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.

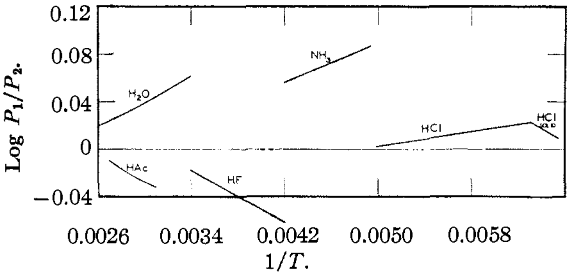

Fig. 1.

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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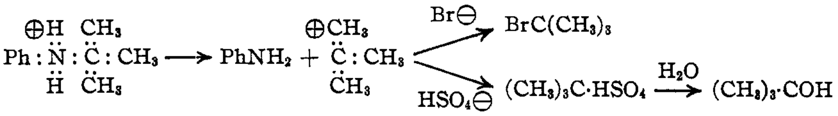
[1] H^2_2O, Lewis and Macdonald, THIS JOURNAL, **55**, 3057 (1933); H^2Cl, Lewis, Macdonald and Schutz, *ibid.*, **56**, 494 (1934); CH_3COOH^2, Lewis and Schutz, *ibid.*, **56**, 493 (1934); H^2CN, Lewis and Schutz, *ibid.*, **56**, 1002 (1934); *cf.* also NH^2_3, Taylor and Jungers, *ibid.*, **55**, 5057 (1933).

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

been found that *tert*-butylaniline and other alkylanilines containing *tertiary* alkyl groupings yield aniline on heating with aqueous mineral acids [Hickinbottom, *J. Chem. Soc.*, 1070 (1933); *Nature*, **131**, 762 (1933)]. Under precisely similar conditions, alkylanilines with *normal* alkyl groupings are unchanged. Further, diphenylamine or triphenylamine appears to be stable to hot mineral acid. Yet, according to Kharasch and Flenner [THIS JOURNAL, **54**, 681 (1932)] a *tertiary* alkyl group is less electronegative than the corresponding *normal* alkyl group and each is less electronegative than phenyl.

A more satisfactory basis for arriving at an explanation of such reactions appears to be the theory of chemical reactions developed by Lapworth and Robinson [Robinson, "Outline of an Electrochemical Theory of the Course of Organic Reactions," London, 1932; compare W. A. Noyes, THIS JOURNAL, **55**, 656 (1933)].

In *tert*-butylaniline, the induced effect of three methyl groups attached to a carbon atom is sufficiently intense to cause the transfer of an electron from the *tert*-butyl group to the nitrogen, provided that conditions are suitable and reagents are present to take advantage of this tendency. The hydrolysis of *tert*-butylaniline in acid solution is represented by the following scheme:



The fate of the *tert*-butyl "ion" obviously depends on the experimental conditions. In concentrated hydriodic acid or hydrobromic acid, the corresponding *tert*-butyl halide is formed, while in more dilute solution increasing amounts of the carbinol result. This has been confirmed experimentally.

The hydrolysis of triphenylmethylaniline [Elbs, *Ber.*, **17**, 702 (1884); Hemilian, *ibid.*, p. 746; Gomberg, *ibid.*, **35**, 1829 (1902)] is represented similarly.

It is evident that, if the induced effect is enhanced by suitable substituents, the tendency to hydrolytic fission is also increased. Recorded examples of this are the elimination of nitrotoluidines from di- and tetranitro-di-*p*-tolylaminobutanes under the influence of hot diluted mineral acid [Morgan and Hickinbottom, *J. Soc. Chem. Ind.*, **43**, 307T (1924); compare Morgan, Hickinbottom and Barker, *Proc. Roy. Soc.*, **A110**, 518 (1926)]; the ready formation of aryl sulfonanilides from the aryl sulfonyl derivatives of *tert*-butylaniline by heating with diluted sulfuric acid.

The same theoretical considerations which have been used to explain the hydrolytic fission of *tert*-butylaniline and triphenylmethylaniline can be applied to account for the sensitivity of the *tert*-butyl halides and triphenylmethyl halides to hydrolysis.

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THE EXCHANGE REACTION BETWEEN DEUTERIUM AND WATER VAPOR ON SURFACES

Sir:

We have observed a rapid conversion of deuterium to hydrogen on catalytic hydrogenating surfaces such as chromium oxide gel and zinc oxide which conversion may be ascribed to the deuterium-water exchange reaction. The existence of this exchange is important, since it may, under favorable circumstances, lead to the practically complete replacement of deuterium by the light isotope in a reaction mixture. In ordinary circumstances it can readily lead to the introduction of hydrogen into what may have been assumed to be pure deuterium.

We have analyzed by the thermal conductivity method of Farkas and Farkas [*Proc. Roy. Soc.* (London), **144A**, 467 (1934)] the gases desorbed by Dr. H. W. Kohlschuetter from a 15.5-g. sample of chromium oxide gel on which the velocity of activated adsorption of pure deuterium gas at 184° was being measured. In successive experiments, during each of which 25 cc. of pure deuterium was adsorbed, the desorbed gases analyzed, respectively, 98.5, 97.5, 92.5 and 87% of the *light isotope*. The adsorbent was then allowed to take up approximately 550 cc. of deuterium at about 350°, in units of 100 cc., the adsorption of each unit being followed by desorption at the same temperature. The gas desorbed from the surface after a further 25 cc. of deuterium had been adsorbed at 184°, in the manner of the first experiments recorded, now analyzed 41% light isotope, pointing to an exhaustion of the hydrogen source on the surface. The exchange was now repeated at 184° in the reverse direction. Hydro-