TABLE II
EXTENT OF REACTION: QUENCHING *vs.* SPECTROPHOTOMETRY[a]

$10^3[Sn(II)]_0$, *M*	$10^3[H_2O_2]_0$, *M*	$10^2[Cu(II)]_0$, *M*	% complete: Quenching	% complete: Spectrophotometry
2.43	1.22	0.00	88 ± 3	38 ± 0.5
1.17	2.34	0.00	71 ± 3	56 ± 1
1.17	1.17	0.00	57 ± 3	46 ± 1
1.17	1.17	1.40	46 ± 3	50 ± 1

[a] Conditions: $[HClO_4] = 1.00\ M$, $\mu = 2.00$ ($LiClO_4$), 25°, λ 255 nm.

Cahill and Taube[5] have demonstrated that isotope fractionation studies of hydrogen peroxide reactions can be used to gain information about the mechanism. An initial 1-equiv step should yield a value of 1.00 for the fractionation factor, as defined by Cahill and Taube, and a value of 0.940 for an initial 2-equiv step. The value observed by Cahill and Taube for the Sn(II)–H_2O_2 reaction in hydrochloric acid was 0.943 indicative of a 2-equiv step.

The results of some fractionation experiments are shown in Table III. The values of the fractionation factors lie between those expected for a 1-equiv or a 2-equiv mechanism and suggest that both types of processes are operative. Our value obtained from HCl solutions does not agree with that reported by Cahill and Taube. A brief series of kinetic experiments indicates that marked deviation from second-order behavior occurs in HCl solutions. Adherence to a second-order rate law should have been observed if the mechanism was a single, 2-equiv step.

TABLE III
RESULTS OF ISOTOPIC FRACTIONATION EXPERIMENTS

$10^2[Sn(II)]_0$, *M*	$10^2[H_2O_2]_0$, *M*	$10^2[Cu(II)]_0$, *M*	$[HClO_4]$, *M*	[HCl], *M*	Fractionation factor[a]
2.1	3.0	0.0	1.24	0.0	0.972
1.9	3.0	6.0	1.29	0.0	0.965
1.5	3.0	0.0	0.00	0.96	0.957

[a] As defined in ref 3.

Higginson has used the induced reduction of $K_3Co(C_2O_4)_3$ as a test for the presence of Sn(III) as an intermediate in the oxidation of Sn(II). In experiments where the initial concentration of the cobalt complex was about equal to the Sn(II) and H_2O_2 concentrations, no induced reduction of $K_3Co(C_2O_4)_3$ could be detected.

Conclusions and Summary

In perchlorate solutions the reaction between Sn(II) and H_2O_2 is complicated. Significant discrepancies in the apparent extent of reaction as determined by spectrophotometry compared to results obtained *via* quenching and titration techniques suggest the existence of a non-steady-state intermediate which absorbs in the wavlength region used to follow the disappearance of tin(II). The addition of Cu(II) ion appears to eliminate the reaction pathway giving rise to the intermediate, which probably is the result of a 1-equiv reduction of H_2O_2. However, even at high concentrations of Cu(II) ion the reaction still takes place and then obeys a second-order rate law which is consistent with a 2-equiv mechanism. It seems likely that the reaction takes place by parallel pathways involving 1- and 2-equivalent mechanisms. Isotope fractionation factors intermediate between those expected for the two mechanisms lend support to the dual nature of the mechanism.

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Acidity Measurements at Elevated Temperatures. VI. Boric Acid Equilibria[1]

BY R. E. MESMER,* C. F. BAES, JR., AND F. H. SWEETON

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Boric acid–borate equilibria have been studied by means of a hydrogen electrode concentration cell from 50 to 290°. The equilibrium in dilute boric acid solution, $B(OH)_3 + OH^- = B(OH)_4^-$, was studied as a function of KCl concentration from 0.13 to 1.0 *m*. A small ionic strength (*I*) dependence of the equilibrium quotient ($Q_{1,1}$) was observed which decreases slightly with temperature. The pressure dependence of the equilibrium quotient is very small up to 2000 psi. Values of $Q_{1,1}$ are given to better than 0.01 log unit by the expression

$$\log Q_{1,1} = \frac{1573.21}{T} + 28.6059 + 0.012078T - 13.2258 \log T + (0.3250 - 0.00033T)I - 0.0912I^{3/2}$$

for values of *I* from 0 to 1 *m* and *T* from 273 to 573°K. Results for more concentrated boric acid solutions (up to 0.6 *m*) in 1.0 *m* KCl have indicated the formation of the polynuclear species $B_2(OH)_7^-$ and $B_3(OH)_{10}^-$ and minor amounts of either $B_4(OH)_{14}^{2-}$ or $B_5(OH)_{18}^{3-}$. The trimeric species is needed to fit the data at all temperatures studied (and previous data at 25°). The dimeric species, which has not been reported previously, is indicated quite strongly by the present results at 200° while the need for a fourth (tetrameric or pentameric) species is indicated by the results at 50°. The two alternative schemes—$B(OH)_4^-$, $B_2(OH)_7^-$, $B_3(OH)_{10}^-$, and $B_4(OH)_{14}^{2-}$ or $B_5(OH)_{18}^{3-}$—are both consistent with the data of Ingri at 25° and give as good a fit as the four-species scheme which he chose. Thermodynamic parameters have been derived for all the species in 1 *m* KCl and for $B(OH)_4^-$ at infinite dilution.

Introduction

Boric acid–borate buffer mixtures serve as pH standards, occur in natural aqueous systems and in detergent solutions, and are used as burnable nuclear poisons in the coolants of pressurized water nuclear reactors. It is not surprising, therefore, that the equilibria which occur in various aqueous solutions of boric acid and borate have been extensively studied,

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although only at temperatures near room temperature. From the results it is clear that, in addition to the mononuclear boric acid and orthoborate ion, which have been well established by infrared and Raman spectroscopy[2–6] to be trigonal ($B(OH)_3$) and tetrahedral ($B(OH)_4^-$) species, a number of polyborate ions also are formed.

Manov, *et al.*,[7] and Owen[8] have carried out careful measurements of the equilibrium

$$B(OH)_3 + OH^- \rightleftharpoons B(OH)_4^- \qquad (1)$$

at boron concentrations as low as 0.01 *m* where interference from polyborates is insignificant. The two sets of measurements, both made over the temperature range 0–60° in cells without liquid junction and containing hydrogen and Ag–AgCl electrodes, are in excellent agreement. They also show that borax ($Na_2B_4O_7 \cdot 10H_2O$) reacts quickly in dilute solution to produce the mononuclear species in the equilibrium amounts.

