

Equilibrium Studies of Polyanions

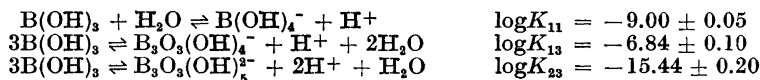
II Polyborates in NaClO₄ Medium

NILS INGRI, GÖSTA LAGERSTRÖM, MINA FRYDMAN, and
LARS GUNNAR SILLÉN

Department of Inorganic Chemistry, The Royal Institute of Technology, Stockholm 70, Sweden

The pH equilibria of boric acid and borate ion have been studied in 3 M sodium (perchlorate) medium at 25°C by electrometric titration using a hydrogen electrode. The total boron concentration B had values between 0.010 and 0.600 M. With the total boron concentration $B \leq 0.025$ M, essentially only the mononuclear species boric acid $B(OH)_3$ and the ion $B(OH)_4^-$ seem to be present; the data for $B > 0.025$ M give evidence also for two polynuclear species, $B_3O_3(OH)_4^-$ and $B_3O_3(OH)_5^{2-}$. (The data may also be explained, though not so well, by assuming $B_3O_3(OH)_4^-$ and $B_4O_4(OH)_5^{2-}$).

Reactions and constants:



In aqueous solution boric acid shows a number of irregularities which indicate the existence of polyborate ions. The aim of this work has been to investigate the pH equilibria of boric acid at various total boron concentrations (B), and from this to deduce the formulas of the predominating species, and the equilibrium constants for their formation.

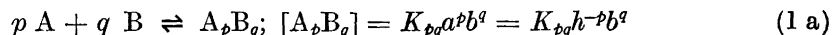
In the following survey we shall for brevity, and to conform with the notations in the general papers¹, use the symbols



The charge of the species A_pB_q will then be $p-$; we shall sometimes write it out, sometimes not. When we apply the law of mass action to the equilibria, we shall write

$$[A] = a = [H^+]^{-1} = h^{-1}; \quad [B] = b$$

and denote by K_{pq} the equilibrium constant for the reaction



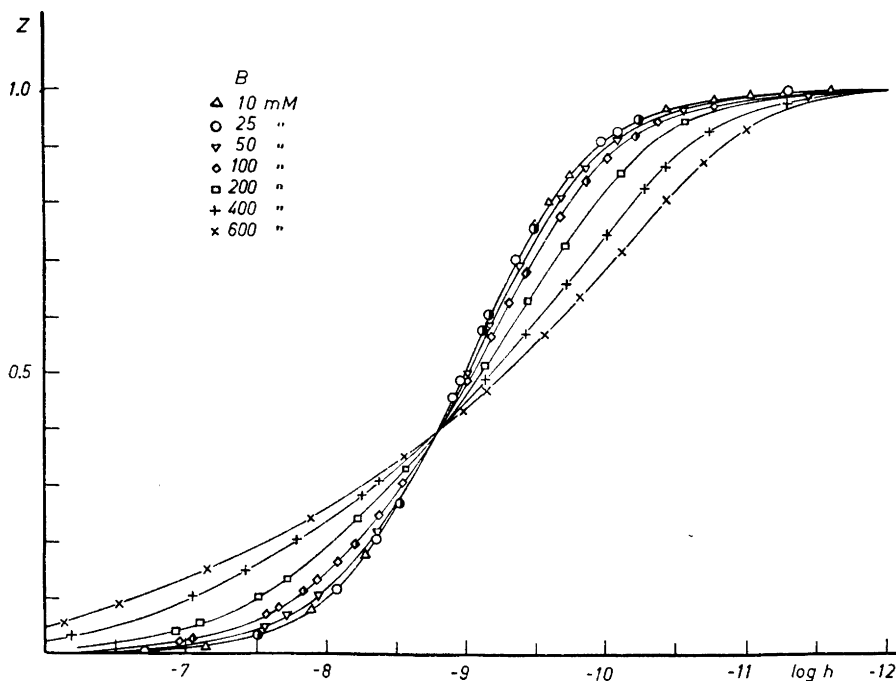
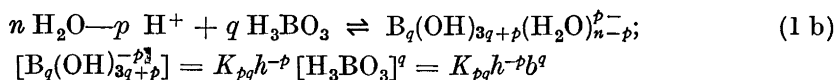


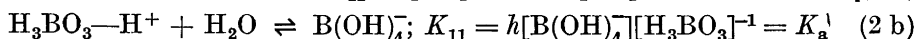
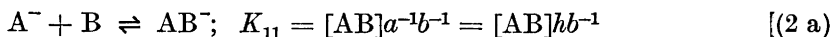
Fig. 1. Average number of OH bound per boron, Z , as a function of $-\log h$. The curve through the points for the two lowest concentrations is that calculated for a normal weak acid with $\log K_a = -9.00$. For the other concentrations smooth curves have been drawn through the experimental points. Half-filled symbols represent points from backtitrations.

OR



The important factors are the number of protons and H_3BO_3 groups. The number of water molecules n cannot be determined from the equilibria.

Then K_{11} for the simplest mononuclear reaction is the acidity constant of boric acid



The behavior of boric acid is well illustrated by Fig. 1, which gives our data for the titration of B (H_3BO_3) with A (Na^+OH^-). Each set of points represents a titration (or rather two duplicate titrations) where the total boron concentration B was maintained constant, at 0.010, 0.025, 0.050, 0.100, 0.200, 0.400 or 0.600 M. The activity factor effects were largely eliminated by keeping $[\text{Na}^+] = 3 \text{ M}$ in all experiments by addition of NaClO_4 . The abscissas represent $\log h$ and the ordinates Z , the average charge per boron atom.

With decreasing B , all of the curves approach the steepest curve, which is the one calculated for a normal weak acid with $\log K_a = -9.00$. At these low concentrations, the only species that need be considered would be B and AB^- . According to Konopik and Leberl², H_3BO_3 should split off two more protons, with $\log K_a$ values of -12.3 and -13.3 ; in our notation A_2B^{2-} and A_3B^{3-} would be formed. With the present data, Z does not seem to exceed 1.0, so there was no definite indication of a dissociation beyond the step AB^- . However, our measurements were not pursued to very high values of the pH.

