ed.[36] In addition, we have redetermined the chemical shifts for liquid ClF_3 since there is some confusion in the literature[17,37,38] concerning its exact values. Most of the data of Table II can be qualitatively rationalized by assuming increasing deshielding of the fluorine ligands with increasing oxidation state of the chlorine central atom (see trends for ClF-ClF_3-ClF_5, ClF_2^+-ClF_4^+-ClF_6^+, or ClF_2O^+-$ClF_2O_2^+$). The effect of oxygen substitution is more difficult to understand. For example, the fluorine in $FClO_2$ is more deshielded than that in $FClO_3$. Also, the high shielding of F in ClF and the increased shielding in the cations when compared to their parent molecules are unexpected. Clearly, our present understanding of the nature of ^{19}F chemical shifts is insufficient to rationalize all these observations.

Registry No. HF, 7664-39-3; AsF_5, 7784-36-3; $ClF_2^+AsF_6^-$, 19154-21-3; $ClF_2^+SbF_6^-$, 30669-19-3; $ClF_2^+BF_4^-$, 36544-26-0; ClF_5, 13637-63-3; SbF_5, 7783-70-2; $ClF_6^+PtF_6^-$, 36609-91-3; $ClF_2O^+AsF_6^-$, 36544-27-1; $ClF_2O^+PtF_6^-$, 36544-28-2; $ClF_2O_2^+PtF_6^-$, 36609-92-4; $NF_2O^+AsF_6^-$, 25562-24-7; ClF, 7790-89-8; $FClO_2$, 13637-83-7; $FClO_3$, 7616-94-6; $ClF_2(F_2)^+$, 36544-30-6.

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Fluoroborate Equilibria in Aqueous Solutions[1a]

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The stability of fluoroborate species has been examined in 1 *m* NaCl solution at 25° by means of potentiometric titrations in which the free fluoride ion concentration was measured with the LaF_3 electrode and the pH was measured with the hydrogen electrode. The procedure consisted of the addition of acid to 0.01 and 0.03 *m* boric acid containing 0.02–0.08 *m* NaF, with variation of the pH from 7 to 2. Under these conditions negligible amounts of BF_4^- ion, which forms only slowly, were produced. The results are explained by the following reactions and equilibrium quotients

$$\begin{array}{ll} B(OH)_3 + F^- \rightleftharpoons BF(OH)_3^- & \log Q = -0.36 \pm 0.2 \\ B(OH)_3 + 2F^- + H^+ \rightleftharpoons BF_2(OH)_2^- + H_2O & \log Q = 7.06 \pm 0.02 \\ B(OH)_3 + 3F^- + 2H^+ \rightleftharpoons BF_3OH^- + 2H_2O & \log Q = 13.689 \pm 0.003 \end{array}$$

Under the conditions of measurement, BF_3OH^- was the major species formed and the species $BF(OH)_3^-$ was barely detectable. Combined with other equilibrium quotients, known previously, these results give the following log *Q* values for the stepwise replacement of OH^- by F^- in the conversion of $B(OH)_4^-$ to BF_4^-: −5.3 ± 0.2, −6.3 ± 0.2, −7.10 ± 0.02, −8.40 ± 0.1. There was no evidence for the formation of the undissociated acids HBF_3OH or $HBF_2(OH)_2$ or for the formation of polyborate species.

The chemistry of fluoroborates has been extensively studied, largely as a result of the technological importance of BF_3 and its derivatives. The work prior to 1949 has been covered in the extensive review of Booth and Martin.[2] In aqueous solutions and in solids the ions BF_4^-, BF_3OH^-, and $B(OH)_4^-$ occur, and possibly the ions $BF_2(OH)_2^-$ and $BF(OH)_3^-$ as well. It is clear from the studies of Wamser,[3] Ryss, *et al.*,[4] and Sen Gupta and Mukherjee[5] that all such species, with the exception of BF_4^-, can undergo rapid and reversible interconversion in aqueous solution at room temperature.

The BF_4^- ion is well established as a stable species both in solid compounds and in aqueous solutions. Its stability toward hydrolysis in neutral or basic solutions is the basis for its determination in mixtures with the other more reactive fluoroborates.[3b] The X-ray studies by Clark and Lynton[6] and by Brunton[7] of crystalline alkali fluoroborates have shown that the BF_4^- ion is a slightly distorted tetrahedron. The Raman spectrum of BF_4^- in aqueous solutions[8,9] and in melts[8] similarly indicates a tetrahedral structure. Nuclear magnetic resonance spectra[10] of the aqueous ion reveal the number of lines and the fine structure for ^{19}F and ^{11}B couplings expected for a symmetrical ion with slow exchange of the fluorides.

Alkali and alkaline earth salts of BF_3OH^- were first prepared by Ryss and by Wamser. Clark and Lynton[11] have determined the crystal structure of $NaBF_3OH$ and also found the anion BF_3OH^- to be very nearly tetrahedral. The nmr

[1] (a) Research sponsored by the U. S. Atomic Energy Commission under contract with Union Carbide Corp. (b) Summer trainee sponsored by Oak Ridge Associated Universities.

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spectrum of BF_3OH^- in aqueous solution has been described by Kuhlmann and Grant.[10] They assigned new nmr peaks appearing in the spectrum of a slightly hydrolyzed solution of $NaBF_4$ to the BF_3OH^- ion. The ^{11}B spectrum consisted of a 1:3:3:1 quartet and the ^{19}F spectrum was a 1:1:1:1 quartet as expected for a species containing one boron atom with three equivalent fluorine atoms.