The equilibria occurring in more concentrated boric acid–borate solutions have been carefully studied in several media by Ingri.[9–13] The species formed appear to be as well established as can be expected considering the number which evidently are formed and the relatively large medium change which must be introduced in order to study them. Ingri found his extensive data to be most consistent with formation of the polymeric species $B_3(OH)_{10}^-$, $B_3(OH)_{11}^{2-}$, and $B_4(OH)_{14}^{2-}$. Ingri also has shown by means of a "self-medium" study[12] that no species are formed with a hydroxide-to-boron ratio greater than 4 in the presence of as much as 0.1 *m* hydroxide. This demonstrates convincingly that the equilibrium constants given by Konopik and Leberl[14] for dissociation of the second and third protons from boric acid (equivalent to the formation of $B(OH)_5^{2-}$ and $B(OH)_6^{3-}$) are much too high.

The recent work of Spessard[15] on the derivation of equilibrium quotients for several assumed species from data up to 90° unfortunately does not contribute to the identification of the actual species present since the total boron concentration was not varied and his technique provided data of very limited accuracy. This latter point is illustrated by the poor agreement of his data with the more precise data of Owen and King[8] in 3 *M* NaCl and the irregular variation of log *Q* with temperature for several of his assumed species in several of the media studied.

Information on the rates of formation of some of the polyborates has been obtained by Anderson, *et al.*,[16] and Osugi, *et al.*,[17] using temperature-jump and pressure-jump techniques. They are in agreement and assign a rate constant of about 3×10^3 M^{-2} sec^{-1} for the reaction

$$2B(OH)_3 + B(OH)_4^- \longrightarrow B_3(OH)_{10}^- \qquad (2)$$

Momii and Nachtrieb[18] found evidence for a slightly slower approach to equilibrium at concentrations of boron between 0.6 and 2.0 *M* at 25° in solutions made up from NaB_5O_8. Two separate ^{11}B resonance peaks with variable relative intensity were observed also by Onak, *et al.*[19] The former authors interpreted their data in terms of equilibria involving pentaborate ion $B_5O_6(OH)_4^-$ although no unique assignment could be made. Equilibria were attained in these studies during the time of mixing. All species in tetraborate solutions ($M_2B_4O_7$) exchange rapidly giving a single nmr line. The surprising observation of apparent slow changes in the infrared spectra of supersaturated boric acid–borate solutions reported by Valyashko and Vlasova[20] was not confirmed by Raman spectra and pH measurements taken by us over a 10-week period at 25° for solutions containing 0.6–0.8 *m* boron in boric acid–borate mixtures.

Because of the importance of borates in general and some of their uses which involve high temperatures, we have employed the high-temperature potentiometric techniques developed recently in this laboratory[21] to examine the hydrolysis of boric acid. The results of such a study in dilute borate solutions should be especially useful in extending the temperature range of pH buffer mixtures and in estimating the pH and other chemical properties of nuclear reactor coolants. Results in more concentrated borate solutions at elevated temperatures should establish more firmly the identity of the polyborate species which are formed in aqueous solutions.

Experimental Section

Materials.—A stock solution of 3.3 *m* KCl prepared from J. T. Baker analyzed reagent was purified by acidifying to pH 3.5 and purging with N_2 to remove CO_2. The fluoride content of the neutralized stock was 7×10^{-6} *m* as determined by the lanthanum fluoride electrode. The protolytic impurities in a 1 *m* solution made from the stock were *ca.* 10^{-5} *m* as determined by titration between pH values of 5 and 9.

The KOH solutions were prepared from KOH pellets and a small stoichiometric amount of $Ba(OH)_2 \cdot 8H_2O$ was added to precipitate the CO_3^{2-} present. The base solutions were stored in paraffin-lined vessels under hydrogen.

The boric acid solutions were prepared from reagent boric acid which had been recrystallized from water. The stock solution was standardized by titration in the presence of mannitol.

Ultrahigh-purity hydrogen (99.999%) from J. T. Baker was used throughout this study.

Potentiometric Apparatus and Techniques.—The pressure cell and electrode assembly employed for this work were described in detail in a previous paper.[21] At the beginning of each experiment the air was removed from the cell by successively pressurizing with hydrogen to 500 psi and venting to the atmosphere. This cycle was repeated three times before addition of hydrogen

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(2) (a) R. R. Servoss and H. M. Clark, *J. Chem. Phys.*, **26**, 1175 (1957); (b) J. D. S. Goulden, *Spectrochim. Acta*, **9**, 657 (1959).

(3) D. E. Bethell and N. Sheppard, *Trans. Faraday Soc.*, **51**, 9 (1955).

(4) J. O. Edwards, G. C. Morrison, V. F. Ross, and J. W. Schultz, *J. Amer. Chem. Soc.*, **77**, 266 (1955).

(5) K. Krishnan, *Proc. Indian Acad. Sci., Sect. A*, **57**, 103 (1963).

(6) J. Goubeau and D. Hummel, *Z. Phys. Chem.*, **20**, 15 (1959).

(7) G. G. Manov, N. J. DeLollis, and S. F. Acree, *J. Res. Nat. Bur. Stand.*, **33**, 287 (1944).

(8) B. B. Owen, *J. Amer. Chem. Soc.*, **56**, 1695 (1934); B. B. Owen and E. J. King, *ibid.*, **75**, 1612 (1943).

(9) N. Ingri, G. Lagerstrom, M. Frydman, and L. G. Sillen, *Acta Chem. Scand.*, **11**, 1034 (1957).

(10) N. Ingri, *ibid.*, **16**, 439 (1962).

(11) N. Ingri, *ibid.*, **17**, 581 (1963).

(12) N. Ingri, *ibid.*, **17**, 573 (1963).

(13) N. Ingri, *Sv. Kem. Tidskr.*, **75**, 199 (1963).

(14) N. Konopik and O. Leberl, *Monatsh.*, **80**, 655 (1949).

(15) J. E. Spessard, *J. Inorg. Nucl. Chem.*, **32**, 2607 (1970).

(16) J. L. Anderson, E. M. Eyring, and M. P. Whittaker, *J. Phys. Chem.*, **68**, 1128 (1964).

(17) J. Osugi, M. Sato, and T. Fujii, *Nippon Kagaku Zasshi*, **89**, 562 (1968).

(18) R. Momii and N. Nachtrieb, *Inorg. Chem.*, **6**, 1189 (1967).

(19) T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1553 (1959).

(20) M. G. Valyashko and E. V. Vlasova, *Geokhimiya*, **7**, 818 (1966).

(21) R. E. Mesmer, C. F. Baes, Jr., and F. H. Sweeton, *J. Phys. Chem.*, **74**, 1937 (1970).

for the equilibration. In the titration experiments, the titrant was delivered from a Zircaloy vessel through platinum capillary tubing to the cell compartment by means of a pressure generator.