At higher total concentrations of B , the curves deviate from the mononuclear one; for low values of Z , the solutions are more acidic and at high values of Z more alkaline, than would be expected, if the mononuclear reaction were the only one.

The curves intersect at $Z \approx 0.40$. Such an intersection point was referred to as an isohydric point by Carpéni³. Byé⁴ and Souchay⁵ have pointed out that at such a point the condensation to polyions must be at a maximum.

Before trying to analyse these curves, we shall survey some previous work on borates in solutions.

PREVIOUS SOLUTION DATA

Reversibility of equilibria. Kahlenberg and Schreiner⁶ were the first to check that whatever reactions there may be between monoborate ions, boric acid, and polyborate ions, they must come very rapidly to equilibrium. For instance, no difference was found between a solution prepared from water and $Na_2B_4O_7 \cdot (H_2O)_{10}$, and one prepared by mixing the corresponding amounts of NaOH and H_3BO_3 . All subsequent work, including our own, seems to lead to the same conclusion.

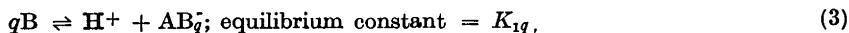
Freezing point data. According to Menzel⁷ the freezing point depression of aqueous solutions of H_3BO_3 is quite normal up to the highest concentrations studied by him, 0.358 M; thus the formation of uncharged polyboric acids, B_q , seems to be negligible. Also freezing point data for $Na+AB^-$ (" $NaBO_2 \cdot (H_2O)_3$ ", $Na+B(OH)_4^-$) up to 2 M solution do not deviate significantly from those of other 1-1 salts like $K^+HCO_3^-$ (Menzel⁷, Menzel and Schulz⁸). Doucet and Rollin⁹ measured the depression of the freezing point of $Na_2SO_4 \cdot (H_2O)_{10}$, which largely eliminates the uncertainty caused by ionic strength effects, and still found no association for B (up to 0.25 M) or $Na+AB^-$ (up to 0.11 M).

Freezing point data for salts like borax, $Na_2B_4O_7 \cdot (H_2O)_{10}$, and $NaB_5O_8 \cdot (H_2O)_5$ in dilute solution indicate that they give chiefly mononuclear species B and AB^- . At higher concentrations there are, however, signs of association (Menzel⁷). Souchay¹⁰ gives curves for the freezing point depression for a series of solutions corresponding to a titration at constant total concentration B (0.10 or 0.25 M) and constant ionic medium. He found that the number of molecules per boron atom is 1.0 at the B and AB^- sides, whereas at the isohydric point it has a minimum value, approximately 0.7 at the higher value for B .

We may thus conclude that the polynuclear species formed are neither polymers B_q nor polymers $(AB)_q^{q-}$ but rather of the mixed type $A_pB_q^{p-}$.

Conductance and pH of pure B solutions. Owen¹¹ has found $\log K_a^0 = -9.236$ for H_3BO_3 (B) at 25°C, using cells without liquid junctions, and extrapolating to zero concentration.

Concentrated solutions of B are more acidic than would correspond to the dissociation of B to H^+ and AB^- . Kolthoff¹² and Thygesen¹³ measured the conductivity of B solutions as a function of concentration. Both assumed that the high acidity is due to the single reaction



and neglected all other species. Kolthoff moreover assumed $q = 4$ and found values for $\log K_{14} \approx -9$ at 18°C. Thygesen tested various values for q ; the equilibrium constant

calculated showed the smallest variation with $q = 3$ ($\log K_{13} \approx -7.5$ at 18°C). However, Thygesen preferred to assume $q = 4$ ($\log K_{14} \approx -7.1$), with a small amount of $q = 2$; probably he was (like Kolthoff) influenced by the net formula of borax. The complexes would then be AB_4^- and AB_2^- ; no attempt was made to estimate the formation constant of the latter.

Stetten¹⁴ measured the pH of various B solutions. Assuming the main reaction (3), he found an average $q = 3.2$ and $\log K_{1,3,2} = -6.86$. From similar pH measurements, Edwards¹⁵ concluded that the main species is AB_3^- with $\log K_{13} \approx -7.5$; deviations at the highest concentrations were ascribed to AB_6^- with $\log K_{16} \approx -6.8$.

Antikainen¹⁶ titrated boric acid of various concentrations B in a number of salt media. From the slope of the titration curve at the isoelectric point (which gives the buffer value of a pure B solution), he calculated the apparent ionization constant of B and concluded the average value for q to be 3.87 ± 0.04 . This would indicate that the main species is AB_4^- , and $\log K_{14} = -7.06$ (extrapolated to zero ionic strength).

Solubilities. From the solubility of B in Na^+AB^- solutions of increasing concentration, Auerbach¹⁷ concluded that the complex formed contained 4 to 5, probably 5, B per Na (B per A^- , in our notation).

pH titrations. A number of pH titrations of B were carried out by Kolthoff and Bosch¹⁸. The data were discussed qualitatively, and the formula AB_5 was favored, in all probability because of the existence of a salt $\text{KB}_5\text{O}_8(\text{H}_2\text{O})_4$. Carpéni and Souchay¹⁹ carried out a series of titrations in 1 M NaCl medium. They obtained curves very much like those given in Fig. 1. These curves gave rise to a rather long discussion in French journals between Carpéni, Souchay and Byé. Whereas Carpéni and Souchay¹⁹ originally concluded that $\text{HB}_2\text{O}_4^-(\text{AB}_2^-)$ and $\text{B}_5\text{O}_8^-(\text{AB}_5^-)$ are formed, Carpéni³ in 1948 coined the name "isohydric point" for such a point of intersection and claimed^{20,21} (1949, 1952) that it proved the existence of a single complex with $Z = 0.40$, which should be $\text{HB}_5\text{O}_9^{2-}(\text{A}_2\text{B}_5^{2-})$. To some extent, Carpéni²² corroborated this conclusion by the preparation of a new solid borate, $\text{K}_2\text{HB}_5\text{O}_9(\text{H}_2\text{O})_3$. On the other hand, Byé⁴ has criticized Carpéni's mathematical arguments. Souchay⁵ prefers to think that the solutions contain the ions $\text{B}_5\text{O}_8^-(\text{AB}_5^-)$ and $\text{B}_4\text{O}_7^{2-}(\text{A}_2\text{B}_4^{2-})$, corresponding to "well known types" of salts.