The most detailed information available at present on the equilibria which occur in aqueous fluoroborate solutions is due largely to the excellent work of Wamser,[3] who performed careful kinetic and equilibrium studies primarily by means of pH and conductance titrimetry. He was one of the first to suggest that the four ions BF_4^-, BF_3OH^-, $BF_2(OH)_2^-$, and $BF(OH)_3^-$ were formed by succession hydrolysis steps, the first of which was slow, the rest being rapid and reversible. He measured the rate of both the forward and the reverse reactions of the slow hydrolysis of BF_4^-

$$BF_4^- + H_2O \underset{k_1}{\overset{k_2}{\rightleftharpoons}} BF_3OH^- + HF \qquad (1)$$

in solutions of HBF_4 and $HBF_3OH + HF$, respectively. He determined k_2 and k_1, both of which increased with the concentration of the acids. From the rate constants at equal concentrations of HBF_4 and HBF_3OH he derived values for the equilibrium quotient of the above reaction ($Q = k_2/k_1$) which were in excellent agreement with his direct measurements of Q in solutions of HBF_4 which had reached hydrolytic equilibrium. Wamser[3b] also approximated the quotient for the next, assumed rapid, hydrolysis step

$$BF_3OH^- + H_2O \rightleftharpoons BF_2(OH)_2^- + HF \qquad (2)$$

$$\frac{[BF_2(OH)_2^-][HF]}{[BF_3OH^-]} = 0.011 \quad (I \approx 0.06, 25^\circ)$$

by studying the effect of the HF concentration on the rate of the slow conversion of BF_3OH^- to BF_4^-. Finally Wamser estimated from conductance measurements that the fluoroboric acids HBF_4, HBF_3OH, and $HBF_2(OH)_2$ were of decreasing strength with HBF_4 a strong acid comparable to HCl, HBF_3OH similar to trichloroacetic acid ($pK = 0.7$), and $HBF_2(OH)_2$ similar to dichloroacetic acid ($pK = 1.48$).

Anbar and Guttmann[12] made additional measurements of the dependence of the rate of the BF_4^- hydrolysis on the acidity, employing ^{18}F-tracer techniques. Their results were completely consistent with those of Wamser, indicating a slow first hydrolysis step followed by subsequent rapid equilibria leading to exchange between BF_3OH^- and HF or F^-. They also observed a monomolecular hydrolysis of BF_4^- in neutral or basic solutions. They concluded that the rate law for the first hydrolysis step was

$$\frac{-d[BF_4^-]}{dt} = k_3[H^+][BF_4^-] + k_4[BF_4^-] \qquad (3)$$

wherein $k_3 = k_2/[H^+]$. The value for k_4 at 100° is 4.2 l. mol^{-1} min^{-1}. Their results, along with those of Wamser, show that k_3 increases with ionic strength. We may represent this by

$$\log k_3\ (\text{l. mol}^{-1}\ \text{min}^{-1}) = -1.85 - \frac{1.022\sqrt{I}}{1 + \sqrt{I}} + 0.21I \qquad (4)$$

$$(I = 0\text{-}1.2, 25^\circ)$$

From the temperature dependence of k_3 and k_4, Anbar and Guttmann found activation energies of 25.1 and 15.5 kcal, respectively. Their measurements of the fluoride-exchange rate in acid solution containing BF_4^- and F^- were consistent with the measurements of the hydrolysis rate in that both showed the same dependence on acidity and temperature. The rate constant for the exchange was 4 times that for hydrolysis as would be expected since the products, primarily $BF_3(OH)^-$ and HF, undergo rapid exchange of fluorides.

In summary, the species BF_4^- and BF_3OH^- have been well established in aqueous solution, along with the equilibrium quotient and the kinetics associated with their interconversion. However, the equilibria relating these species with $B(OH)_3$ and with the other possible fluoroborate species have not been defined. This is no doubt due to the lack, until recently, of a convenient means for the determination of the free fluoride ion concentration in such solutions. It was the purpose of the present study to investigate the hydrolyzed fluoroborate species by use of the lanthanum fluoride electrode to measure the fluoride ion concentration, along with the hydrogen electrode to measure acidity. By a proper choice of experimental conditions, the slow formation of BF_4^- could be minimized in order that the other fluoroborate species and their (metastable) equilibria could be examined. These studies were confined to the pH range 2–7 in which the only other B(III) species expected is boric acid, $B(OH)_3$. Orthoborate ion, $B(OH)_4^-$, does not appear in appreciable amounts below pH 7, nor do the polyborate ions[13] at the low boron concentrations which were employed here.

Experimental Section

The materials used in this study, boric acid, hydrofluoric acid, sodium chloride, and sodium hydroxide, were of reagent grade quality. Sodium hydroxide solutions containing less than 0.1 mol % carbonate and hydrofluoric acid solutions were stored in paraffin-lined flasks to minimize contamination by silicates.

Hydrogen gas for use in hydrogen electrodes was purified by passage through a Serfass hydrogen purifier, Model C-15D, and was saturated with water vapor above a 1 *m* NaCl solution before admission to the cell.

Potentiometric Cells. The potentiometric circuit and cell assembly were similar to the apparatus described previously for the study of fluoride complexes of beryllium.[14] The temperature was maintained at 25.0 ± 0.1° and the medium salt was 1 *m* NaCl. The cell consisted of a Teflon vessel with a Pyrex cap with several inlets for hydrogen, the titrant, and the electrode leads. The assembly had two compartments each containing hydrogen electrodes. The larger outer compartment A contained, in addition, a lanthanum fluoride solid-state electrode. A titrant was added from a syringe microburet to solution A. The reference hydrogen electrode was contained in a smaller inner Teflon compartment B with a porous plug which formed the liquid junction. Hydrogen was bubbled continuously through both compartments; experiments were conducted which demonstrated that HF or volatile fluoroborates were not removed by transpiration with the hydrogen. The cell representation is

$$\begin{array}{l|l||l|l}
 & \text{solution A} & \text{solution B} & \\
LaF_3 & (1-a-c)\ m\ \text{NaCl} & (1-d)\ m\ \text{NaCl} & \\
\text{and} & a\ m\ \text{NaF} & & \\
H_2,\ Pt & b\ m\ H_3BO_3 & d\ m\ \text{HCl} & Pt,\ H_2 \\
 & c\ m\ \text{HCl} & &
\end{array}$$

Reference compartment B contained a solution of 0.01 *m* HCl in 0.99 *m* NaCl and this remained unchanged during each experiment. The concentrations of NaF and boric acid in solution A were varied, and titrations were conducted by adding acid or base.