Corrections were applied to the data for the small amount of solvent in the gas phase at the higher temperatures. The correction was limited to less than 1% at 290° since the gas-to-liquid volume ratio was small in both compartments.

From the data of Byrnes[22] on the distribution coefficient of boric acid between the aqueous and gas phases, the amount in the gas phase under any of the conditions of the present measurements is expected to be $<0.1\%$. This was verified by analysis of the gas phase over a 1 *m* boric acid solution in 1 *m* KCl at 248°.

Potentiometric Measurements.—The cell representation for experiments conducted in dilute boric acid solutions ($\leq$ 0.02 *m*) is

$$\mathrm{Pt,\ H_2}\left|\begin{array}{l} a\ m\ \mathrm{KCl} \\ \sim 0.02a\ m\ \mathrm{B(OH)_3} \\ \sim 0.01a\ m\ \mathrm{KOH} \end{array}\right\|\left.\begin{array}{l} a\ m\ \mathrm{KCl} \\ 0.02a\ m\ \mathrm{KOH} \end{array}\right|\mathrm{Pt,\ H_2} \tag{3}$$

The electrode compartment on the right contains the reference electrode. In these experiments the concentration of KCl *a* was varied from 0.13 to 1 *m*, and the KOH concentration was generally kept at about $^1/_{50}$th of the KCl concentration. The solution on the left contains boric acid and KOH in an approximate ratio of 2:1. The emf was observed as a function of temperature. The resulting values of the equilibrium quotient for reaction 1 ($Q_{1,1}$) are summarized in Table I and Figure 1, wherein I is the ionic strength, m_B is the total boron molality, and $\bar{n}$ is the ligand number, *i.e.*, the number of OH^- ions bound per $B(OH)_3$ group in solution.

TABLE I

DATA FOR LOG $Q_{1,1}$ AS A FUNCTION OF TEMPERATURE AND IONIC STRENGTH IN KCl SOLUTIONS[a]

T°C	I	m_B	$\bar{n}$	log $Q_{1,1}$	$\sigma_{\log Q_{1,1}}$
99.80	1.02	0.01992	0.873	3.423	0.009
150.62	1.02	0.01994	0.752	2.782	0.008
200.03	1.02	0.01998	0.625	2.344	0.008
250.48	1.02	0.02004	0.514	2.034	0.008
290.03	1.02	0.02009	0.450	1.867	0.008
50.54	1.02	0.01999	0.501	4.298	0.005
100.45	1.02	0.02000	0.485	3.422	0.004
150.87	1.02	0.02002	0.440	2.791	0.004
200.53	1.02	0.02005	0.370	2.344	0.005
250.28	1.02	0.02009	0.300	2.022	0.005
49.94	0.51	0.01000	0.498	4.270	0.005
99.60	0.51	0.01000	0.467	3.389	0.004
150.12	0.51	0.01001	0.391	2.759	0.005
200.23	0.51	0.01003	0.299	2.320	0.006
50.34	0.51	0.01000	0.498	4.260	0.005
99.60	0.51	0.01000	0.467	3.387	0.004
150.12	0.51	0.01001	0.391	2.759	0.005
199.88	0.51	0.01003	0.300	2.323	0.006
250.48	0.51	0.01006	0.227	2.023	0.007
290.28	0.51	0.01007	0.188	1.865	0.007
49.79	0.266	0.01002	0.639	4.234	0.005
99.65	0.266	0.01002	0.587	3.359	0.005
150.12	0.266	0.01003	0.479	2.730	0.006
200.43	0.266	0.01005	0.362	2.293	0.006
250.78	0.266	0.01008	0.274	2.000	0.007
290.43	0.266	0.01009	0.232	1.854	0.008
50.19	0.266	0.01002	0.639	4.226	0.005
99.60	0.266	0.01002	0.587	3.359	0.005
149.99	0.266	0.01003	0.479	2.730	0.006
200.33	0.266	0.01005	0.361	2.291	0.006
251.08	0.266	0.01007	0.272	1.991	0.008
50.14	0.129	0.01203	0.395	4.201	0.005
99.55	0.129	0.01203	0.375	3.340	0.004
149.42	0.129	0.01204	0.323	2.721	0.005
199.93	0.129	0.01206	0.252	2.280	0.005
250.43	0.129	0.01209	0.194	1.989	0.006
290.08	0.129	0.01210	0.162	1.830	0.007
49.59	0.129	0.004839	0.629	4.224	0.005
99.67	0.129	0.004842	0.539	3.341	0.005
150.14	0.129	0.004846	0.392	2.713	0.007
198.23	0.129	0.004854	0.267	2.294	0.008
251.58	0.129	0.004867	0.186	2.006	0.010

[a] $Q_{1,1}$ is the molal equilibrium quotient for reaction 1, I is the ionic strength, m_B is the boron molality, and $\bar{n}$ is the number of OH^- ions bound per $B(OH)_3$ group in solution.

At higher concentrations of boron (0.02–0.6 *m*), where the objective was to determine the species present, titration experiments were conducted in which the KCl concentration was kept at 1.0 *m* and the amount of base added was limited arbitrarily to about 8% of the KCl concentration. Some medium change is inherent in such studies where the equilibria can be observed only at relatviely high concentrations. Data were obtained from titrations at 50.3, 100.0, and 199.8°. These results are summarized in Table II and Figure 2.

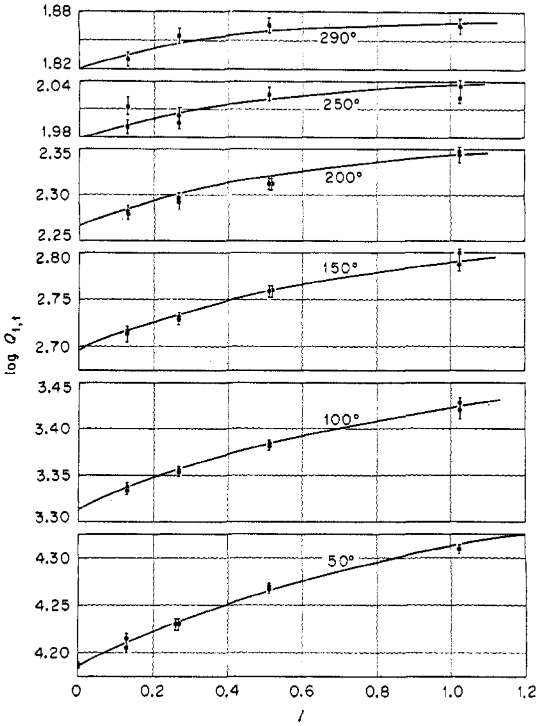

Figure 1.—Log $Q_{1,1}$ as a function of ionic strength. The curves were drawn using the equation in Table III. The dark rectangle at the intercept at 50° is taken from the data of ref 7.