LIST OF SYMBOLS

| | |
|-----------------|--|
| A | total concentration of A = $-\text{H}^+$, proton deficiency = $-H$ |
| a | "concentration of free A" = h^{-1} |
| B | total concentration of B = $\text{B}(\text{OH})_3$ |
| B_1 | total concentration of mononuclear species, $[\text{B}] + [\text{AB}^-] = [\text{B}(\text{OH})_3] + [\text{B}(\text{OH})_4^-]$. |
| B | a normalized quantity corresponding to B (21) |
| E | the measured emf in mV. |
| E_{ca} | = $E + 59.15 \log h - 59.15 \log K_w - E_j$ (eqn. 5 c) |
| E_{oh} | = $E + 59.15 \log h - E_j$ (eqn. 5 a) |
| E_j | = $17 h - 8[\text{OH}^-]$ (eqn. 7), liquid junction emf |
| H | total analytical excess concentration of hydrogen ions assuming no hydrolysis; in most experiments H was negative |
| h | concentration of free hydrogen ions |

| | |
|------------------|---|
| K_a | acidity constant |
| K_{1q} | equilibrium constant for the formation of AB_q^- (3) |
| K_w | ionic product of water |
| K_{pq} | equilibrium constant for formation of A_pB_q from B and A (1 a) |
| p | number of A in complex A_pB_q |
| \bar{p}_{poly} | average number of A per polynuclear complex |
| q | number of B in complex A_pB_q |
| \bar{q}_{poly} | average number of B per polynuclear complex |
| R^{-1} | average degree of condensation of B |
| R_{poly} | $= (\bar{q}_{poly})^{-1}$ |
| u | a normalized quantity corresponding to a (22) |
| v | a normalized quantity corresponding to b (22) |
| α | constant defined by (21) |
| Z | average number of A per B (4) |
| Z_1 | average number of A per B in the mononuclear species |

Chemical symbols are in Roman, concentrations in italic type. Concentrations and equilibrium constants will be expressed in M (mole/l) throughout (except that in Fig. 1 mM is used for B).

METHOD OF MEASUREMENT

This study of the hydrolysis of boric acid has been carried out as a number of potentiometric titrations at 25°C. In order to use concentrations instead of activities in the formulas for emf and equilibrium constants, all solutions were made 3 M in Na^+ by the addition of sodium perchlorate. For the mathematical analysis we decided to give the experimental data in the form $Z(\log h)_B$ or $\log B(\log h)_Z$.

In each titration the total boron concentration, B , was kept constant while the analytical proton deficiency $A = -H$ was varied. A hydrogen electrode was used to determine h . The quantity Z which is the average negative charge per B and may be described as the average number of hydroxyl ions bound per boric acid unit, was calculated from each point of the titration using the relationship

$$BZ = h - H - K_w h^{-1} \quad (4)$$

where K_w is the ionic product of water in 3 M $NaClO_4$.

The hydrogen electrode was used in combination with the half-cell

SE = Ag, AgCl/0.010 M $AgClO_4$, 2.990 M $NaClO_4$ /3 M $NaClO_4$.

For the cell

— Pt, H_2 (1 atm)/ H^+ // SE +

the measured emf, assuming the activity factors to be constant, may be represented by the equations

$$E = E_{oh} - 59.15 \log h + E_j \quad (5 a)$$

$$E = E_{oa} + 59.15 \log [OH^-] + E_j \quad (5 b)$$

$$E = E_{oa} + 59.15 \log K_w - 59.15 \log h + E_j \quad (5 c)$$

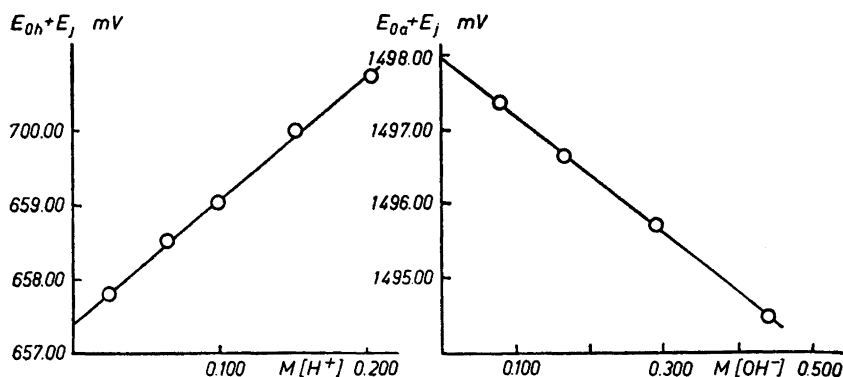


Fig. 2. $E + 59.15 \log h = E_{\text{oh}} + E_j$ as a function of $[\text{H}^+] = h$, and $E - 59.15 \log [\text{OH}^-] = E_{\text{oa}} + E_j$ as a function of $[\text{OH}^-]$.

where E_{oh} and E_{oa} are constants, E_j the liquid junction potential and K_w the ionic product of water in 3 M NaClO_4 .

The ionic product of water was determined in separate titrations by adding a $\text{NaOH} + \text{NaClO}_4$ solution to a $\text{HClO}_4 + \text{NaClO}_4$ solution. The sum $E + 59.15 \log h$ was plotted as a function of h and $E - 59.15 \log [\text{OH}^-]$ as a function of $[\text{OH}^-]$. These functions were approximately straight lines, as shown in Fig. 2, and the slope of the lines was a measure of E_j/h and $E_j/[\text{OH}^-]$. By extrapolation to $h = 0$ and $[\text{OH}^-] = 0$ the constants E_{oh} and E_{oa} were obtained and the ionic product of water in 3 M NaClO_4 was determined as

$$-\log K_w = \frac{E_{\text{oa}} - E_{\text{oh}}}{59.15} = 14.22 \pm 0.02 \quad (6)$$

Ågren²³ has obtained $\log K_w = -14.15 \pm 0.10$ in 3 M sodium perchlorate.

From the slopes E_j/h and $E_j/[\text{OH}^-]$ in the determination of K_w , we found for the liquid junction potential the relation

$$E_j = 17h - 8[\text{OH}^-] \quad (7)$$

where h and $[\text{OH}^-]$ are in M, and E_j in mV. For acid solutions this agrees well with the relation $E_j = +18h$ found by Biedermann and Sillén²⁴.