A run was initiated by addition of a large volume of a dilute,

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neutral sodium fluoride solution in 1 *m* NaCl to compartment A. The boric acid was added to the cell after a stable potential was established between the reference electrode and the fluoride electrode in this dilute solution of known sodium fluoride concentration. Then a titrant was added stepwise by means of a syringe microburet. Equilibrium was established rapidly, usually within a few minutes. Titrations were continued until the pH reached a value in the range 2–3 and then were often reversed by the addition of base to establish the amount of BF_4^- which had been formed during the run. The differences observed in the two directions indicated that less than 1% of the boron was converted to BF_4^- in most of the experiments. As expected, BF_4^- was formed only during periods when the cell solution was relatively acid and allowed to stand for long periods of time.

Results

Acidity and Free Fluoride Measurements. Because the ionic strength and composition of the medium was held nearly constant during these experiments, activity coefficients can be considered constant. The difference in potential between the two hydrogen electrodes gives the acidity h

$$\Delta E_H = (RT/F)\ln(h_r/h) - \Sigma D_i(m_{i,r} - m_i) \quad (5)$$

where h_r is a reference acidity, $m_{i,r}$ and m_i represent the concentrations of each of the ions present in the reference and cell solutions, and D_i is the coefficient for each ion in the Henderson equation for the liquid junction potential (see ref 14). The approximation was made that $D_{Cl^-} = D_{B(OH)_xF_{4-x}^-}$ and that $D_{B(OH)_3} = 0$ in this study.

In an analogous manner the fluoride concentration was calculated from the potential of the fluoride electrode *vs.* the reference hydrogen electrode. In this case the difference (ΔE_F) between the potential given by the pair of electrodes at the initial point in a titration experiment (for which the fluoride ion concentration was known) and each successive point is used to calculate the fluoride concentration at each point

$$\Delta E = -(RT/F)\ln(f_r/f) - \Sigma D_i(m_{i,r} - m_i) \quad (6)$$

where f_r and f are, respectively, the fluoride ion concentrations of the initial solution and at another given point in an experiment.

To reiterate, the reference for the acidity measurements was the solution in the reference compartment. The reference for the fluoride ion measurements was the cell solution at the beginning of the titration.

Data Analysis. For the analysis of these data it is convenient to define two quantities $\bar{n}(H)$ and $\bar{n}(F)$, which represent the average number of hydrogen ions and fluoride ions involved in the general reaction

$$B(OH)_3 + yF^- + zH^+ = BF_y(OH)_{3-z}{}^{z-y} + zH_2O \quad (7)$$

These quantities were calculated for each data point by the relationships

$$\bar{n}(H) = [m_H - h - Q_{HF}hf - Q_{HF_2^-}hf^2 + (Q_W/h)]/m_B \quad (8)$$

$$\bar{n}(F) = [m_F - f - Q_{HF}hf - 2Q_{HF_2^-}hf^2]/m_B \quad (9)$$

where m_H, m_F, and m_B are the total concentrations of hydrogen ion, fluoride ion, and boron, respectively. Previously published values were used for the equilibrium quotients[14] for the formation of HF ($Q_{HF} = 10^{2.89}$) and HF_2^- ($Q_{HF_2^-} = 10^{3.87}$), respectively, and for the ion product for water[15] ($Q_W = 10^{-13.73}$).

Calculated values of these quantities, $\bar{n}(H)_c$ and $\bar{n}(F)_c$, were also determined for each data point by the expressions

$$\bar{n}(H)_c = \Sigma(zQ_{y,z}f^yh^z)/m_B \quad (10)$$

$$\bar{n}(F)_c = \Sigma(yQ_{y,z}f^yh^z)/m_B \quad (11)$$

in which the summations are over all the fluoroborate species assumed to be formed. The equilibrium quotients ($Q_{y,z}$) for the formation of each of these species were adjusted by means of a general least-squares computer program to give the best fit to the data.

Weighing the Data. Uncertainties were assigned to all the observables and parameters involved in obtaining the data and reducing them to sets of m_B, f, $\bar{n}(H)$, and $\bar{n}(F)$ values. The contribution of each of these uncertainties to the variances in the two differences ($\bar{n}(H) - \bar{n}(H)_c$) and ($\bar{n}(F) - \bar{n}(F)_c$) was then determined for each data point by numerical differentiation. Each point was weighed in the least-squares calculation by an amount (W_H or W_F) which was inversely proportional to these variances. The agreement factor used to measure the goodness of fit was defined

$$\sigma(\bar{n}) = \left[\frac{\Sigma W_H(\bar{n}(H) - \bar{n}(H)_c)^2 + \Sigma W_F(\bar{n}(F) - \bar{n}(F)_c)^2}{N_O - N_V}\right]^{1/2} \quad (12)$$

wherein the summations are over the N_O observations, and N_V is the number of adjustable parameters. If all species formed, and only those formed, are included in the scheme assumed, if the weights have been properly assigned, and if there are no unsuspected systemmatic errors, the agreement factor after adjusting the $Q_{y,z}$ values should have a value of unity.

Potentiometric Results. The results of experiments in which acid was added stepwise to nearly neutral solutions containing boric acid and fluoride are summarized in Table I. Potentials usually become constant within a few minutes after each addition, indicating that equilibrium was quickly attained except at relatively high acid concentrations where it has been shown by Wamser[3] and others that the tetrafluoroborate ion slowly forms. Reverse titrations demonstrated that the amount of BF_4^- formed during the additions of acid amounted to no more than 0.5–1% of the boric acid present.

Most of the data were obtained over the pH range from 2 to 6, where the intermediate fluoroborates appeared to be important. In one experiment, in the presence of 0.02 *m* fluoride and 0.01 *m* $B(OH)_3$, the free fluoride measured by the lanthanum fluoride electrode remained within 1% of the stoichiometric value between pH 6 and 10, thus demonstrating the absence of fluoroborates in the region where $B(OH)_3$ is converted to $B(OH)_4^-$. As noted previously, polyborates are not expected at the low boron concentration used in the present study.