TABLE II

POTENTIOMETRIC DATA ON BORIC ACID SOLUTIONS IN 1 *m* KCl[a]

$\bar{n}$ × 10	m_B × 10	−log [OH⁻]	$\bar{n}$ × 10	m_B × 10	−log [OH⁻]	$\bar{n}$ × 10	m_B × 10	−log [OH⁻]
	50.3°			100.0°			199.8°	
0.0021	0.2686	7.750	0.0032	0.2435	6.341	0.0093	0.3301	4.519
0.351	0.2682	5.799	1.203	0.2423	4.323	0.087	0.3299	4.242
1.643	0.2666	5.018	2.212	0.2413	3.989	0.661	0.3287	3.492
2.861	0.2652	4.698	3.566	0.2400	3.701	1.515	0.3269	3.100
3.969	0.2639	4.474	4.846	0.2387	3.465	2.338	0.3251	2.866
5.244	0.2624	4.244	6.126	0.2374	3.237	3.127	0.3233	2.692
6.563	0.2609	4.005	7.285	0.2362	3.012	3.874	0.3216	2.548
7.749	0.2595	3.752	8.367	0.2348	2.735	4.895	0.3190	2.363
8.945	0.2581	3.381	9.068	0.2336	2.490	5.780	0.3164	2.205
9.808	0.2565	2.768	9.555	0.2319	2.181	6.732	0.3131	2.025
9.972	0.2552	2.360	9.755	0.2300	1.971	7.435	0.3098	1.874
10.01	0.2538	2.124	9.838	0.2276	1.772	8.101	0.3051	1.693
10.01	0.2520	1.925				8.537	0.2997	1.536
9.99	0.2493	1.741				8.789	0.2952	1.435
0.0028	1.0001	8.448	0.0015	1.0008	7.300	0.000	1.0048	5.368
0.130	0.9979	6.325	0.325	0.9953	5.051	0.195	1.0020	4.157
0.491	0.9920	5.728	0.649	0.9900	4.682	0.470	0.9966	3.681
1.133	0.9816	5.302	1.299	0.9795	4.328	0.968	0.9880	3.342
1.940	0.9688	4.987	2.598	0.9590	3.915	1.472	0.9794	3.130
3.037	0.9519	4.684	3.892	0.9394	3.626	2.079	0.9691	2.940
4.085	0.9363	4.451	5.177	0.9205	3.369	2.680	0.9590	2.786
5.117	0.9214	4.242	6.447	0.9025	3.127	3.402	0.9469	2.633
6.177	0.9066	4.035	7.973	0.8808	2.776	4.267	0.9324	2.463
7.247	0.8921	3.808	8.790	0.8683	2.507	5.333	0.9140	2.259
8.126	0.8804	3.590	9.370	0.8561	2.187	6.510	0.8919	2.028
9.310	0.8647	3.135	9.594	0.8473	1.970	7.397	0.8728	1.846
9.753	0.8577	2.753	9.711	0.8357	1.750	7.935	0.8566	1.687
9.961	0.8509	2.323				8.330	0.8392	1.538
9.996	0.8393	1.900						
0.0017	1.977	8.513	0.0010	1.978	7.184	0.0005	1.987	5.752
0.091	1.971	6.792	0.090	1.972	5.750	0.072	1.982	4.610
0.278	1.959	6.257	0.263	1.961	5.247	0.270	1.969	4.032
0.576	1.940	5.859	0.600	1.940	4.837	0.514	1.953	3.731
1.028	1.912	5.523	1.063	1.911	4.527	0.912	1.927	3.448
1.530	1.882	5.258	1.630	1.877	4.267	1.409	1.896	3.215
2.158	1.846	5.004	2.210	1.844	4.066	1.908	1.866	3.043
2.744	1.813	4.812	2.834	1.809	3.885	2.393	1.837	2.903
3.248	1.786	4.664	3.394	1.779	3.743	2.903	1.807	2.773
3.827	1.756	4.513	3.950	1.750	3.614	3.391	1.780	2.661
4.456	1.724	4.360	4.553	1.719	3.484	3.941	1.749	2.545
4.997	1.697	4.237	5.120	1.691	3.365	4.489	1.719	2.434
5.536	1.672	4.118				5.038	1.689	2.327
0.0027	3.843	9.014	0.0014	3.846	7.636	0.000	3.862	6.008
0.042	3.833	7.658	0.042	3.835	6.403	0.050	3.850	4.945
0.195	3.796	6.859	0.136	3.812	5.866	0.230	3.805	4.277
0.421	3.742	6.415	0.342	3.763	5.406	0.445	3.754	3.953
0.722	3.673	6.065	0.621	3.699	5.072	0.707	3.693	3.711
1.075	3.596	5.772	0.886	3.639	4.848	0.992	3.628	2.519
1.411	3.525	5.544	1.163	3.579	4.663	1.274	3.567	3.369
1.765	3.453	5.340	1.418	3.525	4.516	1.526	3.513	3.252
2.120	3.384	5.160	1.718	3.464	4.368	1.888	3.439	3.112
2.458	3.320	5.009	2.015	3.406	4.237	2.361	3.346	2.952
2.804	3.258	4.868	2.337	3.344	4.109	2.717	3.279	2.847
			2.701	3.278	3.976			
0.0028	5.936	9.215	0.0022	5.940	8.033	0.001	5.966	6.464
0.033	5.917	8.132	0.029	5.923	6.907	0.030	5.948	5.409
0.130	5.861	7.450	0.124	5.868	6.236	0.127	5.891	4.756
0.300	5.765	6.986	0.243	5.800	5.886	0.305	5.790	4.341
0.492	5.660	6.665	0.425	5.700	5.566	0.481	5.693	4.092
0.974	5.414	6.121	0.606	5.604	5.336	0.651	5.602	3.917
1.193	5.309	5.928	0.794	5.507	5.144	0.842	5.503	3.757
1.410	5.209	5.755	0.986	5.412	4.976	1.067	5.391	3.612
1.628	5.113	5.598	1.194	5.312	4.820	1.289	5.285	3.470
			1.405	5.214	4.678	1.511	5.183	3.355
			1.624	5.117	4.546	1.737	5.082	3.249
			1.836	5.026	4.429			

[a] $\bar{n}$ is the ligand number and m_B is the boron molality.

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[22] D. E. Byrnes, "Some Physicochemical Studies of Boric Acid Solutions at High Temperatures," Report No. 3713, Westinghouse Corp., Atomic Power Division, 1962.