The constants E_{oh} and E_{oa} were, moreover, determined in most borate titrations; E_{oh} was obtained from points in the acid range where boron is practically not hydrolysed ($Z \approx 0$), and E_{oa} from the points with the highest values of $-\log h$ ($Z \approx 1$).

We could then calculate $-\log h$ for each point of the titration in two different ways from E , using either E_{oh} or E_{oa} .

$$-\log h = \frac{E - E_{\text{oh}} - 17h + 8[\text{OH}^-]}{59.15} \quad (8a)$$

$$-\log h = \frac{E - (E_{\text{oa}} + 59.15 \log K_w) - 17h + 8[\text{OH}^-]}{59.15} \quad (8b)$$

These two values of $-\log h$ were not identical. The difference was very small at low total concentrations B but appreciable at higher B .

Since both h and $[\text{OH}^-]$ in (4) are usually negligible in comparison with $-H$ (except for the highest values of $-\log h$), the variation of the E_0 does not significantly affect the values of Z but only $-\log h$.

The variation of E_{oh} and E_{oa} with the boron concentration

In different titrations with the same B , E_{oh} was always the same within ± 1 mV, but in titrations with different B , E_{oh} decreased with increasing boric acid concentration.

In order to investigate this variation we made a separate titration where B was varied and H was constant and positive. The relationship between E_{oh} and B (Table 1) proved to be approximately linear

$$E_{\text{oh}} = \text{const} - 8 B \quad (9 \text{ a})$$

if E_{oh} is expressed in mV and B in M.

This deviation is probably due to a variation of the activity coefficients with the ionic medium. If some more acidic species like H_4BO_3^+ were formed, this would cause a trend in the opposite direction.

In titrations with the same B , E_{oa} was the same within ± 1 mV but varied in titrations with different B . In a separate titration, where $[\text{OH}^-]$ was constant ($Z \approx 1.00$) and B was varied, we found the relationship between E_{oa} and B to be approximately linear (Table 1)

$$E_{\text{oa}} = \text{const} + 5 B \quad (9 \text{ b})$$

if E_{oa} is expressed in mV and B in M. This deviation must also be due to a variation of the activity factors. The formation of species like $\text{H}_3\text{BO}_4^{2-}$ would cause a deviation in the other direction.

Table 1. The variation of E_{oa} and E_{oh} with B .

| The variation of E_{oh} at $[\text{H}^+] = 0.0260 \text{ M}$ | | The variation of E_{oa} at $[\text{OH}^-] = 0.0500 \text{ M}$ | |
|--|----------------------------|---|----------------------------|
| $B \text{ M}$ | $E_{\text{oh}} \text{ mV}$ | $B \text{ M}$ | $E_{\text{oa}} \text{ mV}$ |
| 0.0000 | 657.81 | 0.0000 | 1498.44 |
| 0.0545 | 657.36 | 0.0545 | 1498.63 |
| 0.1000 | 657.03 | 0.1000 | 1498.88 |
| 0.1384 | 656.72 | 0.1384 | 1499.10 |
| 0.2000 | 656.22 | 0.2000 | 1499.45 |
| 0.1471 | 655.84 | 0.2470 | 1499.70 |
| 0.2842 | 655.52 | | |
| 0.4000 | 654.69 | 0.4000 | 1500.03 |
| 0.5000 | 653.83 | | |
| 0.6000 | 653.20 | 0.6000 | 1501.34 |

EXPERIMENTAL DETAILS

Reagents and analysis

Sodium perchlorate was prepared by carefully neutralizing recrystallized Na_2CO_3 (p.a.) with perchloric acid (p.a.). The sodium perchlorate solution was concentrated until a thin layer of the salt formed on the surface, filtered while hot, and the filtrate stirred vigorously while cooling. The salt crystallized well with one molecule of water. The salt was recrystallized twice, after which no Cl^- , ClO_3^- or silica could be detected, and was then found to be free from acid impurities. The NaClO_4 solutions were analysed by evaporating a known weight of solution at 120°C and drying at the same temperature until a constant weight was attained.

Perchloric acid. The ordinary p.a. product was used, and was standardized against KHCO_3 and standard NaOH . The determinations with different standard substances agreed within $\pm 0.1\%$.

Sodium hydroxide. A 50 % solution was prepared from the commercial p.a. material, filtered through a G4 Jena glass filter, and stored in a polyethylene bottle. Dilute solutions were prepared from de-aerated water and 50 % stock solution. The alkali solutions were standardized against HClO_4 which had been standardized in turn against KHCO_3 . Hydrazine sulfate and acid potassium iodate have also been used for the standardizations giving values in good agreement ($\pm 0.1\%$) with the HClO_4 value.

The carbonate ion concentration in the NaOH solutions used was about 0.1 % of the NaOH concentration, as estimated from the difference between the methyl red and the phenolphthalein points in a titration.

Boric acid. The ordinary crystallized p.a. product was used. A stock solution was prepared by weighing a known amount of boric acid and diluting with water to a certain volume. The concentration was checked by adding mannitol and titrating with standard alkali using α -naphtholphthalein as indicator.

Silver perchlorate solutions were prepared by adding a slight excess of Ag_2O to a boiling HClO_4 solution. The excess of Ag_2O was filtered off, and the Ag^+ content in the solution was determined by Volhard's method using a silver wire as a standard.

Titration vessel solution (S_0). Measured quantities of boric acid, perchloric acid, and sodium perchlorate were added to a volumetric flask to give the concentrations wanted. After waiting until the temperature had become equalized, the flask was carefully filled to the mark with de-aerated water.

Buret solution (T). The procedure was the same as described for the titration vessel solution, S_0 , except that the solutions were mixed in a CO_2 -free N_2 atmosphere.

Apparatus

Since the work was carried out with alkaline solutions, all glassware may be appreciably attacked by alkali. To avoid this, polythene or alkali resistant glass vessels may be used. Lagerström²⁵ pointed out in his study of silicate solutions that polythene has so many disadvantages that the use of Jena-Geräte glass was to be preferred. He estimated that an amount of silica corresponding to 0.03 mM is dissolved from the glass vessel during a titration similar to ours (to $\text{pH} \approx 12$). Since this is negligible, Jena-Geräte glass has been used all through this work.