Choice of Species. Figure 1 shows the variation of $\bar{n}(H)$ and $\bar{n}(F)$ with pH as acid is added to solutions containing 0.01 *m* boric acid and 0.02–0.06 *m* fluoride. With increasing acidity and fluoride concentration, the $\bar{n}(H)$ curves approach a limiting value of 2.0 and the $\bar{n}(F)$ curves approach a limiting value of 3.0. Their limits indicate, as expected, that the most fluorinated species formed is BF_3OH^-. Indeed the plots of all the data in Figure 2, wherein the ordinate is log h^2f^3, suggest that this species is the principal fluoroborate species present under most of the conditions studied. If it were the only such species formed, the data points in Figure 2 would fall on a single curve in each case. This would be required by the stoichiometry of reaction 7 for the formation of BF_3OH^-. However, there is an appreciable systematic spread of the data, and,

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Table I. Potentiometric Data on Fluoroborate Solutions in 1 *m* NaCl at 25°

$\bar{n}$(H)	$\bar{n}$(F)	h	$f \times 10^3$	$m_B \times 10^3$
−0.0011	0.0273	1.104×10^{-6}	20.76	9.128
0.0163	0.0497	2.615×10^{-6}	20.52	9.126
0.0898	0.1664	8.723×10^{-6}	19.32	9.119
0.185	0.315	1.579×10^{-5}	17.84	9.110
0.377	0.598	3.366×10^{-5}	15.01	9.092
0.565	0.878	6.306×10^{-5}	12.21	9.075
0.744	1.140	1.156×10^{-4}	9.544	9.057
0.909	1.378	2.218×10^{-4}	7.016	9.040
1.044	1.571	4.573×10^{-4}	4.781	9.022
1.132	1.695	9.807×10^{-4}	3.049	9.005
1.168	1.741	1.935×10^{-3}	1.987	8.988
1.168	1.742	3.278×10^{-3}	1.404	8.971
1.165	1.173	4.789×10^{-3}	1.079	8.953
0.000	0.025	7.348×10^{-7}	29.82	9.824
0.118	0.240	6.274×10^{-6}	27.50	9.811
0.305	0.522	1.375×10^{-5}	24.50	9.791
0.614	0.995	3.385×10^{-5}	19.49	9.759
0.912	1.430	7.394×10^{-5}	14.81	9.727
1.185	1.830	1.716×10^{-4}	10.32	9.696
1.404	2.148	4.578×10^{-4}	6.341	9.664
1.525	2.319	1.317×10^{-3}	3.445	9.633
1.549	2.350	3.133×10^{-3}	1.955	9.601
1.535	2.326	5.609×10^{-3}	1.299	9.570
1.513	2.293	8.388×10^{-3}	0.969	9.540
0.001	0.044	4.863×10^{-7}	40.99	9.851
0.673	1.111	1.898×10^{-5}	29.61	9.781
0.906	1.460	3.109×10^{-5}	25.88	9.757
1.332	2.070	7.918×10^{-5}	19.17	9.710
1.682	2.568	2.338×10^{-4}	12.94	9.664
1.883	2.834	7.441×10^{-4}	7.958	9.618
1.950	2.921	2.134×10^{-3}	4.426	9.573
1.968	2.934	4.788×10^{-3}	2.495	9.528
1.951	2.906	8.420×10^{-3}	1.606	9.484
−0.001	0.051	4.977×10^{-7}	58.86	9.778
0.140	0.283	2.207×10^{-6}	56.36	9.764
0.476	0.817	6.404×10^{-6}	50.67	9.730
0.948	1.536	1.657×10^{-5}	42.95	9.681
1.399	2.200	3.720×10^{-5}	35.62	9.634
1.755	2.689	9.872×10^{-5}	29.02	9.586
1.897	2.864	2.813×10^{-4}	23.32	9.540
1.930	2.889	6.256×10^{-4}	18.31	9.493
1.944	2.906	1.206×10^{-3}	13.76	9.447
1.978	2.952	2.164×10^{-3}	9.843	9.402
2.011	3.006	3.781×10^{-3}	6.696	9.357
0.002	0.028	5.932×10^{-7}	29.29	29.93
0.032	0.080	2.640×10^{-6}	27.64	29.90
0.161	0.289	1.202×10^{-5}	21.12	29.78
0.323	0.531	3.795×10^{-5}	13.62	29.63
0.476	0.753	1.499×10^{-4}	6.635	29.48
0.575	0.887	1.285×10^{-3}	1.746	29.34
0.584	0.888	4.971×10^{-3}	0.7112	29.19
0.579	0.876	9.404×10^{-3}	0.4604	29.05
0.574	0.864	1.395×10^{-2}	0.3498	28.91
−0.005	0.037	2.683×10^{-6}	20.66	9.108
0.088	0.179	9.853×10^{-6}	19.21	9.099
0.183	0.334	1.728×10^{-5}	17.66	9.090
0.375	0.608	3.528×10^{-5}	14.93	9.073
0.563	0.892	6.556×10^{-5}	12.11	9.055
0.742	1.151	1.196×10^{-4}	9.458	9.037
0.905	1.390	2.302×10^{-4}	6.920	9.020
1.038	1.585	4.788×10^{-4}	4.666	9.002
1.123	1.706	1.029×10^{-3}	2.961	8.985
1.155	1.750	2.024×10^{-3}	1.924	8.968
−0.003	0.075	1.057×10^{-6}	40.66	9.835
0.082	0.202	3.162×10^{-6}	39.27	9.826
0.449	0.776	1.224×10^{-5}	33.15	9.788
0.667	1.093	1.978×10^{-5}	29.78	9.766
1.407	2.142	9.726×10^{-5}	18.23	9.686
1.728	2.599	2.893×10^{-4}	12.22	9.640
1.868	2.792	7.349×10^{-4}	8.255	9.604
1.930	2.874	2.072×10^{-3}	4.678	9.559
1.937	2.885	4.673×10^{-3}	2.645	9.514
1.935	2.886	4.695×10^{-3}	2.634	9.514
1.926	2.878	2.074×10^{-3}	4.620	9.469
1.864	2.795	7.256×10^{-4}	8.127	9.424
1.720	2.589	2.837×10^{-4}	12.03	9.389
0.002	0.033	4.045×10^{-7}	41.11	9.837
0.086	0.198	2.914×10^{-6}	39.31	9.828
0.178	0.347	4.758×10^{-6}	37.72	9.818
0.362	0.611	8.590×10^{-6}	34.91	9.799
0.545	0.891	1.368×10^{-5}	31.95	9.781
0.727	1.169	2.034×10^{-5}	29.01	9.762
0.907	1.428	2.920×10^{-5}	26.25	9.743
1.083	1.691	4.208×10^{-5}	23.43	9.725
1.254	1.945	6.131×10^{-5}	20.66	9.706
1.416	2.182	9.074×10^{-5}	17.99	9.688
0.000	0.029	6.216×10^{-7}	29.79	9.812
0.071	0.179	4.748×10^{-6}	28.16	9.804
0.151	0.277	6.997×10^{-6}	27.11	9.796
0.306	0.523	1.346×10^{-5}	24.51	9.780
0.462	0.760	2.169×10^{-5}	22.00	9.764
0.616	0.995	3.280×10^{-5}	19.52	9.747
0.916	1.438	7.165×10^{-5}	14.78	9.715
1.193	1.840	1.658×10^{-4}	10.31	9.684
1.418	2.165	4.415×10^{-4}	6.306	9.652
1.496	2.276	7.575×10^{-4}	4.658	9.636
0.008	0.093	1.591×10^{-7}	84.81	28.63
0.053	0.164	5.572×10^{-7}	82.58	28.59
0.171	0.347	1.421×10^{-6}	76.97	28.49
0.341	0.611	2.889×10^{-6}	68.96	28.35
0.851	1.372	1.218×10^{-5}	46.22	27.94
1.348	2.093	5.632×10^{-5}	24.90	27.54
1.748	2.661	7.515×10^{-4}	6.494	27.15
1.797	2.705	5.299×10^{-3}	1.804	26.89