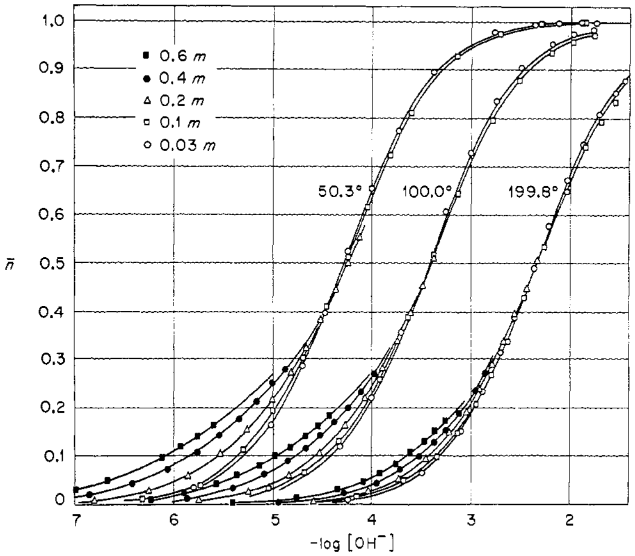

Figure 2.—The effect of boron concentration and temperature on the hydrolysis of boric acid in 1 *m* KCl. The approximate boron concentrations are listed above and the curves were calculated from the equilibrium quotients given by scheme II in Table VI.

Data Reduction and Analyses.—The potentials E for the cell (3) are given by the expression[21]

$$E = (RT/F)\ln([\mathrm{OH^-}]/[\mathrm{OH^-}]_r) - D_{\mathrm{OH}}([\mathrm{OH}]_r - [\mathrm{OH}]) - \Sigma D_i([i]_r - [i]) \quad (4)$$

where [OH] and [i] denote, respectively, the concentration of hydroxide ion and of each other ionic species in the solution. The subscript r refers to the reference solution.

The liquid junction potential is given by the terms on the right containing D_{OH} and D_i which are calculated from the Henderson equation.[21] The limiting equivalent conductances at high temperatures needed for the calculation of D_{OH} and D_i were obtained from Quist and Marshall.[23] Also the approximation that the equivalent conductance of $B(OH)_4^-$ equals that of Cl^- was used, with a large allowance (20%) for error from this assumption in the error analysis. The differences ($[\mathrm{OH^-}]_r - [\mathrm{OH}]$) and ($[i]_r - [i]$) were all small compared to the ionic strength and as a result the maximum liquid junction potentials were about 1 mV.

The data were analyzed and interpreted according to the treatment presented previously for similar studies[24] but here in terms of the average number of OH^- ions, $\bar{n}$, bound to a central moiety ($B(OH)_3$). This was derived from the data using eq 5

$$\bar{n} = ([\mathrm{H^+}] + m_{\mathrm{OH}} - [\mathrm{OH^-}])/m_{\mathrm{B}} \quad (5)$$

where m_{OH} and m_{B} are the stoichiometric concentrations of base and boron in solution. The OH^- concentration in the solution was obtained by a reiterative solution of eq 4. The H^+ concentration, usually a small or negligible contribution to $\bar{n}$, was then obtained from the estimated value of the dissociation quotient for water.[21]

For the evaluation of $Q_{1,1}$ from dilute boric acid experiments (Table I) the following relationship was used

$$\log Q_{1,1} = \log\left[\frac{\bar{n}}{(1-\bar{n})[\mathrm{OH^-}]}\right] \quad (6)$$

The error introduced by neglect of small amounts of polymers on this calculation of the value of log $Q_{1,1}$ was less than the assigned experimental errors in Table I.

The analysis of the data from more concentrated boron solutions in terms of polymeric species was performed by the usual procedure: (1) A set of equilibria

$$x\mathrm{B(OH)_3} + y\mathrm{OH^-} \rightleftharpoons \mathrm{B}_x(\mathrm{OH})_{3x+y}{}^{y-} \quad (7)$$

was chosen, corresponding to a scheme of hydrolysis products. (2) Trial values of the corresponding equilibrium quotients $Q_{x,y}$ were used to calculate a value of $\bar{n}$ for each data point by means of the expression

$$\bar{n}_c = (\Sigma y Q_{x,y}[\mathrm{B(OH)_3}]^x[\mathrm{OH^-}]^y)/m_{\mathrm{B}} \quad (8)$$

wherein the free boric acid concentration was obtained by reiterative solution of the material balance expression

$$[\mathrm{B(OH)_3}] = m_{\mathrm{B}} - \Sigma x Q_{x,y}[\mathrm{B(OH)_3}]^x[\mathrm{OH^-}]^y \quad (9)$$

(3) The $Q_{x,y}$ values were adjusted until the best agreement was obtained between calculated and observed $\bar{n}$ values for all the data. As will be described in the Discussion, a scheme was sought containing a minimum number of species $B_x(OH)_{3x+y}{}^{y-}$ which gives a satisfactory fit to the data.

Weighting of Data.—The data used in the least-squares analyses were weighted according to the assigned experimental errors. Estimated errors were assigned to 17 independently measured quantities involved in solution makeup and in volume, potentiometric, and temperature measurements. The effect of these errors on the quantity ($\bar{n} - \bar{n}_c$) for each data point was obtained by numerical differentiation. Weights (W) were then obtained for use in the least-squares procedure by summing all 17 variances which could then be calculated to obtain the variance in ($\bar{n} - \bar{n}_c$) for each point.

The agreement factor defined in eq 10 was then used as the criterion for the schemes tested. The weight W is the reciprocal

$$\sigma(\bar{n}) = [\Sigma(W(\bar{n} - \bar{n}_c)^2)/(N_o - N_v)]^{1/2} \quad (10)$$

of the variance for the data point and ($N_o - N_v$) is the difference in the number of observations and the number of variables. The $\sigma(\bar{n})$ should be unity when the weights are accurately set and the data fit the model exactly.

Discussion

$B(OH)_3$–$B(OH)_4^-$ Equilibrium.—Figure 1 shows the dependence of log $Q_{1,1}$ for equilibrium 1 on I up to an ionic strength of unity at rounded temperatures.[25] The equilibrium quotient has a small dependence on ionic strength and this dependence decreases as the temperature increases.

A relatively small dependence of the equilibrium quotient on ionic strength was expected since it depends only on the ratio $\gamma_{\mathrm{OH^-}}/\gamma_{\mathrm{B(OH)_4^-}}$. For this ratio we have elected to use the two-term expression

$$\log(\gamma_{\mathrm{OH^-}}/\gamma_{\mathrm{B(OH)_4^-}}) = aI + bI^{3/2} \quad (11)$$

This simple relationship results when the usual Debye–Hückel expression for this ratio is expanded as a power series in I.[26] This expression is not to be construed as a uniquely significant form but simply an adequate description of the data.

