Short Communication

New Enthalpy Data on the Formation of Chiolite, Na$_5$Al$_3$F$_{14}$, and Sodium Tetrafluoroaluminate, NaAlF$_4$

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A new value for the enthalpy of formation of chiolite, Na$_5$Al$_3$F$_{14}$, 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$_3$AlF$_6$(s) + 0.575 AlF$_3$(s)  
= 0.255 Na$_3$Al$_3$F$_{14}$(s) + 0.235 AlF$_3$(s)  \( \text{(1)} \)

0.333 Na$_3$AlF$_6$(s) + 0.667 AlF$_3$(s)  
= 0.2 Na$_3$Al$_3$F$_{14}$(s) + 0.4 AlF$_3$(s)  \( \text{(2)} \)

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$_3$AlF$_6$(s) + 4/3 AlF$_3$(s) = Na$_3$Al$_3$F$_{14}$(s)  \( \text{(3)} \)

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:

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

From this value, combined with available data for Na$_3$AlF$_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$_3$Al$_3$F$_{14}$(s)  \( \text{(4)} \)

A value of $\Delta H_f(900 \text{ K}) = -129.5 \text{ kJ mol}^{-1}$ is obtained. This value should be compared with the enthalpy of formation, $\Delta H_f(900 \text{ K}) = -181.4 \text{ kJ mol}^{-1}$, 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.$^{1,5}$ The calculated value is $\Delta H_f(900 \text{ K}) = -7513.6 \text{ kJ mol}^{-1}$. 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

$H_f(H' f(298.15 \text{ K})) = -184,702 + 574.31 T$

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:

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

This value is in disagreement with the recommended

<table>
<thead>
<tr>
<th>Compound (mixture)</th>
<th>$H_f' - H_f(298.15 \text{ K})/\text{J mol}^{-1}$</th>
<th>$\sigma/\text{J mol}^{-1}$</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_3$Al$<em>3$F$</em>{14}$(s)</td>
<td>-184,975 + 574.588 T</td>
<td>1138</td>
<td>1</td>
</tr>
<tr>
<td>0.425 Na$_3$AlF$_6$(s) + 0.575 AlF$_3$(s)</td>
<td>-66,927 + 182.297 T</td>
<td>364</td>
<td>1</td>
</tr>
<tr>
<td>0.333 Na$_3$AlF$_6$(s) + 0.667 AlF$_3$(s)</td>
<td>-53,614 + 159.127 T</td>
<td>556</td>
<td>1</td>
</tr>
<tr>
<td>$\beta$-Na$_3$AlF$_6$(s)</td>
<td>-90,629 + 288.497 T</td>
<td>1079</td>
<td>2, 3</td>
</tr>
<tr>
<td>$\beta$-AlF$_3$(s)</td>
<td>-30,870 + 100.167 T</td>
<td>88</td>
<td>4</td>
</tr>
</tbody>
</table>

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Table 2. Standard enthalpy of formation of solid Na₆Al₃F₁₄ at 900 K.

<table>
<thead>
<tr>
<th>Source</th>
<th>ΔHᵣ/kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dewing</td>
<td>-7539.8</td>
</tr>
<tr>
<td>Grijthoime et al.</td>
<td>-7472.9</td>
</tr>
<tr>
<td>Cantor et al.</td>
<td>-7488.5</td>
</tr>
<tr>
<td>Sterten et al.</td>
<td>-7462.5</td>
</tr>
<tr>
<td>This work</td>
<td>-7513.6 ± 12.0</td>
</tr>
</tbody>
</table>

![Diagram showing ΔHᵣ values](image)

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:

ΔHᵣ(298.15 K) = -7581.4 ± 16 kJ mol⁻¹

From the new enthalpy value for reaction (4)

ΔHᵣ(900 K) = -129.5 kJ mol⁻¹, and the enthalpy of the disproportionation reaction

5 NaAlF₄(s) = Na₄Al₁F₁₄(s) + 2 AlF₃(s)

ΔHᵣ(900 K) = -66.9 kJ reported by Björseth et al., the enthalpy of formation of the metastable compound NaAlF₄, sodium tetrafluoroaluminate, can be calculated.

One obtains for the reaction

NaF(s) + AlF₃(s) = NaAlF₄(s);

ΔHᵣ(900 K) = -12.5 kJ mol⁻¹

This value should be compared with earlier values calculated by Holm (−16.7 kJ mol⁻¹) and by Björseth et al. (−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 Na₄Al₁F₁₄, Na₆Al₃F₁₄ and NaAlF₄. The data for Na₆Al₃F₁₄ and NaAlF₄ are based on this work, while the data for cryolite has been taken from the literature. The diagram clearly demonstrates the instability of NaAlF₄ with respect to Na₆Al₃F₁₄ + AlF₃.

References


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