moreover, the assumption of BF_3OH^- only gives an agreement factor of 3.0, a relatively poor fit of the data. Thus at least one additional species must be formed in minor amounts.

Assumption of $BF_2(OH)_2^-$ as an additional species gives a very good fit of the data, with an agreement factor of 1.45. The equilibria and the quotients derived are

$$B(OH)_3 + 3F^- + 2H^+ = BF_3(OH)^- + 2H_2O \quad \log Q_{3,2} = 13.689 \pm 0.003 \qquad (13)$$

$$B(OH)_3 + 2F^- + H^+ = BF_2(OH)_2^- + H_2O \quad \log Q_{2,1} = 7.06 \pm 0.02 \qquad (14)$$

By introducing the third species, $BF(OH)_3^-$, to complete the sequence of expected tetrahedral monomers, the agreement factor was 1.43. This represents an insignificant improvement in the overall fit and the quotients for the other two equilibria are unaffected; however, the improvement is somewhat systematic and is greatest in runs at the highest total fluoride concentration, where this species would be most significant. If $BF(OH)_3^-$ is formed, the equilibrium and its quotient are

$$B(OH)_3 + F^- = BF(OH)_3^- \quad \log Q_{1,0} = -0.36 \pm 0.19 \qquad (15)$$

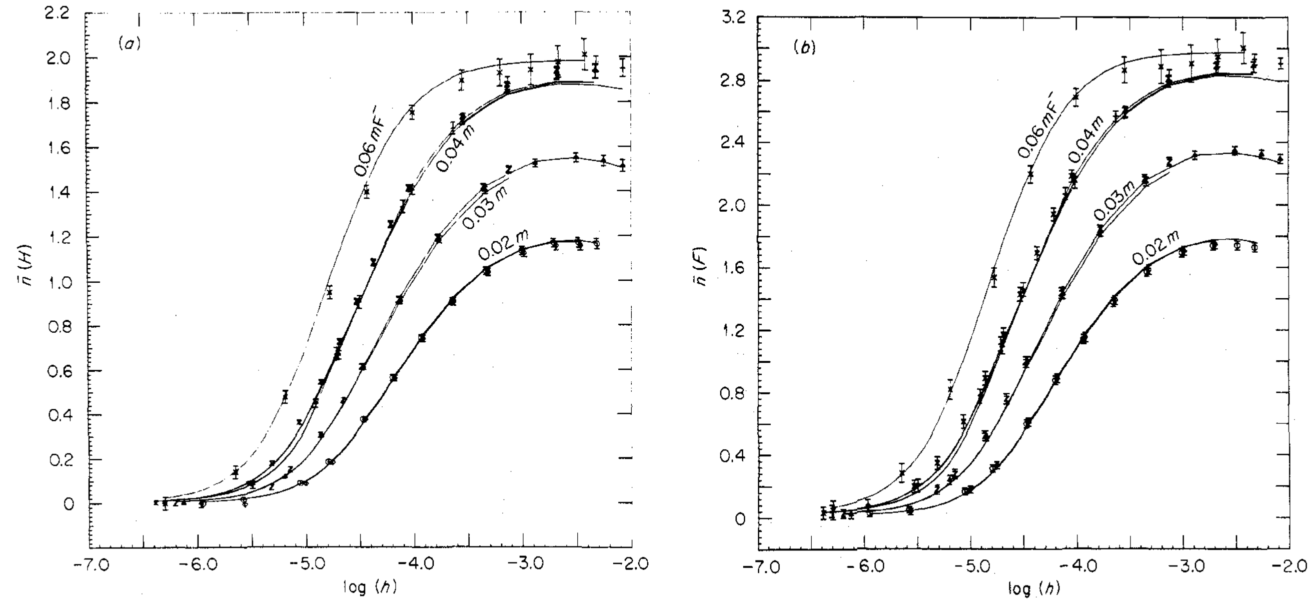

Figure 1. The average number of hydrogen ions (a) and the average number of fluoride ions (b) consumed per mole of boric acid in reaction 7. The data result from titrations in the presence of total fluoride concentrations from 0.02 to 0.06 *m* and a boric acid concentration of 0.01 *m* in NaCl at 25°. The curves were calculated assuming the species BF_3OH^-, $BF_2(OH)_2^-$, and $BF(OH)_3^-$.