A complete analysis of the temperature dependence of the log $Q_{1,1}$ requires a knowledge of the pressure coefficient of the equilibrium quotient since the total pressure in these experiments varies from about 500 to 1900 psi. By experiment it was found that within the experimental error of the measurements (~0.004 unit in log Q) there was no effect of a change of 1300 psi at 50° and 1400 psi at 200°. The upper limit for the absolute magnitude of ΔV for the reaction based on these data is 3–4 cm³/mol. The pressure coefficient is therefore not a factor in setting the standard state for reaction 1 when expressing thermodynamic quantities at pressures below about 150 atm.

Table III shows the least-squares results of analyses

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(23) A. S. Quist and W. L. Marshall, *J. Phys. Chem.*, **69**, 2984 (1965).

(24) C. F. Baes, Jr., N. J. Meyer, and C. E. Roberts, *Inorg. Chem.*, **4**, 518 (1965); R. E. Mesmer and C. F. Baes, Jr., *ibid.*, **6**, 1951 (1967).

(25) The small correction for temperature (less than 2°) was made by fitting the data at a given ionic strength to the expression $\log Q_{1,1} = -A/T + B + CT - D\log T$ and then using the derivative ($d\log Q/d(1/T)$) to calculate the correction in log $Q_{1,1}$.

(26) If the ionic strength dependence for the activity coefficient of each ion has the form $\log\gamma_i = -\alpha I^{1/2}/(1 + \beta I^{1/2}) + \epsilon I$ from Debye–Hückel theory and if β and ϵ are different for the two ions by $\Delta\beta$ and $\Delta\epsilon$, then $\log(\gamma_{\mathrm{OH^-}}/\gamma_{\mathrm{B(OH)_4^-}}) = (\Delta\epsilon - \alpha\Delta\beta)I + (2\alpha\beta\Delta\beta + \alpha\Delta\beta^2)I^{3/2} + \ldots.$

TABLE III

FITS TO THE $Q_{1,1}$ DATA OBTAINED WITH SEVERAL ASSUMPTIONS FOR THE FORM OF THE TEMPERATURE DEPENDENCE

Case	ΔC_p	I	Agreement factor
1	c	$(i_1 + i_2T)I + i_3I^{3/2}$	2.62
2	cT	$(i_1 + i_2T)I + i_3I^{3/2}$	1.96
3[a]	$c_1 + c_2T$	$(i_1 + i_2T)I + i_3I^{3/2}$	0.97
4	$c_1 + c_2T$	$i_1I + i_3I^{3/2}$	1.75

[a] Case 3 gives $\log Q_{1,1} = 1573.21/T + 28.6059 + 0.012078T - 13.2258 \log T + (0.3250 - 0.00033T)I - 0.0912I^{3/2}$.

according to several assumptions for the form of the temperature dependence ΔC_p and for the temperature dependence of the ionic strength terms. The agreement factors (from eq 10) shown are in terms of the estimated experimental error in log Q. Case 3, where the ΔC_p is given linear dependence on temperature and one of the ionic strength terms is made temperature dependent, gives a satisfactory fit to the data. The other cases give poorer fits with pronounced systematic deviations.

Thermodynamic Quantities at Infinite Dilution.—The thermodynamic quantities (Table IV) for reaction 1 were derived from the values of $Q_{1,1}$ at $I = 0$ (*i.e.*, the equilibrium constant $K_{1,1}$) as given by the expression from case 3 in Table III. The uncertainties are three standard deviations as calculated from the experimental errors assigned to individual determinations of log $Q_{1,1}$. This should allow for any systematic errors in the derived thermodynamic quantities introduced by the restriction that ΔC_p changes linearly with temperature.

TABLE IV

THERMODYNAMIC PARAMETERS AT INFINITE DILUTION DERIVED FOR THE EQUILIBRIUM[a]

$$B(OH)_3 + OH^- \rightleftharpoons B(OH)_4^-$$

Temp, °C	$\Delta H°$, kcal mol^{-1}	$\Delta S°$, cal deg^{-1} mol^{-1}	$\Delta C_p°$, cal deg^{-1} mol^{-1}
0	−10.25 ± 0.13	−12.65 ± 0.46	3.9 ± 2.6
25	−10.12 ± 0.08	−12.18 ± 0.27	6.7 ± 2.1
50	−9.92 ± 0.05	−11.54 ± 0.16	9.4 ± 1.6
75	−9.65 ± 0.05	−10.73 ± 0.13	12.2 ± 1.2
100	−9.31 ± 0.05	−9.79 ± 0.14	15.0 ± 0.8
125	−8.90 ± 0.06	−8.73 ± 0.15	17.7 ± 0.7
150	−8.42 ± 0.06	−7.57 ± 0.16	20.5 ± 0.8
175	−7.88 ± 0.06	−6.32 ± 0.16	23.3 ± 1.2
200	−7.26 ± 0.08	−4.98 ± 0.18	26.0 ± 1.6
225	−6.58 ± 0.11	−3.57 ± 0.23	28.8 ± 2.1
250	−5.82 ± 0.15	−2.09 ± 0.32	31.5 ± 2.6
275	−5.00 ± 0.22	−0.56 ± 0.43	34.3 ± 3.0
300	−4.11 ± 0.29	1.04 ± 0.56	37.7 ± 3.5

[a] The uncertainties listed correspond to 3σ, wherein σ is based on the fit obtained with the expression in Table III, derived from case 3.

The value of $\Delta H°_{298}$ in Table IV is −10.12 ± 0.08 kcal mol^{-1}. Although there have been no precision calorimetric measurements of this quantity, Harries[27] has recently reported the nearly identical value of −10.2 ± 0.2 kcal mol^{-1} based on a thermometric titration procedure. As is general for weak acids this heat is less than the heat of neutralization of a strong acid (−13.34 kcal mol^{-1}).[28] The formation of borate is opposed by the $\Delta S°$ and favored by the $\Delta H°$. Since the addition of an OH^- ion to boric acid does not lead to a charge neutralization whereas the neutralization of the hydronium ion does, this probably accounts for the much more negative value of the ΔS for the former reaction compared to the latter (−12.2 *vs.* 19.3 cal deg^{-1} mol^{-1}). The ΔC_p values calculated for reaction 1 using the expression from case 3, Table III, change from 3.9 cal deg^{-1} mol^{-1} at 0° to 37.7 cal deg^{-1} mol^{-1} at 300°.

Polyborate Equilibria.—That polyborates do exist in aqueous solutions is clearly evident in Figure 2 from the dependence of the $\bar{n}$ *vs.* $-\log [OH^-]$ curves on boron concentration above about 0.03 m at each of the three temperatures shown. This was also shown by the previous work at 25° and especially by the extensive work of Ingri in a number of different salt media. Trends with increasing temperature can be seen (Figure 2) in the shift of equilibria to higher hydroxide concentrations and also in the decreasing spread of the curves with boron concentration; these reflect a decreasing amount of polymerization.

