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The Hammett Acidity Function H_0 for Hydrofluoric Acid Solutions[1]

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The Hammett acidity function H_0 value has been determined for hydrogen fluoride in the concentration range from anhydrous material down to about 40% hydrogen fluoride. The dryest hydrogen fluoride prepared had an H_0 value of -10.2. In the course of this investigation, improved spectrophotometric cells were developed for handling hydrofluoric acid solutions and the spectrum of anhydrous hydrogen fluoride in the near infrared was determined. The effect of sodium fluoride and water on the near infrared hydrogen fluoride spectrum was investigated and an analytical method for water in hydrogen fluoride was developed based on measurements of the water absorption at 1.95 μ.

Liquid anhydrous hydrogen fluoride has long been recognized as a very acidic substance despite the fact that in dilute aqueous solution it behaves as a rather weak acid.[2,3] A wide variety of compounds are readily soluble in liquid hydrogen fluoride. These solutions usually exhibit substantial ionic conductivity that can be attributed to proton transfer from the acid to the solute.

Hammett has discussed the use of organic indicators for the determination of relative acidity and suggested an acidity scale based on the relative concentration of protonated and non-protonated species in the medium under investigation.[4]

Paul and Long[5] recently have reviewed the determination and use of the H_0 function. In particular, the acidity of any solution on the H_0 scale is determined by the fraction of the neutral indicator which is converted from an uncharged molecule to a protonated species. Hammett also discussed the H_- and H_+ scales in which the original indicator was an anion or cation rather than a neutral molecule.

For practical use of the H_0 acidity functions, it is defined by the equation

$$H_0 = pK_a{}^{\mathrm{I}} + \log (C_{\mathrm{I}}/C_{\mathrm{IH^+}})$$

$$pK_a{}^{\mathrm{I}} = -\log \frac{C_{\mathrm{H^+}}C_{\mathrm{I}}}{C_{\mathrm{IH^+}}} - \log \frac{f_{\mathrm{H^+}}f_{\mathrm{I}}}{f_{\mathrm{IH^+}}}$$

for the indicator, I, is determined by a series of intercomparisons with indicators of decreasing $pK_a{}^{\mathrm{I}}$. The activity coefficient term for a constant charge type is supposed to be independent of the medium or indicator, and H_0 approaches pH in dilute aqueous solution.

Paul and Long have reviewed previous intercomparisons and extrapolations and suggest a best value for each indicator which has been studied. As they point out, these values are not entirely self-consistent within the expected limit of error. Different indicators will give different values for the same solution. Other workers[6] have questioned the general applicability of the H_0 concept, or sought more satisfying acidity functions.[7] In spite of this, the H_0 function is very useful in correlating and predicting for different media properties such as solubility or catalytic effects which depend on acidity. In the highly acid, high dielectric solvents, such as those considered here, it is probably fair to assume that a medium which shows a more negative H_0 value for a specific indicator is the more acidic medium.

Hammett and his students determined the H_0 function for several aqueous acid solutions, including 0–100% sulfuric acid.[8,9] Lewis and Bigeleisen[10] and more recently Brand[11] extended these measurements into the fuming sulfuric acid range. The development of a variety of cells with polychlorotrifluoroethylene windows,[12] now make it possible to study optical absorption spectra in hydrogen fluoride solutions with relative ease, and a determination of the Hammett acidity function for hydrofluoric acid solutions becomes practical. R. P. Bell has previously investigated the dilute aqueous range up to about 40% hydrogen fluoride[13] and it has now been possible to complete the study of the water–hydrogen fluoride system using the same indicators used by Hammett for his sulfuric acid study.

Experimental

Materials.—The indicators used in this work were Aldrich Chemical Company products sold for use as Hammett indicators and no further purification was attempted.

Two separate methods of purification were used for the hydrogen fluoride. For most of the earlier runs commercial hydrogen fluoride was absorbed on sodium fluoride, and the resulting $NaHF_2$ heated *in vacuo* at 150° to remove volatile impurities. Hydrogen fluoride was then regenerated by heating at 300°. The material was stored over cobaltic fluoride in a nickel vessel. Hydrogen fluoride was distilled from this vessel as needed directly into a conductivity cell or an optical absorption cell. Hydrogen fluoride purified in this way showed conductivities in the range 4 to 6 $\times$ 10^{-4} ohm^{-1} cm.$^{-1}$ at 0° indicating a water content of 0.01% or less. More recently a better quality acid has been obtained. As suggested by Runner, Balog and Kilpatrick, the hydrogen fluoride was purified by fractional distillation in an efficient column.[14] The product was collected and handled entirely in polychlorotrifluoroethylene and gold lined fittings thus avoiding contact with base metal (nickel). Under these conditions, batches of acid have been obtained with conductivities below 10^{-5} ohm^{-1} cm.$^{-1}$. Measurably higher acidities (more negative H_0 values) were found for

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] J. H. Simons, "Fluorine Chemistry," Chap. 6, Academic Press, New York, N. Y., 1950, p. 225.

