

# An Experimental Search for Gaseous Reactivity Between $\text{AlF}_3$ and HF Near 1200 K\*

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Using an accurate transpiration method,  $\text{AlF}_3$  was sublimed near 1200 K into argon containing 0, 0.02, and 0.76 atm of HF, but no reaction between  $\text{AlF}_3$  and the HF was detected within the precision (about 1%). Two alternative structures of  $\text{HAlF}_4$  are postulated. An upper bound for extent of reaction corresponds to  $\Delta H_{298}^\circ > -33$  kcal ( $-138$  kJ) for  $\text{AlF}_3(\text{g}) + \text{HF}(\text{g}) = \text{HAlF}_4(\text{g})$ ; this indicates a far lower stability of  $\text{HAlF}_4(\text{g})$  than that of  $\text{LiAlF}_4(\text{g})$  or  $\text{NaAlF}_4(\text{g})$  when formed similarly.

Key words: Aluminum fluoride; aluminum hydrofluorides; equilibrium constant; hydrogen fluoride; stability limits; transpiration measurements.

## 1. Introduction

The transpiration technique affords precise measurement of not only vapor pressures but also gaseous equilibria, since the vaporization equilibria themselves are fixed. Hence, when a new gas is added to the inert carrier gas, any enhancement of vaporization may ordinarily be attributed to chemical reaction between the extra vapor and the new gas. From earlier such studies at temperatures near 1200 K we determined the vapor pressures of crystalline  $\text{AlF}_3$  [1]<sup>1</sup> and the heats of formation of the gases  $\text{AlF}_2\text{Cl}$  and  $\text{AlFCl}_2$  [2]. In the present study, in the same temperature range,  $\text{AlF}_3$  was sublimed in the presence of HF in search of measurable formation of hydrofluorides of aluminum. Mass spectrometric studies [3] have shown that under the same conditions Li or Na in place of H would lead to almost complete reaction. As high-temperature gas species, some hydroxides of metals are known to be of considerable importance, though apparently no gaseous metallic hydrofluorides have been reported. No reactivity between  $\text{AlF}_3$  and HF was detectable in the present study within experimental error, and the implications deduced regarding the stability of  $\text{HAlF}_4(\text{g})$ , presumably the most likely product, are discussed.

## 2. Experimental Procedure and Results

$\text{AlF}_3$  was allowed to sublime into flowing pure argon or argon containing a known proportion of HF, the

volume of argon and mass of sublimed  $\text{AlF}_3$  being subsequently determined. The apparatus, high-purity  $\text{AlF}_3$  and carrier-gas argon, procedure, and precautions were (when applicable) as described earlier [1, 2]. The vessels attached to the original apparatus to handle the HF were of monel, whose surface was conditioned by preliminary flushes of HF. Commercial anhydrous liquid HF, claimed to be 99.9 mol percent pure, was distilled into place, and served to create the desired partial pressure of this gas by bubbling argon at 1 atm through it at either the Dry-Ice or ice temperature. The partial pressures of HF were subsequently determined by absorption in "activated" NaF and weighing. The argon itself had been dried by commercial molecular sieves (claimed residue, 1.5 ppm by volume).

The significant data obtained are given (one run per line) in table 1. In the last column the apparent vapor pressure of  $\text{AlF}_3$  calculated for each run is compared with that of the smoothed value at the same exact temperature from the earlier work [1], in which  $\text{AlF}_3$  was sublimed into pure argon. (At these temperatures and pressures HF vapor is nearly all monomer, and it was convenient to count each mole of  $\text{Al}_2\text{F}_6$  as two moles of  $\text{AlF}_3$ .)

The deviations (last column of the table) should be nearly independent of the systematic error (possibly as high as 1%) of the earlier measurements [1] (eight runs from 1194 to 1258 K; standard deviation, 0.15%; flow rates, 1–2 ml/s). The deviations at 1200 K when HF was present are zero within their limited precision, and require no further consideration since the results at 1260 K involve a partial pressure of HF 40 times as great and hence form a much more sensi-

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<sup>1</sup>Figures in brackets indicate the literature references at the end of this paper.