The principal species which have been invoked by Ingri in analysis of his data are $B(OH)_4^-$, $B_3O_3(OH)_4^-$, $B_3O_3(OH)_5^{2-}$, and $B_4O_5(OH)_4^{2-}$. In discussing such species we will use the notation (x,y) to represent the species according to the formula $B_x(OH)_{3x+y}{}^{y-}$. Hence, the polyborate species of Ingri become (3,1)-$B_3(OH)_{10}^-$, (3,2)-$B_3(OH)_{11}^{2-}$, and (4,2)-$B_4(OH)_{14}^{2-}$. Of course, since no information can be derived from potentiometric studies alone regarding the hydration of such species, it is optional whether one writes $B_3O_3(OH)_4^-$ or $B_3(OH)_{10}^-$, etc.

Because the present data are of a precision comparable to that of Ingri and, in particular, because they cover a wide temperature range, it should be possible to test rather sensitively for the best scheme of polyborate species. By "best scheme" we mean the simplest scheme consistent with all the data. If such a scheme involves a sufficiently small number of species, it is likely to be the correct one, since an incorrect scheme with the same small number of species is not likely to fit data covering a wide range of conditions. In short, the simplest consistent scheme has the best chance of being the correct one.

The data of Ingri at 25° and our own data indicate that the maximum value of $\bar{n}$ is 1 and hence that no species exists which has a y/x ratio greater than unity. In addition, Ingri's self-medium study at very high concentrations of boron (2.5 M) show that at $\bar{n} > 0.9$ the predominant polyborate species has an $x - y$ difference of 2.0.

Applying these constraints we have limited our analysis to the following array of 14 possible polymeric species: (x,y) = (2,0), (2,1), (2,2); (3,0), (3,1), (3,2), (3,3); (4,0), (4,1), (4,2), (4,3); (5,1), (5,2), (5,3). In each scheme tested we have, of course, included $B(OH)_4^-$, (1,1), which has been well established as the only mononuclear borate species by the data in dilute solutions.

Least-squares analyses of the data at 50°, wherein we assumed that only one polymeric species was formed, not surprisingly failed in every case to give a satisfactory fit, thus indicating agreement with Ingri that at least two polymeric species are formed.

Least-squares analyses were next performed for all the possible pairs from the above array with the data at each of the three temperatures. The results as represented by the agreement factors for the four best

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(27) R. J. N. Harries, *Talanta*, **5**, 1345 (1968).

(28) C. E. Vanderzee and J. A. Swansen, *J. Phys. Chem.*, **67**, 2608 (1963).

TABLE V
FIT OF THREE-SPECIES MODELS EACH
INCLUDING THE (1,1) AND (3,1) SPECIES ALONG WITH A THIRD

Third species	$\sigma(\bar{n})$			Third species	$\sigma(\bar{n})$		
(x,y)	50.3°	100.0°	199.8°	(x,y)	50.3°	100.0°	199.8°
2,1	2.66	1.60	1.44	4,2	2.37	2.18	2.48
3,2	2.02	1.92	2.12	5,3	1.96	2.19	2.56

schemes are shown at each temperature in Table V. The important outcome of this analysis is that the (3,1) species is common to all the best schemes and that at the higher temperatures the (2,1) gives a much better fit as the second polymeric species than does any of the other three species ((4,2), (3,2), and (5,3)). At the lowest temperature, 50.3°, each of the last three species gives a significantly better fit than does the (2,1) species.

The conclusion to be drawn from this analysis then is that while two polymeric species can account for the data at a single temperature, quite clearly more than two are required to account for all the data. Moreover, the identity of the correct species at the highest temperature seems quite clear in view of the uniquely good fit given by the scheme (1,1), (2,1), (3,1). At 50°, however, an additional polymeric species evidently becomes important while the (2,1) species becomes less important. Since it is known from Ingri's "self-medium" results that a polymeric species is formed at high $\bar{n}$ values in which the difference $x - y$ equals 2.0, it is not surprising that improved fits to the lower temperature data are obtained when the (4,2) or the (5,3) species replaces the (2,1) species. Thus it seems clear that the best overall interpretation of the present data should be in terms of the scheme

$$(1,1),\ (2,1),\ (3,1),\ (4,2) \qquad \text{(I)}$$

or the scheme

$$(1,1),\ (2,1),\ (3,1),\ (5,3) \qquad \text{(II)}$$

wherein we expect that the fourth species will be minor at the higher temperatures while the second species will be minor at the lower temperatures.

This expectation is borne out by the least-squares analysis in terms of schemes I and II given in Table VI. The relative importance of each species in fitting the data may be judged by the uncertainty generated for its stability constant. It is noteworthy that the contributions of the (4,2) and the (5,3) species are so similar that replacement of one by the other has no significant effect on the formation quotients of the other species.

TABLE VI
LOG $Q_{x,y}$ VALUES FROM DATA IN 1 *m* KCl

	Log $Q_{x,y}$			
	25°[a]	50.3°	100.0°	199.8°
		Scheme I		
1,1	5.278 ± 0.004	4.301 ± 0.004	3.428 ± 0.002	2.332 ± 0.002
2,1	5.95 ± 0.06	3.8 ± 0.4	3.45 ± 0.06	2.47 ± 0.04
3,1	7.319 ± 0.002	5.98 ± 0.01	4.707 ± 0.008	2.98 ± 0.04
4,2	13.29 ± 0.07	10.75 ± 0.11	8.1 ± 0.2	5.2 ± 0.6
$\sigma(\bar{n})$		2.38	1.55	1.45
		Scheme II		
1,1	5.279 ± 0.003	4.296 ± 0.003	3.427 ± 0.002	2.332 ± 0.002
2,1	6.02 ± 0.04	3.7 ± 0.4	3.43 ± 0.05	2.47 ± 0.04
3,1	7.378 ± 0.003	5.997 ± 0.008	4.712 ± 0.008	2.98 ± 0.04
5,3	19.20 ± 0.08	16.43 ± 0.07	12.9 ± 0.1	8.6 ± 0.5
$\sigma(\bar{n})$		1.95	1.47	1.45

Analytical Expressions

$$\log Q_{1,1}{}^{b} = \frac{1573.21}{T} + 28.8397 + 0.011748T - 13.2258 \log T$$

$$\log Q_{2,2}{}^{d} = \frac{2756.1}{T} - 18.966 + 5.835 \log T$$

$$\log Q_{3,1}{}^{d} = \frac{3339.5}{T} - 8.084 + 1.497 \log T$$

$$\log Q_{4,2}{}^{c} = \frac{12820}{T} - 134.56 + 42.105 \log T$$

$$\log Q_{5,3}{}^{d} = \frac{14099}{T} - 118.115 + 36.237 \log T$$

[a] These values are derived from Ingri in 3 *M* $NaClO_4$. Because of the difference in medium, these quotients are not included in the derivation of the analytical expressions. [b] Based on data from Tables I and II. [c] Based on scheme I. [d] Based on scheme II.