[3] L. Pauling, *J. Chem. Ed.*, **33**, 16 (1956).

[4] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940.

[5] M. A. Paul and F. A. Long, *Chem. Revs.*, in press.

[6] R. G. Bates and G. Schwarzenbach, *Helv. Chim. Acta*, **38**, 699 (1955).

[7] B. Gutbezahl and E. Grunwald, THIS JOURNAL, **75**, 565 (1953).

[8] L .P. Hammett and A. J. Deyrup, *ibid.*, **54**, 2721 (1932).

[9] L. P. Hammett and M. A. Paul, *ibid.*, **56**, 827 (1934).

[10] G. N. Lewis and J. Bigeleisen, *ibid.*, **65**, 1144–50 (1943).

[11] J. C. D. Brand, *J. Chem. Soc.*, 997 (1950).

[12] J. J. Katz and H. H. Hyman, *Rev. Sci. Instr.*, **24**, 1066 (1953).

[13] R. P. Bell, K. N. Bascombe and I. C. McCowbrey, *J. Chem. Soc.*, 1286 (1956).

[14] M. E. Runner, G. Balog and M. Kilpatrick, THIS JOURNAL, **78**, 5183 (1956).

hydrogen fluoride purified by distillation than for the earlier material.

Sodium fluoride was reagent grade material and was dried before use.

Optical Equipment.—The optical cells employed polychlorotrifluoroethylene bodies and windows. The cells were made vacuum and pressure tight with external metal fittings but no metal was in contact with the solution. At the beginning of the work the cells were fitted with small metal valves of the bellows type; however, a polythene tubing and pinch clamp arrangement was found more convenient and made it possible completely to eliminate base metal from contact with the solution.

The absorption cells are connected to a vacuum line through the polythene tubing. After evacuating and filling the cell, the tubing is pinched shut, and the cell removed from the line.

For highly absorbing solutions, variable spacer cells of the type described by Quarterman, Hyman and Katz[15] were employed. These could be closed down to useful thicknesses of 50 μ with sapphire windows and 10 μ with selected polychlorotrifluoroethylene windows. These cells have nickel bodies, some of which have been gold plated, and because of the difference of expansion between the window and body cannot be subjected to severe temperature changes without leaking. This problem introduces minor changes in filling procedure. For example, hydrogen fluoride must be condensed in a separate vessel and transferred to the cell as a liquid, rather than condensed directly in the cell. However, if severe temperature changes are avoided these cells may be evacuated, filled and emptied, and the optical path changed repeatedly without incident.

A Beckman DK-1 automatic spectrophotometer was equipped with a secondary container to prevent damage in case of leaky cells. With the exception of this precaution, the instrument was used in a conventional way. The instrument was in a constant temperature room and all measurements were made at 25 ± 2°.

The electrical conductivity equipment has been described elsewhere.[15]

Solution Preparation.—Solutions were prepared in a variety of ways, usually using vacuum line technique. In most cases the indicator was made up to a known concentration in benzene and a measured volume pipetted directly into the cell. The solution was frozen, cooled to below 0° and the cell evacuated. The benzene sublimed off leaving a known amount of indicator much smaller than could be conveniently weighed directly. The hydrogen fluoride could then be distilled in, and water or other diluent added. Additions were made to a partially filled cell without significant loss or exposure of the contents to the atmosphere. This was accomplished by pinching the tubing shut, and making the addition to the length of tubing above the closure. After capping the cell, the pinch clamp was opened and the solution mixed. In other cases, the indicator was dissolved in dilute hydrofluoric acid whose concentration was determined by titration with standard base. The indicator concentration in this stock solution was usually determined optically. A known weight of this acid was added to the cell and anhydrous hydrogen fluoride distilled in to yield the desired concentration.

Hydrofluoric acid concentrations were determined by titration below 50% and by direct weighing in the cell in the 50 to 98% region. Above 98% the most convenient determination of water content was found to be that based on optical absorbancy at 1.95 μ described below.

The solutions of indicator as prepared were all stable for at least 24 hours. In preliminary experiments where optical cells with nickel bodies were employed, the nitro aromatic indicators were decolorized slowly on standing, presumably by reduction of the nitro group. Indicators in the acid form usually could be destroyed by heating the solution, yielding in most cases deeply colored compounds, that did not behave as indicators at least in similar acidity ranges. The composition or nature of these colored materials was not investigated further. Solutions of the basic form of the aniline type indicators used appear to be stable indefinitely when stored in all plastic containers.