TABLE 1. *Experimental data*

Approx. temp., K	Gas flow over AlF <sub>3</sub> , ml/s	P <sub>HF</sub> , atm	AlF <sub>3</sub> enhancement in vapor, % <sup>a</sup>
1200	2.6	0	+0.3
	2.7	0.02	+0.8
	2.7	0.02	-0.5
1260	2.3	0	-0.2
	6.0	0	-1.1
	6.3	0	-1.0
	7.2	0.76	-1.3
	7.4	0.76	-1.2

<sup>a</sup> The vapor pressure of AlF<sub>3</sub> varies from approximately 0.002 atm at 1200 K to 0.007 atm at 1260 K.

tive test of reaction between AlF<sub>3</sub> and HF. There is no reason to believe that HF would appreciably raise the effective activity coefficient of AlF<sub>3</sub>(g) under these conditions; hence the distinctly negative trend of the deviations at 1260 K for the higher flow rates must be considered to reflect appreciable deviations from vaporization equilibrium (lower flow rates were not feasible when so much of the carrier gas was HF). An attempt to correct empirically for the supposed lack of saturation of the AlF<sub>3</sub> vapor gives, for the proportion of the AlF<sub>3</sub>(g) reacting with HF in the last two runs, no value different from zero with certainty. However, one type of extrapolation gave us 1 percent; we arbitrarily double this,<sup>2</sup> and conclude that less than 2 percent of the AlF<sub>3</sub>(g) reacted with HF under these conditions. This corresponds to a limiting Gibbs-energy value of  $\Delta G_{1260}^{\circ} > 9$  kcal (38 kJ) for the reaction



In contrast, appropriate thermal functions [3] indicate that the same reaction except with Li or Na replacing H proceeds to more than 99,999 percent completion under the same initial conditions.

### 3. Discussion

An estimate of the molecular constants of HALF<sub>4</sub> allows calculation of a free energy function and a corresponding bound on the heat of reaction (1). Two alternative structures were assumed, as follows. *Structure I*: Tetrahedral AlF<sub>4</sub> (Al-F, 1.69 Å), with a linear H-F-Al group (H-F, 1.0 Å). (Similar structures had been assumed for LiAlF<sub>4</sub> and NaAlF<sub>4</sub> [3].) Vibrational fundamentals, the same as those of AlF<sub>3</sub> and HF [3], plus (in cm<sup>-1</sup> and with degeneracies in parentheses) 500(1), 300(2), and 800(2). *Structure II*: Planar. Unaltered AlF<sub>3</sub>

<sup>2</sup>This factor of 2 makes only minor differences in the rough limiting values for HALF<sub>4</sub> deduced later in this paper.

[3] attached to HF (H-F, 1.0 Å) through a hydrogen bond 1.5 Å long. Vibrational fundamentals, same as for Structure I except with 500(1) replaced by 200(1). These two structures give for  $-(G_{1260}^{\circ} - H_{298}^{\circ})/1260$  respectively 90.4 and 94.0 cal mol<sup>-1</sup>K<sup>-1</sup> (378 and 393 J mol<sup>-1</sup>K<sup>-1</sup>), and for reaction (1) (with  $\Delta G_{1260}^{\circ} > 9$  kcal) values of  $\Delta H_{298}^{\circ} > -33$  and  $> -29$  kcal ( $> -138$  and  $> -121$  kJ). When H in reaction (1) is replaced by Li or Na, the respective values of  $\Delta H_{298}^{\circ}$  are -73 and -88 kcal (-305 and -368 kJ) [3].

One may seek the principal reason why  $\Delta H$  for reaction (1) is so much greater than for the Li or Na analog. Considering Structure I for HALF<sub>4</sub>, perhaps the large difference can be traced principally to the far greater energy of decomposition to ions for HF than for LiF or NaF. On the other hand, Structure II would make reaction (1) simply the formation of a hydrogen bond. The hydrogen-bond energy in HF<sub>2</sub>(g) has been evaluated as lying between 37 and 63 kcal mol<sup>-1</sup> (155 and 264 kJ mol<sup>-1</sup>) by several semi-experimental and theoretical methods, but in other species it is very generally much lower, typically being approximately 6 kcal mol<sup>-1</sup> (25 kJ mol<sup>-1</sup>) in the gaseous polymers of HF [4].

The present study has shown that gaseous reaction products between AlF<sub>3</sub> and HF are not important species near 1200 K (except possibly under high pressures of HF). Assuming their formation to be somewhat exothermic, they would be even less important at higher temperatures and the same pressures, and also at lower temperatures because of the much smaller vapor pressures of AlF<sub>3</sub>. The transpiration technique, despite its high precision for overall results, is less promising than spectroscopic techniques for detecting and measuring such distinctly minor species.

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### 4. References

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