3. Castellano, S. and Bothner-By, A. A. In
   Detar, D. F. and Benjamin, W. A., Eds.,
   Computer Programs for Chemistry, 1968,
   Vol. 1.
4. Aksnes, D. and Albriktsen, P. *Private
   communication.*
5. Jackman, L. M. and Sternhell, S. *Applica-
   tions of NMR Spectroscopy in Organic
   Chemistry*, 2nd Ed., Pergamon, London-
   New York 1969, p. 368.
6. Emsley, J. W., Feeney, J. and Sutcliffe,
   L. H. *High Resolution NMR Spectroscopy*,
   Pergamon, London-New York 1966.
7. Abraham, R. J. and Cavalli, L. *Mol. Phys.*
   9 (1965) 67.
8. Almenningen, A., Bastiansen, O., Haaland,
   A. and Seip, H. M. *Angew. Chem.* **77** (1965)
   877; *Int. Edition* **4** (1965) 819.
9. Bastiansen, O., Seip, H. M. and Boggs,
   J. E. In Dunitz, J. D. and Ibers, J. A.,
   Eds., *Perspectives in Struct. Chem.*, Wiley,
   New York 1971, Vol. 4.
10. Klæboe, P. and Rud Nielsen, J. *J. Chem.
    Phys.* **33** (1960) 1764.

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

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Auf Seite 225, Zeile 4 ff. muss es richtig heissen: Der Niederschlag wurde abgesaugt und verworfen. Das Filtrat wurde im Vakuum eingeengt und der Rückstand schnell mit 50 ml kaltem Wasser digeriert. Nach Trocknen und Umkristallisieren usw.

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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 [2,3] 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,[4] 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.[5]

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

$$\Delta G_{(\text{AlF}_3,\text{l})} = \Delta G_{(\text{AlF}_3,\text{s})} + \Delta H_\text{f} - T \Delta S_\text{f} \quad (1)$$

where ΔH_f and ΔS_f 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.[6] 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 AlF_3 was taken from the JANAF Thermochemical Tables.[7]

For temperatures above 1000 K these data fit the equation

$$\Delta G_{(AlF_3,s)} = -356.682 + 0.0606T + 1.66 \times 10^{-7}T^2 \text{ kcal} \quad (2)$$

with an accuracy of ± 1.5 kcal.

The enthalpy of fusion of AlF_3 has recently been measured by Holm[5] and found to be 9.5 ± 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

$$\Delta H_f = 6.5 + 0.003T \pm 1.0 \text{ kcal/mol} \quad (3)$$

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.[6] Ketelaar[8] has shown that solid aluminium fluoride has a distorted rhenium oxide structure where each aluminium atom is coordinated with 6 fluorine atoms.

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 Alcock.[6]

Compound	Entropy of fusion
HgF_2	1.9
ZrF_3	2.0
TiF_3	2.0
FeF_6	1.4
UF_6	1.9

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

$$\Delta G_{(AlF_3,l)} = -350.2 + 0.0504T + 1.66 \times 10^{-7}T^2 \text{ kcal/mol} \quad (4)$$

with an uncertainty of ± 2.5 kcal/mol.

As would be expected, this Gibbs free energy curve lies between those for solid and for gaseous aluminium fluoride[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.

1. Grjotheim, K., Holm, J. L., Krohn, C. and Thonstad, J. In Førland, T., Grjotheim, K., Motzfeldt, K. and Urnes, S., Eds., *Selected Topics in High Temperature Chemistry*, Universitetsforlaget, Oslo 1966, pp. 151–178.
2. Dewing, E. W. *Met. Trans.* **2** (1971). *In press.*
3. Mitchell, J. C. and Samis, C. S. *Trans. Met. Soc. AIME* **245** (1969) 1227.
4. Ruff, O. and Boucher, L. *Z. anorg. Chem.* **219** (1934) 376.
5. Holm, J. L. *Thermodynamic Properties of Molten Cryolite and Other Fluoride Mixtures*, Dr. thesis, Institute of Inorganic Chemistry, The Technical University of Norway, May 1971.
6. Kubaschewski, O., Evans, E. L. and Alcock, C. B. *Metallurgical Thermo-Chemistry*, 4th Ed., Pergamon, London 1967, p. 215.
7. JANAF, *Thermochemical Tables*, The Dow Chemical Company, Midland, Mich. 1966.
8. Ketelaar, J. A. *Z. Krist.* **85** (1933) 119.