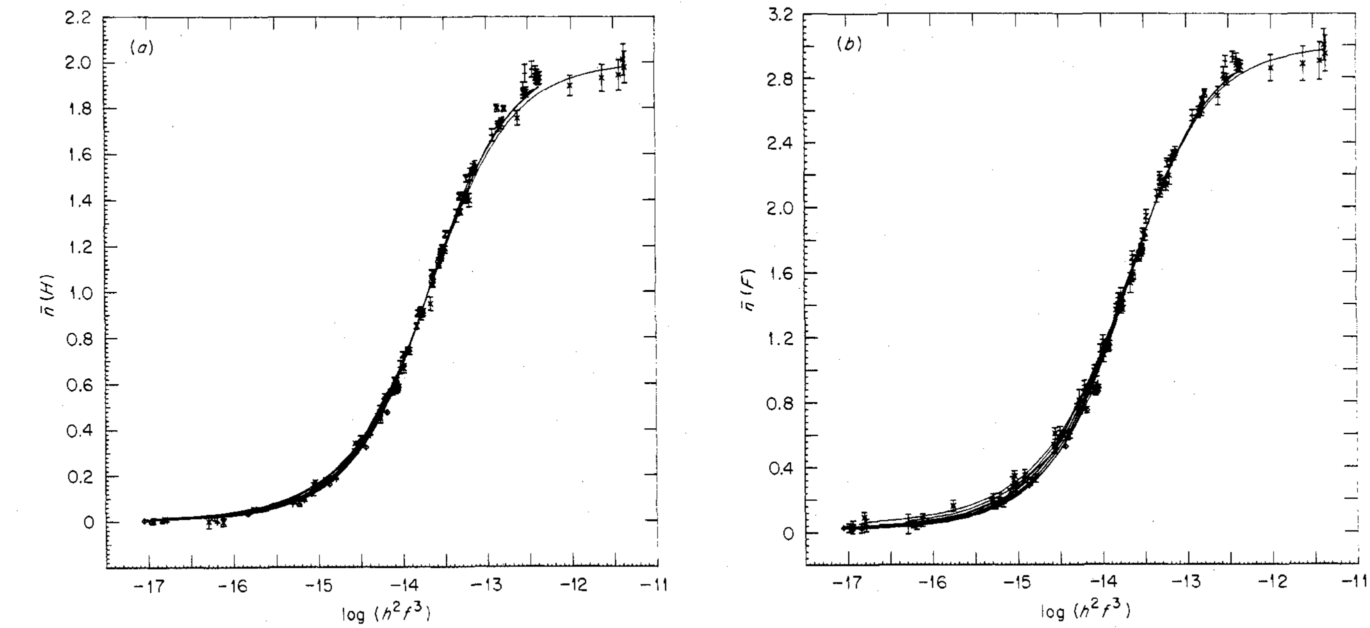

Figure 2. The average number of hydrogen ions (a) and the average number of fluoride ions (b) consumed per mole of boric acid in reaction 7. The near superposition of the curves with h^2f^3 as the abscissa indicates the importance of BF_3OH^-.

The protonated forms of the two important fluoroborate species HBF_3OH and $HBF_2(OH)_2$, when introduced one at a time, did not lead to a further improvement of the fit. Finally, it is clear that no polyfluoroborate species were formed since there was no systematic deviation of observed from calculated $\bar{n}$ values as the boron concentration changed from 0.01 *m*, used in most runs, to 0.03 *m*.

The smooth curves shown in Figures 1 and 2, were generated by use of the three species BF_3OH^-, $BF_2(OH)_2^-$, and $BF(OH)_3^-$ with the above equilibrium quotients.

The present data can be accounted for quite well by the assumption that only two fluoroborate species were formed, BF_3OH^- and $BF_2(OH)_2^-$. Moreover, introduction of the third species, $BF(OH)_3^-$, to complete the sequence of tetrahedral fluoroborate ions, yields a stability for it which is about what would be expected. This can be seen from reactions 9-12 in Table II, representing the stepwise addition of F^- ion to the orthoborate ion. The corresponding equilibrium quotients—which should not be very dependent on the medium—show a regular pattern, decreasing about 1 log unit per fluoride added. Interestingly this is very nearly the same decrease which we found previously[14] for stepwise addition of fluorides to complexes of a number of metal ions.

From an appropriate combination of the equilibrium quotients in Table II we calculate the equilibrium quotient for the hydrolysis of BF_3OH^- to produce $BF_2(OH)_2^-$ and undissociated HF (reaction 2) to be $(1.83 \pm 0.09) \times 10^{-4}$. This is considerably lower than the value (0.011) estimated by Wamser.[3b]

Discussion

The formation of BF_4^- ion was suppressed in the present measurements by restricting the acidity, the fluoride ion con-

Table II. Equilibrium Quotients in 1 *m* NaCl at 25°

Reaction	Log *Q*	Source
Protolytic Equilibria		
1. $H^+ + F^- \rightleftharpoons HF$	2.887 ± 0.009	*a*
2. $H^+ + 2F^- \rightleftharpoons HF_2^-$	3.87 ± 0.11	*a*
3. $H_2O \rightleftharpoons H^+ + OH^-$	−13.725	*b*
4. $B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$	−8.809	*c*
Fluoride-Boric Acid Equilibria		
5. $B(OH)_3 + F^- \rightleftharpoons BF(OH)_3^-$	−0.36 ± 0.19	*d*
6. $B(OH)_3 + 2F^- + H^+ \rightleftharpoons BF_2(OH)_2^- + H_2O$	7.06 ± 0.02	*d*
7. $B(OH)_3 + 3F^- + 2H^+ \rightleftharpoons BF_3(OH)^- + 2H_2O$	13.689 ± 0.003	*d*
8. $B(OH)_3 + 4F^- + 3H^+ \rightleftharpoons BF_4^- + 3H_2O$	19.0 ± 0.1	*e*
Fluoride-Hydroxide Exchange		
9. $B(OH)_4^- + F^- \rightleftharpoons BF(OH)_3^- + OH^-$	−5.3 ± 0.2	*f*
10. $BF(OH)_3^- + F^- \rightleftharpoons BF_2(OH)_2^- + OH^-$	−6.3 ± 0.2	*f*
11. $BF_2(OH)_2^- + F^- \rightleftharpoons BF_3(OH)^- + OH^-$	−7.10 ± 0.02	*f*
12. $BF_3(OH)^- + F^- \rightleftharpoons BF_4^- + OH^-$	−8.40 ± 0.1	*f*

[a] Reference 14. [b] Reference 15. [c] B. B. Owen and E. J. King, *J. Amer. Chem. Soc.*, 65, 1612 (1943). [d] From present results. [e] From equilibrium quotient in Table III combined with that for reactions 1 and 7 in this table. [f] From combination of equilibrium quotients for reaction 3 with those for reactions 3-8.

