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Berichtigung der Arbeit "Reaktionen von Trichlormethansulfenychlorid mit Stickstoffverbindungen. V. Sulfenylierung von Acylhydrazinen" *

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The Gibbs Free Energy of Formation of Liquid Aluminium Fluoride

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The Gibbs free energy of formation of liquid aluminium fluoride is necessary for discussions of the dissociation equilibria in molten sodium cryolite. This dissociation has been shown to be a complex one (see for instance Grjotheim et al.¹) and correlation of the structural and thermodynamic measurements has been hindered by the absence of accurate thermodynamic data. This lack of data has forced some authors " to use the Gibbs free energy of formation of solid aluminium fluoride in their calculations instead of more correctly the Gibbs free energy of formation of liquid aluminium fluoride.

As aluminium fluoride does not melt, but sublimes, with an equilibrium pressure over the pure solid of 1 atmosphere at 1533 K, the Gibbs free energy of formation of liquid aluminium fluoride cannot be measured directly. In this paper we have made an estimate of this quantity, utilizing recent measurements of the enthalpy of fusion of aluminium fluoride.

The Gibbs free energy of formation of liquid aluminium fluoride at a temperature T is related to that of solid aluminium fluoride by the relation

$$\Delta G_{(\text{AlF}_3 \text{sol})} = \Delta G_{(\text{AlF}_3 \text{sol})} + \Delta H_f^T - T \Delta S_f^T$$ (1)

where $\Delta H_f^T$ and $\Delta S_f^T$ are the enthalpy and entropy of fusion at the temperature T. If the entropy of fusion is assumed to be independent of temperature, the entropy of fusion at any temperature can be found from the enthalpy of fusion at the melting point of the pure compound. If the latter is not known, the entropy of fusion can often be estimated fairly accurately from the structure. This method, too, is based on the assumption that the entropy of fusion is independent of temperature. In

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most systems little error is introduced by making this assumption.

The Gibbs free energy of formation of solid $\text{AlF}_3$ was taken from the JANAF Thermochemical Tables.\textsuperscript{7} For temperatures above 1000 K these data fit the equation

$$
\Delta G(\text{AlF}_3) = -356.682 + 0.0606 T + 1.66 \times 10^{-7} T^2 \text{ kcal}
$$

(2)

with an accuracy of $\pm 1.5$ kcal.\textsuperscript{6}

The enthalpy of fusion of $\text{AlF}_3$ has recently been measured by Holm\textsuperscript{6} and found to be $9.5 \pm 1.0$ kcal at 1000 K. Holm also estimated that at this temperature the difference in heat capacity between the liquid and the solid would be 3 cal/mol deg. Hence the enthalpy of fusion is given by the relation

$$
\Delta H_f = 6.5 + 0.003 T \pm 1.0 \text{ kcal/mol}
$$

valid in the temperature range 1000–1300 K.

As pure aluminium fluoride does not melt at normal pressure, its entropy of fusion has to be estimated from its structure. Compounds of the same structural type generally have similar entropies of fusion.\textsuperscript{8} Ketelaar\textsuperscript{8} has shown that solid aluminium fluoride has a distorted rhenium oxide structure where each aluminium atom is coordinated with 6 fluorine atoms.

In Table 1 are given enthalpies of fusion per g atom for a range of fluorides with structures similar to that of aluminium fluoride. From these values we estimate the entropy of fusion of aluminium fluoride to be 1.8 cal degree$^{-1}$ g atom$^{-1}$ or 7.2 cal degree$^{-1}$ mol$^{-1}$.

Inserting these values in eqn. (1) we find the Gibbs free energy of formation of liquid aluminium fluoride to be given by

$$
\Delta G(\text{AlF}_3) = -350.2 + 0.0504 T + 1.66 \times 10^{-7} T^2 \text{ kcal/mol}
$$

(4)

with an uncertainty of $\pm 2.5$ kcal/mol.

As would be expected, this Gibbs free energy curve lies between those for solid and for gaseous aluminium fluoride\textsuperscript{7} at temperatures well below the sublimation point, and it intercepts the curve for gaseous aluminium fluoride at a temperature a few degrees below the sublimation point of the compound.


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**Table 1.** The entropy of fusion (cal deg$^{-1}$ g atom$^{-1}$) of six co-ordinated fluorides at their melting points, from Kubaschewski, Evans and Alocok.\textsuperscript{8}

<table>
<thead>
<tr>
<th>Compound</th>
<th>Entropy of fusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{HgF}_2$</td>
<td>1.9</td>
</tr>
<tr>
<td>$\text{ZrF}_4$</td>
<td>2.0</td>
</tr>
<tr>
<td>$\text{TIF}_3$</td>
<td>2.0</td>
</tr>
<tr>
<td>$\text{FeF}_3$</td>
<td>1.4</td>
</tr>
<tr>
<td>$\text{UF}_4$</td>
<td>1.9</td>
</tr>
</tbody>
</table>