The electrode vessel and the salt bridge were of the "Wilhelm" type described in previous papers²⁶ from this institute.

Commercially available hydrogen was purified by passing it through a) a column of activated copper at around 180°C to remove traces of oxygen, b) a wash bottle containing 10 % H_2SO_4 to remove alkaline impurities, and c) a wash bottle with 10 % NaOH to remove acidic impurities. Before entering the titration vessel, the gas was saturated with water by passage through two wash bottles containing the ionic medium, 3.0 M NaClO_4 .

The *hydrogen electrode* was prepared according to Bates²⁷ (p. 166). Immediately after the preparation, the electrode was electrolysed as the cathode in 0.1 M H_2SO_4 for 20 min. An even distribution of H_2 bubbles on the electrode surface was good evidence of a completely active surface. Electrodes with an uneven distribution of bubbles were immediately taken out of service. A new hydrogen electrode was prepared for each titration,

and the electrode gave a steady potential after 10 to 20 min, regardless of the velocity of the hydrogen stream.

The *silver-silver chloride electrode* was prepared by electro-depositing Ag on a Pt foil and afterwards electrolyzing the silver electrode in dilute HCl.

The emf measurements were made with a Jensen compensator (type 10A) and a Multiflex galvanometer. The compensator could be read to a hundredth of a mV.

Titration procedure

The titrations were carried out at $25.0 \pm 0.1^\circ\text{C}$ with the cell and the titration vessel immersed in an oil thermostat and the whole equipment in a thermostated room at $25.0 \pm 0.5^\circ\text{C}$.

For each titration two solutions were prepared: S_0 (in the titration vessel) and T (in the buret), with the following analytical composition.

| Solutions | [Na ⁺] M | B M | H M | [ClO ₄ ⁻] M |
|----------------------------|----------------------|-----|--------------------------|------------------------------------|
| Titration vessel (S_0) | 3 | B | $C_1(C_1\text{M H}^+)$ | $3 + C_1$ |
| Buret (T) | 3 | B | $-C_2(C_2\text{M OH}^-)$ | $3 - C_2$ |

The manner of titration is best described by an example, and Table 2 gives a representative part of a titration with $B = 0.100\text{ M}$.

In the titration shown in Table 2, the analytical hydrogen ion concentration was checked with aid of the points obtained in the unhydrolysed acid range and in the alkaline part with $Z = 1$. The end-point was found by Gran's method²⁸ of extrapolation. The two straight lines, corresponding to free H^+ and free OH^- , intersect in two points on the volume axis. The total hydrogen ion concentration obtained from the intersection of the H^+ line agreed very well with that calculated from the analytical concentrations of solutions S_0 and T. The distance between the intersections of the H^+ and OH^- lines on the volume axis corresponds to the amount of A, necessary to give the species AB^- .

In some cases the hydrolysed solution was back-titrated with acid; the points $Z(\log h)$ always fell on the same curve as the points obtained by adding alkali, indicating that the equilibria are completely reversible. (Half-filled symbols in Fig. 1.)

TREATMENT OF THE DATA AND RESULTS

Using the eqns. (4), (8 a) and (8 b), the $Z(\log h)_B$ curves have been obtained from the emf measurements. The data are shown in Table 3 and plotted in Fig. 1.

For values of $B \leq 0.025$ essentially the same $Z(\log h)$ curve was obtained, which indicates that for these low boron concentrations only the mononuclear species $\text{B} = \text{B}(\text{OH})_3$ and $\text{AB}^- = \text{B}(\text{OH})_4^-$ need be considered. Moreover, the curve has the shape characteristic of equilibria with only two mononuclear species.

Table 2. A titration with $B = 0.100$ M

S_0 : $H_3BO_3 = 0.100$ M, $HClO_4 = 0.0434$ M, $NaClO_4 = 3.000$ M, 50.0 ml
 T_1 : $H_3BO_3 = 0.100$ M, $NaOH = 0.1083$ M, $NaClO_4 = 2.892$ M, v_1 ml
 T_2 : $H_3BO_3 = 0.100$ M, $NaOH = 0.3777$ M, $NaClO_4 = 2.622$ M, v_2 ml

Atmospheric pressure = 772.0 mm Hg. The vapor pressure of pure water at 25.0°C = 23.7 torr. This value has been used instead of that valid for 3 M $NaClO_4$. The correction 29.58 $\log p_{H_2O}$ is +0.20 mV. E_{oh} from the first acid points (8 a) = 658.20 mV. $E_{oa} = 1500.00$ mV at $Z \approx 1.0$; E_{oh} from E_{oa} and K_w (8 b) = 658.89 mV.