Table III. Equilibrium Quotient for the Hydrolysis of BF_4^- at 25° from Wamser[3a]

Medium	$[BF_3OH^-] \cdot [HF]/[BF_4^-]$[a]	Medium	$[BF_3OH^-] \cdot [HF]/[BF_4^-]$[a]
0.0	0.0020	0.2 *M* HBF_4	0.0028
0.01 *M* HBF_4	0.0020	0.5 *M* HBF_4	0.0041
0.05 *M* HBF_4	0.0022	1 *M* HBF_4	0.0056
0.1 *M* HBF_4	0.0024	1 *m* NaCl	0.0037

[a] These are smoothed values in which we have included minor corrections for the dissociation of HF and for the further hydrolysis of BF_3OH^-. The value for 1 *m* NaCl reflects the expected change in the salt effect on HF (see text).

centration, and the equilibration time to values small enough that the rate of formation of BF_4^- by the reverse of reaction 1 was negligibly slow. This may be seen by combining the rate constant for the forward reaction (k_3 = 0.007 at I = 1 *m* from eq 4) with the equilibrium quotient (Q = 0.0037 in 1 *m* NaCl from Table III) to give

$$\frac{-d[BF_3OH^-]}{dt} = 1.9[H^+][HF][BF_3OH^-] \text{ mol l.}^{-1} \text{ min}^{-1} \quad (16)$$

The maximum value of the concentration product $[H^+] \cdot [HF]$, approached briefly in a few runs, was 8×10^{-5} mol^2 l.$^{-2}$. Under these most unfavorable conditions about 1 hr would have been required for the conversion of 1% of the BF_3OH^- to BF_4^-.

Equilibrium quotients for the first hydrolysis step of BF_4^- ion (reaction 1) are shown in Table III. These are smoothed values based on the data of Wamser[3a] in HBF_4 and in HBF_3OH + HF solutions. The increase in this equilibrium quotient with ionic strength is more rapid than would be expected for a reaction in which ΔZ^2 is zero and may well be due to a salting-in of HF.[16] Our estimate for this equilibrium quotient in 1 *m* NaCl, therefore, includes a correction for the expected change in the salt effect resulting from the change in medium. Onda, *et al.*,[17] recently reviewed a large amount of data on salting effects in various aqueous media and, for a given nonelectrolyte, separated them into contributions from each ion. From these effects

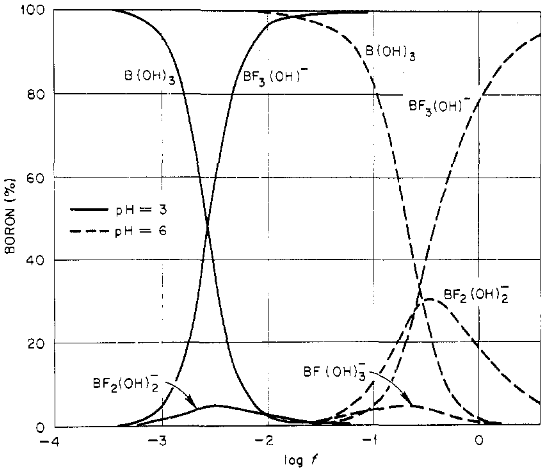

Figure 3. The relative amounts of the fluoroborates formed at pH values of 3 and 6 plotted as a function of the free fluoride concentration in the metastable system in which the tetrafluoroborate has not formed.

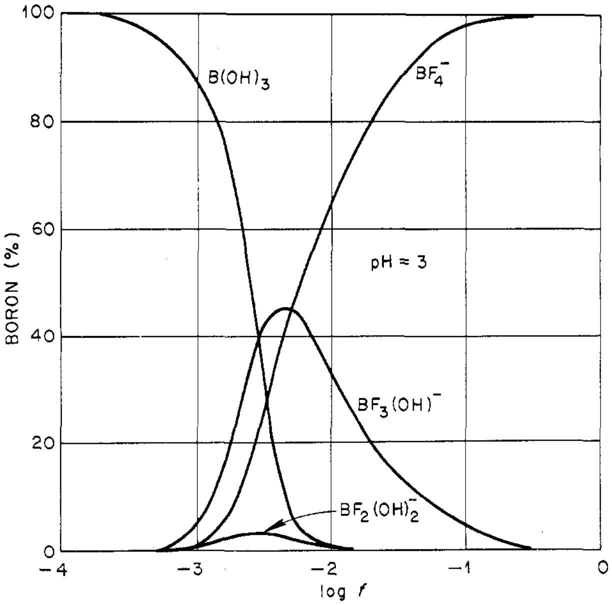

Figure 4. The relative amounts of the fluoroborates formed at pH 3 as a function of the free fluoride concentration in the equilibrium system in which the tetrafluoroborate has formed.

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(16) The increase in this equilibrium quotient with HBF_4 concentration could also be explained by assuming that HBF_3OH has an acid dissociation constant of ~0.01; however, this would be inconsistent with the conductance measurements of Wamser and with the fact that detectable amounts of undissociated HBF_3OH were not formed in the present measurements.

