Strong Hydrogen Bonds. II. The Hydrogen Difluoride Ion

Sir:

There has been much interest in the bond energy of the hydrogen difluoride ion. Current textbooks list values ranging from ~27 to 58 kcal./mole. The first value is just slightly greater than the experimental heat of reaction of cesium fluoride with hydrogen fluoride, while the latter is due to a value corrected for lattice effects by Waddington.[1] We have now determined an enthalpy of −37 kcal./mole for the reaction

$$(CH_3)_4NF(s) + HF(g) \longrightarrow (CH_3)_4NHF_2(s)$$

This is the largest experimentally determined hydrogen bond energy reported to date. Further, lattice expansion should be slight for this reaction.[2] Thus the value of −37 kcal./mole should be within 1 to 2 kcal. of the heat of the hydrogen bond in HF_2^-.

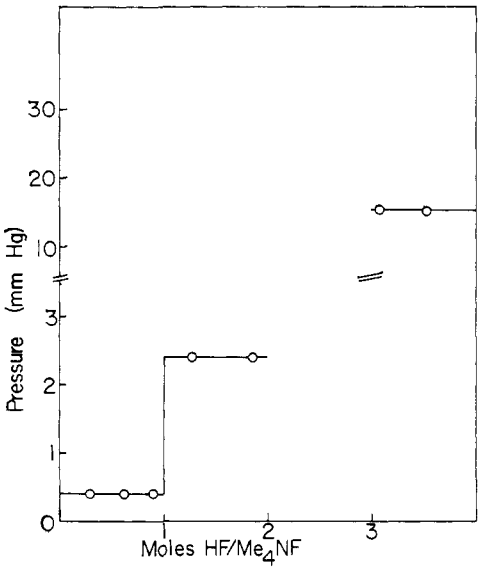

Fig. 1.—Pressure–composition isotherm for the system hydrogen fluoride–tetramethylammonium fluoride at 90.5°.

Tetramethylammonium fluoride was prepared under anhydrous conditions by the method of Tunder and Siegel[3] with slight modification. Anhydrous hydrogen fluoride was prepared by the thermal decomposition of potassium hydrogen difluoride which had been dried according to the method of Kilpatrick.[4] The interaction of hydrogen fluoride with tetramethylammonium fluoride was carried out in a vacuum line constructed of type K copper tubing with all joints silver alloy brazed. The sample tube and valves were constructed of monel. Pressure was measured by means of Wallace and Tiernan Model 145 gauges constructed of monel with actuating bellows of Ni-Span-C. The entire copper apparatus, except the gauges, was thermostated at the desired temperatures. The temperatures used were high enough so that the hydrogen fluoride was present as a monomer. The pressure–composition isotherm for this system is shown in Fig. 1, and the variation of pressure with temperature, for 90.5 to 122.0°, is shown in Fig. 2.

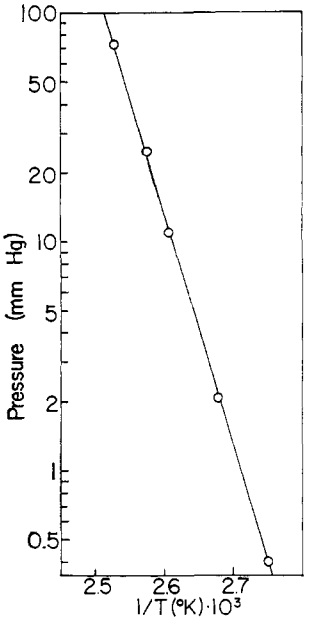

Fig. 2.—Variation of decomposition pressure of tetramethylammonium hydrogen difluoride with temperature.

The region of composition between 2 and 3 moles of HF to $(CH_3)_4NF$ was not studied owing to a failure of one of the gauges.

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The Occurrence of the Re_3Br_9 Group in Compounds Derived from Rhenium(III) Bromide

Sir:

It has been shown recently[1] that rhenium(III) chloride is built up of Re_3Cl_9 groups which contain a triangular Re_3 metal atom cluster. This result had been anticipated from, and, in turn, provides an explanation for, the fact that numerous compounds prepared directly from rhenium(III) chloride contain the Re_3Cl_9 group.[1-5]

We now wish to report evidence that rhenium(III) bromide similarly gives rise to numerous compounds containing the Re_3Br_9 group which also contains the triangular Re_3 metal atom cluster. Several new compounds,[6] the spectra of their solutions, and spectra of solutions of rhenium(III) bromide will be described in support of this statement.

The presence of the Re_3Br_9 group has been conclusively demonstrated in $M_2Re_4Br_{15}$, where M represents quinolinium, pyridinium, or tetraethylammonium

(1) T. C. Waddington, *J. Chem. Soc.*, 1708 (1958).

(2) See Fig. 7 of D. H. McDaniel and R. E. Vallee, *Inorg. Chem.*, **2**, 996 (1963), for the effect of cation size on the heat of reaction of hydrogen halides with tetraalkylammonium halides.

(3) R. Tunder and B. Siegel, *J. Inorg. Nucl. Chem.*, **25**, 1097 (1963).

(4) M. E. Runner, G. Balog, and M. Kilpatrick, *J. Am. Chem. Soc.*, **78**, 5183 (1956).

(1) F. A. Cotton and J. T. Mague, *Proc. Chem. Soc.*, 233 (1964); *Inorg. Chem.*, **3**, 1402 (1964).

(2) F. A. Cotton, *et al.*, *Science*, 1305 (1964).

(3) F. A. Cotton and J. T. Mague, *Inorg. Chem.*, **3**, 1094 (1964).

(4) J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *ibid.*, **2**, 1166 (1963); B. H. Robinson, J. E. Fergusson, and B. R. Penfold, *Proc. Chem. Soc.*, 116 (1963).

(5) J. E. Fergusson, B. R. Penfold, and W. T. Robinson, *Nature*, **201**, 181 (1964).

(6) Elemental analyses have been carried out on all new compounds mentioned and agree satisfactorily with the proposed formulas.