The Spectrum of Anhydrous Hydrogen Fluoride.

—Anhydrous hydrogen fluoride is a water-white liquid, essentially completely transparent in the visible region of the spectrum. While the infrared spectrum in the region above 2 μ appears to have been studied adequately by Maybury, Gordon and Katz,[16] their data below 2 μ are not adequate and the earlier values reported by Safari[17] for this region appear to be entirely incorrect. A portion of Safari's curve is drawn with a dotted line and it is not clear that any significant measurements were made by him below 2 μ. There seems to be no doubt about the existence of the 1.45 μ peak which might readily be expected as the overtone of the 2.9 μ polymer peak. The 0.98 μ overtone is shown by Safari, but slightly displaced and with much too high an extinction coefficient. While we cannot account for the difference between our spectrum and that reported by Safari, the curve given in Fig. 1 has been obtained repeatedly on a number of different samples of purified hydrogen fluoride. In the region above 2 μ, Fig. 1 agrees perfectly with data reported by Maybury, Gordon and Katz for different samples, with different cells using silver fluoride rather than polychlorotrifluoroethylene windows, using a Perkin–Elmer spectrophotometer rather than a Beckman DK.

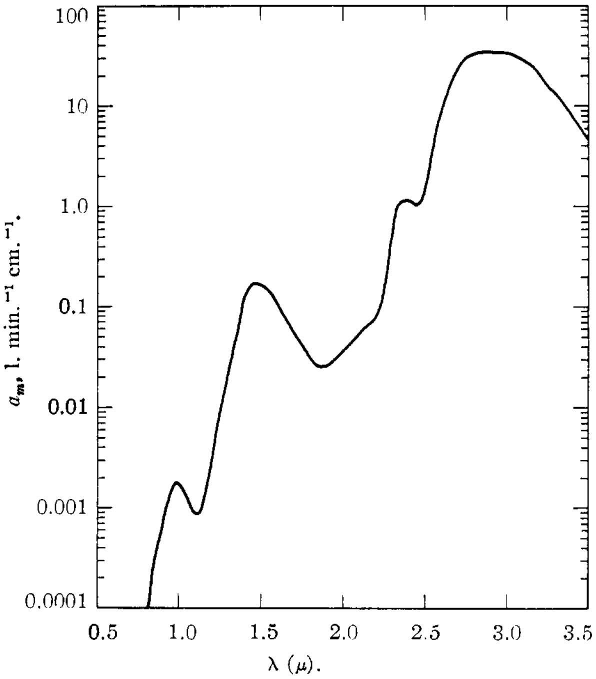

Fig. 1.—Near infrared absorption spectrum of anhydrous liquid hydrogen fluoride.

The Effect of Water and Sodium Fluoride on the Hydrogen Fluoride Spectrum.—These observations are summarized in Fig. 2. Since water has a significant absorption peak near 1.9 μ where hydrogen fluoride is relatively transparent, it appeared reasonable to develop an analytical method for water content based on this difference in behavior. This proved to be possible, since water as a solute

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(15) I. A. Quarterman, H. H. Hyman and J. J. Katz, to be published.

(16) R. H. Maybury, S. Gordon and J. J. Katz, *J. Chem. Phys.*, **23**, 1277 (1955).

(17) E. Safari, *Ann. Physik*, **9**, 203 (1954).

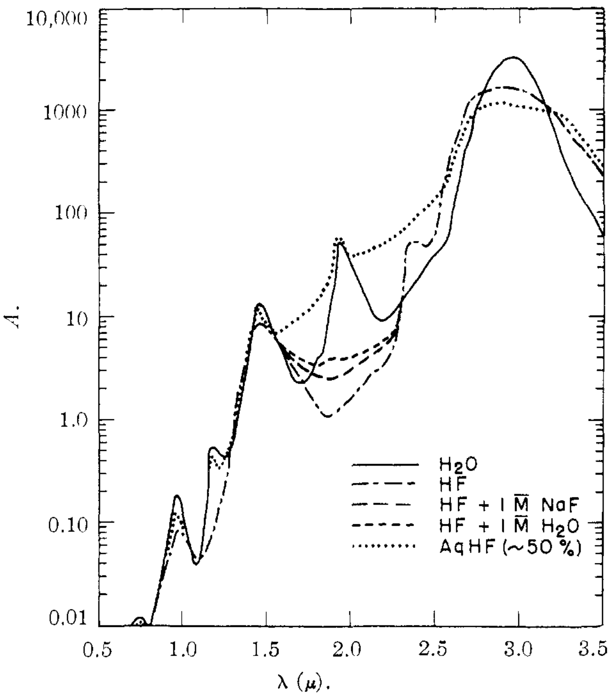

Fig. 2.—Near infrared spectrum of some fluoride solutions. Absorbancy of 1 cm. of liquid.