| v_1 ml | v_2 ml | Total volu- me | E mV | E_{corr} mV | -log h calc with | | $K_w h^{-1}$ 10^{-3} M | $H \cdot 10^{-3}$ M | $\frac{h-H-K_w h^{-1}}{B} = Z$ |
|-------------|-------------|----------------------|-----------|------------------|--------------------|--------------------------------|-----------------------------|------------------------|--------------------------------|
| | | | | | E_{oh} | $E_{oa} + 59.15$ $\log K_w$ | | | |
| 0.00 | | 50.00 | 739.00 | 739.20 | | | | 43.40 | |
| 3.52 | | 53.52 | 745.54 | 745.74 | | | | 33.42 | |
| 7.13 | | 57.13 | 753.66 | 753.66 | | | | 24.47 | |
| 10.56 | | 60.56 | 762.85 | 763.05 | | | | 16.95 | |
| 16.08 | | 66.08 | 788.10 | 788.30 | | | | 6.48 | |
| 20.04 | | 70.04 | 1011.07 | 1011.27 | | | | | |
| | 1.28 | 71.32 | 1107.00 | 1107.20 | 7.590 | 7.580 | | - 6.78 | 0.068 |
| | 2.28 | 72.32 | 1125.29 | 1125.49 | 7.899 | 7.890 | | -11.90 | 0.119 |
| | 3.27 | 73.31 | 1139.00 | 1139.20 | 8.131 | 8.121 | | -16.84 | 0.168 |
| | 5.19 | 75.24 | 1154.04 | 1154.24 | 8.440 | 8.430 | | -26.05 | 0.261 |
| | 7.52 | 77.56 | 1174.10 | 1174.30 | 8.724 | 8.715 | | -36.62 | 0.366 |
| | 9.32 | 79.36 | 1185.09 | 1185.29 | 8.910 | 8.900 | | -44.35 | 0.444 |
| | 12.28 | 82.32 | 1201.05 | 1201.25 | 9.179 | 9.170 | | -56.34 | 0.563 |
| | 13.92 | 83.96 | 1209.20 | 1209.40 | 9.317 | 9.308 | 0.01 | -62.62 | 0.626 |
| | 15.33 | 85.37 | 1216.21 | 1216.41 | 9.436 | 9.426 | 0.02 | -67.82 | 0.678 |
| | 16.84 | 86.88 | 1223.75 | 1223.95 | 9.563 | 9.554 | 0.02 | -73.20 | 0.732 |
| | 18.10 | 88.14 | 1230.38 | 1230.58 | 9.675 | 9.666 | 0.03 | -77.56 | 0.775 |
| | 20.04 | 90.08 | 1241.66 | 1241.86 | 9.866 | 9.857 | 0.04 | -84.02 | 0.838 |
| | 21.32 | 91.36 | 1250.71 | 1250.91 | 10.019 | 10.009 | 0.06 | -88.14 | 0.881 |
| | 23.39 | 93.43 | 1271.74 | 1271.94 | 10.374 | 10.365 | 0.14 | -94.55 | 0.944 |
| | 24.54 | 94.58 | 1295.88 | 1296.08 | 10.782 | 10.773 | 0.37 | -98.00 | 0.973 |
| | 26.22 | 96.26 | 1352.68 | 1352.88 | | | | -102.88 | |
| | 29.38 | 99.42 | 1385.48 | 1385.68 | | | | -111.61 | |
| | 34.75 | 104.79 | 1405.00 | 1405.20 | | | | -125.25 | |
| | 40.08 | 110.12 | 1414.98 | 1415.18 | | | | -137.47 | |
| | 45.21 | 115.25 | 1421.35 | 1421.55 | | | | -148.16 | |
| | 49.77 | 119.81 | 1425.54 | 1425.74 | | | | -156.90 | |
| | 60.12 | 130.16 | 1432.25 | 1432.45 | | | | -174.46 | |

For concentrations > 0.025 M, different $Z(\log h)$ curves were obtained for different values of B . This shows that besides the mononuclear complexes there must also be polynuclear complexes.

The first step in our calculation has been an approximate determination of the average number of boron atoms and the average charge of the polynuclear complexes, \bar{q}_{poly} and \bar{p}_{poly} .

With aid of the values \bar{q}_{poly} and \bar{p}_{poly} , we have then tested various hypotheses and determined the equilibrium constant for the most probable complexes.

Table 3. *Experimental data.* The $-\log h$ values calculated with ($E_{\text{ca}} + 59.15 \log K_w$) are omitted in the table for $B = 0.010, 0.020, 0.025$ and 0.050 M since these values are approximately the same as calculated with E_{oh} .

| $B = 0.010$ M | | $B = 0.020$ M | | $B = 0.025$ M | | $B = 0.050$ M | | $B = 0.100$ M | |
|---------------|--|---------------|--|---------------|--|---------------|--|---------------|---|
| Z | $-\log h$ calc. with E_{oh} | Z | $-\log h$ calc. with E_{oh} | Z | $-\log h$ calc. with E_{oh} | Z | $-\log h$ calc. with E_{oh} | Z | $-\log h$ calc. with $E_{\text{ca}} + 59.15 \log K_w$ |
| 0.010 | 7.137 | 0.052 | 7.757 | 0.033 | 7.510 | 0.006 | 6.538 | 0.024 | 7.090 |
| 0.062 | 7.794 | 0.107 | 8.065 | 0.116 | 8.073 | 0.047 | 7.573 | 0.068 | 7.590 |
| 0.174 | 8.293 | 0.200 | 8.367 | 0.202 | 8.361 | 0.068 | 7.717 | 0.108 | 7.833 |
| 0.265 | 8.541 | 0.302 | 8.608 | 0.287 | 8.572 | 0.105 | 7.938 | 0.119 | 7.899 |
| 0.530 | 9.052 | 0.398 | 8.792 | 0.459 | 8.843 | 0.105 | 7.960 | 0.131 | 7.939 |
| 0.609 | 9.194 | 0.513 | 9.996 | 0.488 | 8.874 | 0.182 | 8.293 | 0.168 | 8.131 |
| 0.705 | 9.385 | 0.803 | 9.587 | 0.583 | 9.141 | 0.191 | 8.269 | 0.202 | 8.232 |
| 0.752 | 9.488 | 0.986 | 10.657 | 0.604 | 9.160 | 0.217 | 8.372 | 0.261 | 8.440 |
| 0.847 | 9.751 | | | 0.700 | 9.354 | 0.298 | 8.558 | 0.300 | 8.530 |
| 0.896 | 9.946 | | | 0.749 | 9.490 | 0.345 | 8.680 | 0.366 | 8.724 |
| 0.944 | 10.238 | | | 0.911 | 9.973 | 0.371 | 8.719 | 0.444 | 8.910 |
| 0.985 | 10.769 | | | 0.925 | 10.091 | 0.461 | 8.902 | 0.563 | 9.179 |
| 0.993 | 10.911 | | | 0.965 | 10.441 | 0.459 | 8.920 | 0.607 | 9.254 |
| 0.999 | 11.241 | | | 0.984 | 10.801 | 0.586 | 9.161 | 0.626 | 9.317 |
| 1.002 | 11.416 | | | 1.001 | 11.317 | 0.611 | 9.203 | 0.678 | 9.436 |
| | | | | | | 0.690 | 9.387 | 0.732 | 9.563 |
| | | | | | | 0.709 | 9.445 | 0.775 | 9.675 |
| | | | | | | 0.812 | 9.683 | 0.838 | 9.666 |
| | | | | | | 0.869 | 9.864 | 0.881 | 10.009 |
| | | | | | | 0.917 | 10.081 | 0.897 | 10.073 |
| | | | | | | 0.972 | 10.583 | 0.944 | 10.374 |
| | | | | | | 0.990 | 11.433 | 0.973 | 10.782 |
| | | | | | | 0.991 | 11.835 | | |
| | | | | | | 0.999 | 12.031 | | |