Schemes I and II were also used to fit Ingri's unweighted data in 3 *M* $NaClO_4$ at 25°. Both schemes I and II were found to give fits as good as Ingri's—(1,1), (3,1), (3,2), and (4,2). The values for log $Q_{2,1}$, however, are somewhat higher than expected based on our results in the chloride medium. Regarding the question of which one of these alternative four-species schemes is the correct one, we believe that scheme I or II is a better choice than Ingri's scheme because each is consistent with all the present data and Ingri's is not.

The analytical expression for the temperature dependence of the log $Q_{x,y}$ for each species is also given in Table VI. Thermodynamic parameters calculated from these expressions at 298°K are given in Table VII (uncertainties are 1σ). The variations of the polymer distribution with concentration of boron and with temperature are shown in Figure 3 at 50 and 200°.

TABLE VII

THERMODYNAMIC QUANTITIES FOR BORATE EQUILIBRIA AT 298° IN 1 *m* KCl

$$x\mathrm{B(OH)_3} + y\mathrm{OH^-} \rightleftharpoons \mathrm{B}_x\mathrm{(OH)}_{3x+y}{}^{y-}$$

x,y	ΔH_{298}, kcal mol^{-1}	ΔS_{298}, eu	x,y	ΔH_{298}, kcal mol^{-1}	ΔS_{298}, eu
1,1	-10.3 ± 0.2	-12.0 ± 0.6	4,2	-34 ± 6	-55 ± 19
2,1	-9.2 ± 1	-9.1 ± 3	5,3	-43 ± 4	-58 ± 14
3,1	-14.4 ± 0.3	-17.1 ± 1			

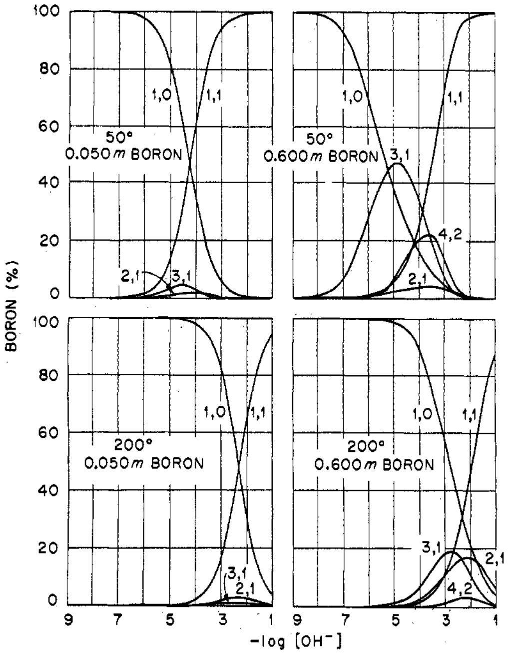


Figure 3.—Distribution of species calculated for solutions containing 0.05 and 0.60 *m* boron at 50 and 200°. The species are represented by the notation (x,y) for the formula $\mathrm{B}_x\mathrm{(OH)}_{3x+y}{}^{y-}$.

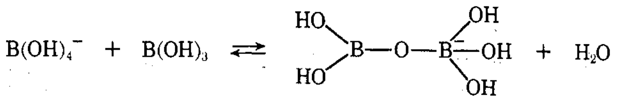
As the temperature increases, there is a decrease in the amount of polyborates at a given boron concentration and $\bar{n}$ value, as was evidenced by the reduction in spread of the curves in Figure 2.

Stability of Polyborates.—The reality of the species $\mathrm{B(OH)_4^-}$ can scarcely be doubted in view of the extensive data here, as well as elsewhere, which support equilibrium 1. The reality of the (3,1) species, while somewhat less certain, is nonetheless highly probable since it was found in all the better schemes at all temperatures in the present study and had previously been proposed by Ingri to interpret his data at 25°. The (2,1) species also seems highly probable in view of the fact that it, along with the (1,1) and the (3,1) species, is uniquely sufficient to explain the present data above 100°. The identity of the fourth species (*e.g.*, (4,2) or (5,3)) is relatively much less certain.

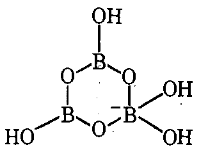
While the sequence of the first two polynuclear species might suggest the successive addition of $\mathrm{B(OH)_3}$ groups to the orthoborate ion

$$\mathrm{B(OH)_4^-} \xrightarrow{\mathrm{B(OH)_3}} \mathrm{B_2(OH)_7^-} \xrightarrow{\mathrm{B(OH)_3}} \mathrm{B_3(OH)_{10}^-}$$

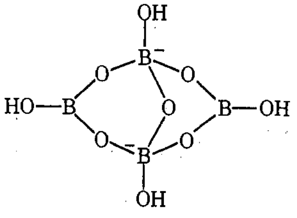
by –OH– bridging, the positive ΔS associated with the first step (2.9 ± 3 eu from Table VII) is in contrast to the negative ΔS associated with the combination of $\mathrm{OH^-}$ ion and $\mathrm{B(OH)_3}$ (-12.0 ± 0.9 eu) and hence would seem more consistent with the formation of an –O– bridge

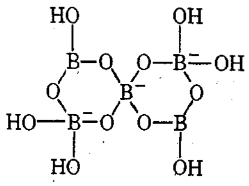


since this is accompanied by the additional entropy contributed by the molecule of water liberated. Moreover, the triborate species is more stable than would be predicted from the stability of the dimer if a stepwise addition process were all that was occurring. This stability of the trimer led Ingri to suggest that it has the ring structure



Such a structure is consistent with the following rules proposed by Edwards and Ross[29] for the structures of crystalline hydrated polyborates. (i) Boron atoms exist in threefold and fourfold coordination, the former having a neutral charge and the latter a 1– charge. (ii) The basic structure of the polyborates is a six-membered ring with alternate boron and oxygen atoms. (iii) To be stable the ring must contain one or two tetrahedral boron atoms. (iv) Other discrete anions may be formed by the fusion of two rings at a tetrahedral boron atom. (v) Long-chain polyanions may be formed from the rings by repeated dehydration. When applied to the polyborate ions which appear to exist in aqueous solution, these rules lead to the above structures for the dimer and trimer and to the following structures for the remaining alternative species





Finally, rule (iii) is consistent with the absence of a cyclic trimer of boric acid ($\mathrm{B_3O_3(OH)_3}$) in aqueous solution.

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[29] J. O. Edwards and V. Ross, *J. Inorg. Nucl. Chem.*, **15**, 329 (1960).