was found to obey the Beer–Lambert law with a molar absorbancy of 2.7 at 1.95 μ. At this wave length the molar absorbancy of water was constant within experimental error, from about 50% water down to anhydrous acid. Over the concentration range 0.1–2M the experimental error in measuring increased optical absorption due to added water is probably less than 10%. For both higher and lower water concentrations, with the equipment available, the method is less precise. The measured extinction is more than twice that found for the 1.92 μ peak in pure water and at least part of the extra absorption appears to be due to the solvated F^- ion. This could be the 2 μ overtone of the 4 μ peak found by Maybury, *et al.* Note in Fig. 2 the effect of NaF added to anhydrous hydrogen fluoride. When an aqueous hydrofluoric acid solution (~50%) was saturated with NaF, no difference in the near infrared spectrum could be detected. The study of Jones and Penneman[18] on similar solutions did indicate spectral changes, but the measurements were at lower frequencies, the particular absorbing species were not identified, and the data are not necessarily in disagreement.

The Acidity Function.—All solutions were scanned in the visible region and the percentage of acid or basic form calculated in the usual way from the optical density near the peak of the colored species.

The measured H_0 values are summarized in Tables IA and B. In Fig. 3 these values are combined with those of Bell to give the H_0 values for 0–100% hydrofluoric acid and compared with the sulfuric acid values. All of the hydrogen fluoride points plotted were selected from indicator measurements in the 10% acid to 10% basic range (±1 H_0 unit).

TABLE IA

THE H_0 FUNCTION FOR HYDROFLUORIC ACID SOLUTIONS

Concn. wt. %	HF in H_2O mole %	H_0	Concn. wt. %	HF in H_2O mole %	H_0
39.6	37.2	-2.07^a	83.5	82.0	-7.65^d
42.6	40.1	-2.53^a	87.8	86.6	-7.94^d
45.4	43.8	-2.94^a	90.2	89.2	-8.17^d
48.7	46.1	-3.55^a	92.3	91.5	-8.27^d
55.3	52.7	-5.04^b	93.9	93.3	-8.39^d
61.4	58.8	-6.30^c	97.0	96.7	-8.54^d
71.0	68.8	-6.79^c	100	100	-10.0^d
80.9	79.2	-7.52^d			

[a] Indicator used: *p*-nitrodiphenylamine, $pK = -2.50$. [b] Indicator used: 2,6-dinitro-4-methylaniline, $pK = -4.44$. [c] Indicator used: 6-bromo-2,4-dinitroaniline, $pK = -6.71$. [d] Indicator used: anthraquinone, $pK = -8.27$.

TABLE IB

THE H_0 FUNCTION FOR HYDROFLUORIC ACID SOLUTIONS.

Concn. H_2O in HF, mole/l.[a]	Concn. wt. %	HF in H_2O mole %	H_0[b]
<0.001			−10.2
< .01	100.0	100.0	−9.96
.12	99.78	99.76	−9.59
.38	99.29	99.22	−9.47
.50	99.07	98.97	−9.31
.63	98.83	98.70	−9.34
.83	98.48	98.31	−9.12
.87	98.40	98.23	−9.09
.89	98.38	98.20	−9.11
1.03	98.13	97.93	−8.86

[a] Concentration determined by optical absorption at 1.95 μ. [b] The indicator used in this set of measurements was 2,4,6-trinitroaniline, $pK = -9.41$.

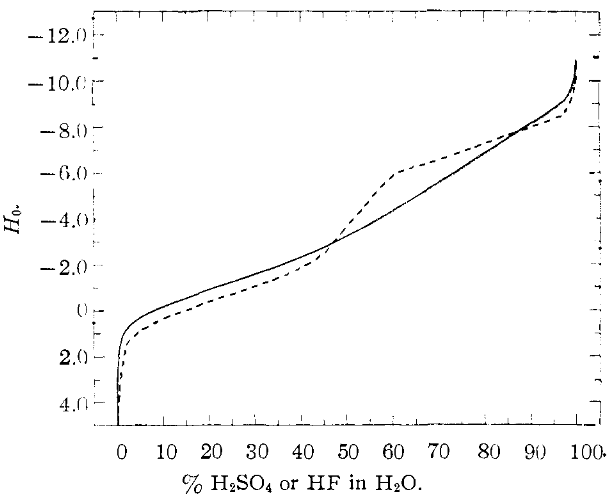

Fig. 3.—The H_0 function for aqueous sulfuric and hydrofluoric acids: ———, H_2SO_4; --------, HF.