(17) K. Onda, E. Sada, T. Kobayashi, S. Kito, and K. Ito, *J. Chem. Eng. Jap.*, 3, 18 (1970).

the replacement of H^+ by Na^+ should lower Q (salt in HF) by 0.09 log unit. We estimate that replacing BF_4^- by Cl^- should produce a further reduction of Q by about 0.09 log unit. This is based on the difference in the salting effects reported for 1 M NaCl and 1 M $NaClO_4$,[18] and the assumption that BF_4^- will have the same salt effect as ClO_4^-.

Figure 3 shows the relative amounts of the fluoroborates formed at pH values of 3 and 6 plotted as a function of the free fluoride concentration. At the higher pH the amounts of $BF_2(OH)_2^-$ and $BF(OH)_3^-$ which are formed are greater and the fluoride concentrations at which these species appear are higher. The distribution data in Figure 3 represent the metastable system in which tetrafluoroborate has not formed. At equilibrium (Figure 4) the predominant product at high fluoride concentrations is BF_4^-.

Since there was no significant improvement in the fit to the data by the assumption that the undissociated acids HBF_3OH and $HBF_2(OH)_2$ are formed, we may conclude that in the present measurements these species could have reached concentrations no higher than ~5 and ~25%, respectively, of the concentration of the corresponding ion. From this the acid dissociation constants are judged to have the following lower limits: HBF_3OH, 0.2; $HBF_2(OH)_2$, 10^{-4}. These are consistent with the values (~0.2 and ~0.03, respectively) estimated from conductance measurements by Wamser.[3b]

These results provide very strong evidence in support of the existence of $BF_3(OH)^-$ and $BF_2(OH)_2^-$ in water as well as evidence for $BF(OH)_3^-$. They have also permitted the evaluation of equilibrium quotients relating all the species BF_4^-, $BF_3(OH)^-$, $BF_2(OH)_2^-$, $BF(OH)_3^-$, and $B(OH)_3$. Recent ^{19}F nmr studies in our laboratory will be reported soon which have confirmed the conclusions from these potentiometric results.

Registry No. $B(OH)_4^-$, 15390-83-7; $BF(OH)_3^-$, 32554-53-3; $BF_2(OH)_2^-$, 32554-52-2; $BF_3(OH)^-$, 18953-00-9; BF_4^-, 14874-70-5; $B(OH)_3$, 10043-35-3; F^-, 16984-48-8.

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[18] W. F. McDevit and F. A. Long, *J. Amer. Chem. Soc.*, 74, 1773 (1952).

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High-Resolution Boron-11 Nuclear Magnetic Resonance. III. Diborane(6) and Tetraborane(10)[1,2]

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The upper limits for the ^{11}B-^{11}B nuclear spin coupling constant, J_{BB}, have been obtained for a three-center, two-electron BHB bond in diborane(6)-^{11}B (<1.1 Hz) and in tetraborane(10)-^{11}B (<0.3 Hz) under conditions of double and triple resonance, respectively. The efficiency of the triple-resonance technique, used for the first time in ^{11}B nmr studies, is discussed for pentaborane(9). The value of J_{BB} in a three-center, two-electron BHB bond is compared with that found for the boron-boron coupling constant in pentaborane(9).

Since the first determination of a ^{11}B-^{11}B coupling constant (J_{BB})[4] in our laboratories,[5] we have been engaged in a systematic investigation of the factors which influence the value of J_{BB}. This has included a study of substituent effects on the magnitude of J_{BB} in pentaborane(9) derivatives in which various groups are substituted for hydrogen in the apex position.[6] In addition, studies have been conducted to determine boron-boron coupling constants in which boron is engaged in different bonding situations (*i.e.*, two-center, two-electron BB bonds, three-center, two-electron BBB bonds, and three-center, two-electron BHB bonds).[7] A molecule of fundamental importance and also one in which the value of J_{BB} has been reported is diborane(6). Recent studies by Farrar, *et al.*,[8] resulted in a "best fit" value of $|J_{BB}| = 5 \pm 2$ Hz. Similarly, Hopkins, *et al.*,[9] inferred from a detailed spectral analysis of the ^1H and ^{11}B nmr spectra of B_4H_{10} that the value of J_{BB} (*i.e.*, B_1-B_2[10]) was equal to zero.

In this study we have examined the B_2H_6 and B_4H_{10} molecules in an attempt to determine experimentally the value of J_{BB} in these compounds. Comparisons of the spin coupling constants for these molecules with that determined for B_5H_9 provide the opportunity to attempt a correlation between J_{BB} and the nature of the bonding between the two boron atoms under consideration.

Experimental Section

Nmr Measurements. Boron-11 nmr measurements were made on a Varian XL-100-15 nmr spectrometer operating at 32.1 MHz. Field/frequency lock was employed by locking to either ^2H or ^{19}F. The double-resonance experiments were conducted using the Varian Gyrocode decoupler. The triple-resonance experiments (observing ^{11}B, homonuclear decoupling ^{11}B, and heteronuclear noise decoupling ^1H) were accomplished with the Gyrocode decoupler in conjunction with a Varian V-3512-1 heteronuclear spin decoupler. For

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[1] Part II: D. W. Lowman, P. D. Ellis, and J. D. Odom, *J. Magn. Resonance*, 8, 289 (1972).

[2] Presented in part at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972. This paper is based, in part, on the thesis submitted by D. W. L. to the Graduate School of the University of South Carolina in partial fulfillment of the requirements for the M.S. degree.

[3] (a) University of South Carolina. (b) Varian Associates.

[4] Unless stated otherwise, J_{BB} is used to represent a ^{11}B-^{11}B spin coupling constant.

[5] J. D. Odom, P. D. Ellis, and H. C. Walsh, *J. Amer. Chem. Soc.*, 93, 3529 (1971).

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[7] W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963.

[8] T. C. Farrar, R. B. Johannesen, and T. D. Coyle, *J. Chem. Phys.*, 49, 281 (1968).

[9] R. C. Hopkins, J. D. Baldeschwieler, R. Schaeffer, F. N. Tebbe, and A. Norman, *J. Chem. Phys.*, 43, 975 (1965).

[10] The numbering system employed here is that set forth in *Inorg. Chem.*, 7, 1945 (1968).