THE VAPOR PRESSURES OF HYDROGEN AND DEUTERIUM FLUORIDES

Sir:

The vapor pressures of several deuterium compounds have been measured before in this Laboratory and elsewhere.[1] Since the hydrogen bond has been regarded by Lewis as largely responsible for the differences in vapor pressures between the corresponding light and heavy compounds, it occurred to us that a comparison of the two hydrogen fluorides, in which this bond is particularly strong, would be interesting.

Two runs each with the light and heavy compounds were made as follows: hydrogen made from water and zinc dust at about 400° was pumped through a liquid air drier into a silver vessel containing silver fluoride made by the action of fluorine gas on its inner walls. This vessel was then heated to 110° until the pressure became constant. The hydrogen fluoride thus produced was frozen with liquid air, the residual hydrogen pumped off and distilled into a small copper cell, of total volume 6.3 cc., embedded in a large copper block. The block was surrounded by a cold alcohol-bath in a large Dewar vessel. The temperature rose about 1° per hour at the lower temperatures and 0.1° per hour at the higher. This system was closed off and the vapor pressure measured by means of a diaphragm gage,[2] and temperature by means of a three junction copper–constantan thermocouple.

The H^1F was made from 0.15 and 0.13 cc. of light water in the respective runs. The vapor pressure of H^1F between the pressures of 5 and 76 cm. of mercury is given by the equation

$$\log_{10} P_1 \text{ (cm.)} = 6.3739 - 1316.79/T$$

The average deviation of the points is 0.08°. All pressure readings were reduced to 0°. Our results differ by only 0.13° from those of Simons [THIS JOURNAL, **46**, 2179 (1924)] which lie within the accuracy of his measurements.

The two runs with H^2F were begun with 0.12 and 0.18 cc. of 99.5% H^2_2O kindly furnished us by Professor G. N. Lewis. The vapor pressures of the second sample came out slightly higher than the first and we give them the principal weight since the first sample would tend to clean H^1 out of the apparatus. The vapor pressure of H^2F is given by the equation

$$\log P_2 \text{ (cm.)} = 6.2026 - 1261.16/T$$

The average deviation is 0.07°.

The table gives vapor pressures of both forms at rounded temperatures.

T, °K.	H^1F, cm.	H^2F, cm.	P_2/P_1
240	7.71	8.87	1.150
250	12.78	14.39	1.126
260	20.38	22.49	1.104
270	31.40	34.01	1.083
280	46.89	49.95	1.065
290	68.11	71.42	1.049
Boiling points	293.07°	291.81°K.	Diff. = 1.26°

For comparison with other compounds, Fig. 1 is included.

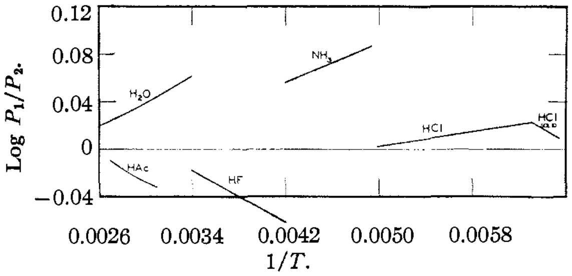

Fig. 1.

The deviation of the HF is in the same direction as with acetic acid but larger in magnitude. The most striking connection between acetic and hydrofluoric acids is that both are highly associated in the gas phase. It is evident that HF might lend itself to economic distillation at low pressure for the separation of the hydrogen isotopes. The heavy hydrogen would be removed, of course, at the top of the still, which would be very advantageous.

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THE HYDROLYTIC FISSION OF AMINES

Sir:

In a recent paper, Kharasch and Howard [THIS JOURNAL, **56**, 1370 (1934)] suggest that the elimination of groups by hydrolytic fission from amines of suitable constitution is determined by the electronegative nature of the groups attached to the nitrogen.

It seems doubtful, however, whether this hypothesis can be extended to the other known examples of this type of reaction. Thus it has

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(1) H^2_2O, Lewis and Macdonald, THIS JOURNAL, **55**, 3057 (1933); H^2Cl, Lewis, Macdonald and Schutz, *ibid.*, **56**, 494 (1934); CH_3-$COOH^2$, Lewis and Schutz, *ibid.*, **56**, 493 (1934); H^2CN, Lewis and Schutz, *ibid.*, **56**, 1002 (1934); *cf.* also NH^2_3, Taylor and Jungers, *ibid.*, **55**, 5057 (1933).

(2) Claussen, *ibid.*, **56**, 614 (1934).