On the whole hydrogen fluoride is a weaker acid than sulfuric. The dryest hydrogen fluoride obtainable by us had an H_0 value of −10.2 while 100% sulfuric acid has an H_0 value of −11.0. Due to the lower molecular weight of hydrogen fluoride, however, a 60–80% hydrogen fluoride solution in water is more acid than a similar weight

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(18) L. H. Jones and R. A. Penneman, *J. Chem. Phys.*, **22**, 781 (1954).

% H_2SO_4 solution, although on an equivalent concentration basis, sulfuric acid is always stronger.

Neither gram nor moles of hydrogen fluoride per unit volume are satisfactory units for plotting hydrogen fluoride concentration in aqueous solutions. The density increases rapidly as water is added to hydrogen fluoride to a maximum near 75% hydrogen fluoride.[19] This is reflected in a maximum in the molar hydrogen fluoride concentration well below 100%.

A plot of acidity *vs.* weight or mole % hydrogen fluoride rises steadily and shows no such maximum. However it is not a smooth continuous curve from pure water to pure HF. In fact there appear to be several separate regions in this plot. In dilute aqueous solutions, the actual acidic species present is H_3O^+, according to the equation

$$HF + H_2O \rightleftarrows H_3O^+ + F^-$$

Even for infinitely strong acids, the acidity of a solution in which the concentration of H_2O molecules exceeds that of the acid molecule cannot exceed a value fixed by the inherent acidity of H_3O^+. In this region, hydrofluoric acid solutions are significantly less acid than equal concentrations of any of the group of strong acids studied by Hammett but the acidity rises more rapidly with concentration. Of these strong acids, only sulfuric acid has been studied by anyone in the range where there are fewer water molecules than acid molecules. In hydrogen fluoride, as the 1-1 point is approached the acidity rises sharply, then increases steadily until a region close to 100% acid, where it again rises sharply.

Bell[13] has discussed the rise in acid strength below 50 mole % in terms of increasing concentration of HF_2^-, $H_2F_3^-$, and even longer chains as the HF concentration is increased. Several authors have commented on the occurrence of such polymeric ions.[18,20] Presumably as the 1-1 point is passed, the much more acidic species HF_2^+ appears, and acidity then increases regularly with concentration. At the high hydrogen fluoride end of the scale a further sharp rise in acidity is encountered which may also be correlated with the occurrence of polymer chains stabilized by ionization. In this case, however, the increase in chain length serves to decrease the acidity.

As water is added to hydrogen fluoride, the acidity of the solution is reduced by substituting H_3O^+ for H_2F^+. The equilibria involved may be represented as

$$H_2O + nHF \rightleftarrows H_3O^+ + F^-(HF)_{(n-1)}$$
$$HF + nHF \rightleftarrows H_2F^+ + F^-(HF)_{(n-1)}$$

The relative effect of H_2O is enhanced beyond its molar concentration as n is increased. The observed anomalous density behavior of hydrofluoric acid solutions mentioned above may well be correlated with this hypothesis. We hope to discuss the subject more fully elsewhere.

The effect of water on acidity is probably not specific since sodium fluoride is a slightly stronger base as is shown in Table II.

TABLE II

H_0 VALUE FOR HF–NaF SOLUTION

Solution	H_0
100% HF	−10.13
0.447% NaF = 0.103 $\bar{M}$	−9.62
4.32% NaF = 1.0 $\bar{M}$	−8.4

Qualitatively other reagents such as ethyl alcohol similarly yield the basic form of trinitroaniline when added in small amounts to a solution of this indicator in anhydrous hydrogen fluoride.

The addition of liquid SO_2 has little effect. Anhydrous hydrogen fluoride (H_0 = −10.25) was diluted to 82.3% hydrogen fluoride, 17.7% SO_2 and the H_0 value found was −9.98. A second sample (H_0 = −10.21) was similarly diluted to 81.7% hydrogen fluoride, 18.3% SO_2 and the H_0 value found was −9.93.

The addition of SO_3 to 100% sulfuric acid leads to a regular increase in acidity. There is no simple analog of this behavior in hydrogen fluoride, but the addition of fluoride ion acceptors such as boron trifluoride or antimony pentafluoride might well increase the acidity of hydrogen fluoride.[21–23]

An investigation of the acidity of such solutions is planned.

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