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Short Communication

New Enthalpy Data on the Formation of Chiolite, $Na_5Al_3F_{14}$, and Sodium Tetrafluoroaluminate, $NaAlF_4$

Markus Bruno and Jan L. Holm*

Department of Inorganic Chemistry, The Norwegian University of Science and Technology, N-7034 Trondhiem, Norway

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A new value for the enthalpy of formation of chiolite, $Na_5Al_3F_{14}$, has been calculated from the enthalpy increment data obtained by drop calorimetry and reported by Holm[1] in 1974. The data are recalculated from calories to joules and given in Table 1.

From the two reactions given as eqns. (1) and (2)

$$0.425\ Na_3AlF_6(s) + 0.575\ AlF_3(s) = 0.255\ Na_5Al_3F_{14}(s) + 0.235\ AlF_3(s) \quad (1)$$

$$0.333\ Na_3AlF_6(s) + 0.667\ AlF_3(s) = 0.2\ Na_5Al_3F_{14}(s) + 0.4\ AlF_3(s) \quad (2)$$

one obtains, by taking the difference between the right-hand side and the left-hand side of the two equations, the following reaction as a result:

$$5/3\ Na_3AlF_6(s) + 4/3\ AlF_3(s) = Na_5Al_3F_{14}(s) \quad (3)$$

From the enthalpy data for the two mixtures and literature data for solid cryolite,[2,3] and solid aluminium fluoride[4] given in Table 1, the following value for the standard enthalpy for reaction (3) from the two series of drop experiments is obtained:

$$\Delta H^\circ(900\ K) = -34.9 \pm 1.5\ kJ\ mol^{-1}$$

From this value, combined with available data for Na_3AlF_6,[2,3] NaF[2,3] and AlF_3,[4] it is possible to calculate the enthalpy of formation of chiolite from the component fluorides:

$$5\ NaF(s) + 3\ AlF_3(s) = Na_5Al_3F_{14}(s) \quad (4)$$

A value of $\Delta H_f^\circ(900\ K) = -129.5\ kJ\ mol^{-1}$ is obtained. This value should be compared with the enthalpy of formation, $\Delta H_f^\circ(900\ K) = -181.4\ kJ\ mol^{-1}$, calculated from Ref. 3. As can be seen, the discrepancy between the new value and the JANAF value is more than 50 kJ.

The formation of chiolite from the elements at 900 K can be calculated by use of available literature data.[3,5] The calculated value is $\Delta H_f^\circ(900\ K) = -7513.6\ kJ\ mol^{-1}$. This value has been compared with different enthalpies of formation reported in the literature in Table 2.

By use of the standard enthalpy increment equation for chiolite given in Table 1

$$H_T^\circ - H^\circ(298.15\ K) = -184\,702 + 574.31T$$

together with the same data for NaF and AlF_3 in Ref. 3, a new value for the standard enthalpy of formation of chiolite at 298.15 K has been obtained:

$$\Delta H_f^\circ(298.15\ K) = -7539.5 \pm 12.0\ kJ\ mol^{-1}$$

This value is in disagreement with the recommended

Table 1. Standard enthalpy increments $H_T^\circ - H^\circ(298.15\ K) = a + bT$ as a function of temperature and standard deviations.

Compound (mixture)	$H_T^\circ - H^\circ(298.15\ K)/J\ mol^{-1}$	$\sigma/J\ mol^{-1}$	Literature
$Na_5Al_3F_{14}(s)$	$-184\,975 + 574.588T$	1138	1
$0.425\ Na_3AlF_6(s) + 0.575\ AlF_3(s)$	$-66\,927 + 182.297T$	364	1
$0.333\ Na_3AlF_6(s) + 0.667\ AlF_3(s)$	$-53\,614 + 159.12T$	556	1
β-$Na_3AlF_6(s)$	$-90\,629 + 288.49T$	1079	2, 3
β-$AlF_3(s)$	$-30\,870 + 100.16T$	88	4

*To whom correspondence should be addressed.

Table 2. Standard enthalpy of formation of solid $Na_5Al_3F_{14}$ at 900 K.

Source	ΔH_f°/kJ mol^{-1}
Dewing[8]	−7539.8
Grjotheim *et al.*[9]	−7472.9
Cantor *et al.*[10]	−7488.5
Sterten *et al.*[11]	−7462.5
This work	−7513.6 ± 12.0

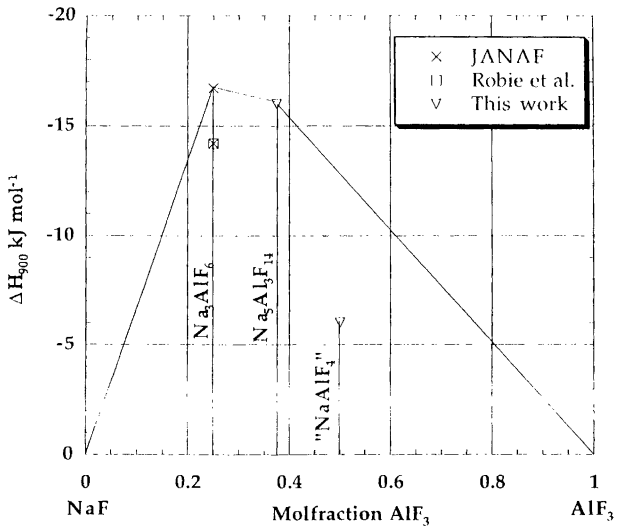

Fig. 1. Standard molar enthalpies of reaction at 900 K for cryolite, chiolite and sodium tetrafluoroaluminate from the component fluorides sodium fluoride and aluminium fluoride.

value given in Ref. 3:

$$\Delta H_f^\circ(298.15\ \mathrm{K}) = -7581.4 \pm 16\ \mathrm{kJ\ mol^{-1}}$$

From the new enthalpy value for reaction (4) $\Delta H_f^\circ(900\ \mathrm{K}) = -129.5\ \mathrm{kJ\ mol^{-1}}$, and the enthalpy of the disproportionation reaction

$$5\ NaAlF_4(s) = Na_5Al_3F_{14}(s) + 2\ AlF_3(s) \qquad (5)$$

$\Delta H^\circ(900\ \mathrm{K}) = -66.9$ kJ reported by Bjørseth *et al.*,[6] the enthalpy of formation of the metastable compound $NaAlF_4$, sodium tetrafluoroaluminate, can be calculated. One obtains for the reaction

$$NaF(s) + AlF_3(s) = NaAlF_4(s); \qquad (6)$$

$$\Delta H_f^\circ(900\ \mathrm{K}) = -12.5\ \mathrm{kJ\ mol^{-1}}$$

This value should be compared with earlier values calculated by Holm[7] (-16.7 kJ mol^{-1}) and by Bjørseth *et al.*[6] (-6.9 kJ mol^{-1}).

In Fig. 1 are plotted the standard molar enthalpies of formation from the component fluorides in kJ (mol mixture)$^{-1}$ at 900 K for the three compounds Na_3AlF_6, $Na_5Al_3F_{14}$ and $NaAlF_4$. The data for $Na_5Al_3F_{14}$ and $NaAlF_4$ are based on this work, while the data for cryolite has been taken from the literature.[3,5] The diagram clearly demonstrates the instability of $NaAlF_4$ with respect to $Na_5Al_3F_{14} + AlF_3$.

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