Table 3. Continued.

| Z | B = 0.200 M | | B = 0.400 M | | B = 0.600 M | |
|-------|-------------------------------------|--|-------------------------------------|--|-------------------------------------|--|
| | $-\log h$ calc. with E_{oh} | $-\log h$ calc. with $E_{oa} + 59.15 \log K_w$ | $-\log h$ calc. with E_{oh} | $-\log h$ calc. with $E_{oa} + 59.15 \log K_w$ | $-\log h$ calc. with E_{oh} | $-\log h$ calc. with $E_{oa} + 59.15 \log K_w$ |
| 0.040 | 6.927 | 6.894 | 0.030 | 6.192 | 0.032 | 5.820 |
| 0.050 | 7.085 | 7.050 | 0.035 | 6.298 | 0.033 | 6.020 |
| 0.052 | 7.104 | | 0.064 | 6.691 | 0.090 | 6.420 |
| 0.099 | 7.484 | 7.451 | 0.066 | 6.680 | 0.102 | 6.592 |
| 0.100 | 7.506 | | 0.102 | 7.051 | 0.148 | 7.042 |
| 0.130 | 7.723 | 7.688 | 0.119 | 7.173 | 0.177 | 7.276 |
| 0.148 | 7.812 | | 0.136 | 7.337 | 0.240 | 7.771 |
| 0.173 | 7.913 | 7.880 | 0.149 | 7.429 | 0.266 | 7.952 |
| 0.186 | 8.020 | 7.984 | 0.178 | 7.619 | 0.283 | 8.065 |
| 0.237 | 8.231 | | 0.201 | 7.788 | 0.348 | 8.453 |
| 0.241 | 8.223 | 8.190 | 0.219 | 7.921 | 0.369 | 8.564 |
| 0.263 | 8.356 | 8.320 | 0.222 | 7.904 | 0.405 | 8.751 |
| 0.304 | 8.457 | 8.425 | 0.281 | 8.259 | 0.431 | 8.872 |
| 0.327 | 8.572 | | 0.304 | 8.384 | 0.466 | 9.040 |
| 0.357 | 8.695 | 8.661 | 0.333 | 8.505 | 0.536 | 9.332 |
| 0.374 | 8.700 | 8.667 | 0.374 | 8.700 | 0.565 | 9.453 |
| 0.411 | 8.837 | | 0.388 | 8.774 | 0.631 | 9.697 |
| 0.427 | 8.861 | 8.828 | 0.415 | 8.879 | 0.653 | 9.786 |
| 0.482 | 9.022 | 8.989 | 0.471 | 9.093 | 0.715 | 9.999 |
| 0.511 | 9.134 | | 0.485 | 9.152 | 0.733 | 10.067 |
| 0.550 | 9.209 | 9.177 | 0.545 | 9.365 | 0.793 | 10.269 |
| 0.557 | 9.288 | 9.253 | 0.567 | 9.443 | 0.803 | 10.324 |
| 0.603 | 9.351 | 9.319 | 0.597 | 9.543 | 0.862 | 10.528 |
| 0.626 | 9.438 | | 0.642 | 9.691 | 0.872 | 10.578 |
| 0.661 | 9.563 | 9.528 | 0.655 | 9.720 | 0.933 | 10.874 |
| 0.661 | 9.501 | 9.468 | 0.711 | 9.866 | | |
| 0.728 | 9.726 | | 0.717 | 9.931 | | |
| 0.730 | 9.686 | 9.653 | 0.745 | 10.010 | | |
| 0.753 | 9.811 | 9.776 | 0.787 | 10.158 | | |
| 0.849 | 10.053 | 10.020 | 0.799 | 10.192 | | |
| 0.852 | 10.117 | 10.082 | 0.826 | 10.280 | | |
| 0.860 | 10.123 | | 0.865 | 10.434 | | |
| 0.941 | 10.532 | | 0.868 | 10.448 | | |
| 0.947 | 10.576 | 10.541 | 0.901 | 10.573 | | |
| 0.989 | 11.301 | | 0.929 | 10.740 | | |
| | | | 0.983 | 10.804 | | |
| | | | 0.990 | 11.583 | | |

The average charge and the average number of boron atoms in the polynuclear complexes.

It has been possible to obtain the average composition of the polynuclear complexes from the experimental $Z(\log h)_B$ curves without any special assumptions about the complexes formed using the formulas given by Sillén²⁰, which give the quantities B_1 and R .

$$\log B_1 = \log B - \int_{-11.60}^{\log h} \left[(Z_1 - Z) - \left(\frac{\partial Z}{\partial \log B} \right)_h \right] d \log h \text{ at constant } B \quad (10)$$

$$R = 1 - \int_{-11.60}^{\log h} \left(\frac{\partial Z}{\partial \log B} \right)_h d \log h \text{ at constant } B \quad (11)$$

where B is the total concentration of boron, B_1 the boron concentration in the mononuclear species, R the reciprocal of the average degree of condensation of B and $Z_1 =$ the average number of A per B in the mononuclear species.

The average charge of the polynuclear complexes \bar{p}_{poly} , has been calculated from the equation

$$\bar{p}_{\text{poly}} = \frac{Z_{\text{poly}}}{R_{\text{poly}}} = \frac{BZ - B_1 Z_1}{BR - B_1} \quad (12)$$

and the average number of boron, \bar{q}_{poly} , from

$$\bar{q}_{\text{poly}} = \frac{1}{R_{\text{poly}}} = \frac{B - B_1}{BR - B_1} \quad (13)$$

where $BZ =$ the number of moles A that are bound to B per liter, $B_1 Z_1 =$ the number of moles A that are bound to B in the mononuclear species, and $BR =$ the sum of the molar concentration of B and of all complexes containing boron.

Previous solution data, especially the freezing-point data⁹, make it appear very likely that the species at the highest and lowest pH are mononuclear, *i.e.* H_3BO_3 (B) at the acid, and $\text{B}(\text{OH})_4^-$ (AB) at the alkaline end. In the above formulas borate is assumed to be mononuclear with $Z = 1.00$ for $-\log h \geq 11.60$.

