norges Tekniske Hogskoles Fond* is gratefully acknowledged.

1. Spedding, F. H. and Daane, A. H. *The Rare Earths*, Wiley, New York 1961.
2. King, E. G. and Christensen, A. U. *U. S. Bur. Mines, Rep. Invest. 5510*, 1959.
3. Brewer, L. In Quill, L. L., Ed., *The Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics*, McGraw, New York 1950.
4. Besenbruch, G., Charlu, T. V., Zmbov, K. F. and Margrave, J. L. *J. Less-Common Metals* **12** (1967) 375.
5. Phipps, T. E., Sears, G. V., Seifert, R. L. and Simpson, O. C. *J. Chem. Phys.* **18** (1950) 713.
6. Grønvold, F. *Acta Chem. Scand. In press.*
7. Jenssen Holm, B. and Grønvold, F. *To be published.*
8. Thoma, R. E. *Progress in Science and Technology of the Rare Earths*, Pergamon, New York 1960, Vol. 2, p. 110.
9. Westrum, E. F., Jr. and Beale, A. F. *J. Phys. Chem.* **65** (1961) 353.
10. *JANAF Thermochemical Tables*, Clearinghouse Springfield, Virginia 1965.
11. Charlu, T. V., Chaudhuri, A. K. and Margrave, J. L. *High Temp. Sci.* **2** (1970) 2.

Received March 24, 1972.