The integration has been carried out numerically from the experimental $Z(\log h)$ curves at given value of B . As is clear from the above formulas, the determination of R is a step in calculating B_1 . Keeping h constant, the slope $(\partial Z / \partial \log B)_h$ from any experimental value for B was assumed to be the average of the difference quotients $(\Delta Z / \Delta \log B)$ for the two neighboring intervals.

An example of the various steps in the calculation is given in Table 4. As follows from (10) and (11), the values of B_1 and R have a minimum at the intersection point. B_1 approaches the value B , and R approaches 1 at the highest values of h when $Z \approx 0$; this fact corroborates our assumption that boric acid and borate ion are chiefly mononuclear at $Z = 0$ and $Z = 1.00$. In Table 4, natural logarithms were used when (10) and (11) were applied.

Table 5 gives \bar{p}_{poly} and \bar{q}_{poly} for $B = 0.100, 0.200,$ and 0.400 M at various $-\log h$. The data in this table indicate that the most probable complexes in the solution contain three boron and have the charge one or two; however, the

Table 4. Analysis of the Z ($\log h$) curve for $B = 0.100$ M

| $-\log h$ | $Z_1 - Z$ | $-\left(\frac{\partial Z}{\partial \ln B}\right)_a$ | $\Delta \ln a$ | $\Delta \ln B/B_1$ | $\ln B/B_1$ | $\ln B_1$ | $\log B_1$ | B_1 | $\Delta (1-R)$ | R | BR | q_{poly} | p_{poly} |
|-----------|-------------|---|----------------|--------------------|-------------|-----------|------------|-------|----------------|-------|------|-------------------|-------------------|
| 11.80 | 0.000 | | 0.461 | 0.001 | 0.001 | -2.304 | -1.000 | 99.9 | 0.001 | 1.000 | 99.9 | | |
| 11.60 | 0.002 | 0.002 | 0.461 | 0.003 | 0.004 | -2.307 | -1.002 | 99.6 | 0.001 | 0.999 | 99.8 | 2.0 | 0.5 |
| 11.40 | 0.003 | 0.004 | 0.461 | 0.004 | 0.008 | -2.311 | -1.004 | 99.2 | 0.002 | 0.998 | 99.8 | 2.0 | 0.5 |
| 11.20 | 0.006 | 0.006 | 0.461 | 0.005 | 0.013 | -2.316 | -1.006 | 98.7 | 0.003 | 0.996 | 99.6 | 1.8 | 0.6 |
| 11.00 | 0.007 | 0.004 | 0.461 | 0.007 | 0.020 | -2.323 | -1.009 | 98.0 | 0.006 | 0.994 | 99.4 | 1.8 | 0.9 |
| 10.80 | 0.010 | 0.009 | 0.461 | 0.011 | 0.031 | -2.334 | -1.014 | 97.0 | 0.010 | 0.991 | 99.1 | 2.0 | 1.1 |
| 10.60 | 0.013 | 0.016 | 0.461 | 0.017 | 0.048 | -2.351 | -1.021 | 95.3 | 0.016 | 0.985 | 98.5 | 2.1 | 1.3 |
| 10.40 | 0.017 | 0.027 | 0.461 | 0.025 | 0.073 | -2.376 | -1.032 | 93.0 | 0.023 | 0.975 | 97.5 | 2.4 | 1.5 |
| 10.20 | 0.022 | 0.041 | 0.461 | 0.035 | 0.108 | -2.411 | -1.047 | 89.8 | 0.026 | 0.959 | 95.9 | 2.7 | 1.6 |
| 10.00 | 0.032 | 0.057 | 0.461 | 0.042 | 0.150 | -2.453 | -1.065 | 86.1 | 0.027 | 0.910 | 91.0 | 2.8 | 1.5 |
| 9.80 | 0.045 | 0.055 | 0.461 | 0.049 | 0.199 | -2.502 | -1.086 | 82.0 | 0.028 | 0.883 | 88.3 | 2.9 | 1.5 |
| 9.60 | 0.052 | 0.062 | 0.461 | 0.053 | 0.252 | -2.555 | -1.109 | 77.7 | 0.024 | 0.855 | 85.5 | 2.9 | 1.4 |
| 9.40 | 0.055 | 0.061 | 0.461 | 0.048 | 0.300 | -2.603 | -1.130 | 74.1 | 0.014 | 0.831 | 83.1 | 2.9 | 1.2 |
| 9.20 | 0.048 | 0.042 | 0.461 | 0.032 | 0.332 | -2.635 | -1.144 | 71.8 | 0.005 | 0.817 | 81.7 | 2.9 | 1.2 |
| 9.00 | 0.027 | 0.020 | 0.461 | 0.011 | 0.343 | -2.646 | -1.149 | 71.0 | -0.006 | 0.812 | 81.2 | 2.8 | 1.1 |
| 8.80 | ± 0.000 | ± 0.000 | 0.461 | -0.011 | 0.332 | -2.635 | -1.144 | 71.8 | -0.015 | 0.818 | 81.8 | 2.8 | 1.1 |
| 8.60 | -0.024 | -0.024 | 0.461 | -0.030 | 0.302 | -2.605 | -1.131 | 74.0 | 0.021 | 0.833 | 83.8 | 2.8 | 1.0 |
| 8.40 | -0.040 | -0.041 | 0.461 | -0.042 | 0.260 | -2.563 | -1.113 | 77.1 | -0.024 | 0.854 | 85.4 | 2.8 | 1.0 |
| 8.20 | -0.047 | -0.052 | 0.461 | -0.046 | 0.214 | -2.517 | -1.093 | 80.7 | -0.024 | 0.878 | 87.8 | 2.5 | 0.9 |
| 8.00 | -0.048 | -0.054 | 0.461 | -0.045 | 0.169 | -2.472 | -1.073 | 84.5 | -0.021 | 0.902 | 90.2 | 2.7 | 0.8 |
| 7.80 | -0.044 | -0.049 | 0.461 | -0.039 | 0.130 | -2.433 | -1.057 | 87.8 | -0.019 | 0.923 | 92.3 | 2.7 | 1.1 |
| 7.60 | -0.035 | -0.043 | 0.461 | -0.033 | 0.097 | -2.400 | -1.042 | 90.8 | -0.016 | 0.942 | 94.2 | 2.7 | 0.9 |
| 7.40 | -0.026 | -0.038 | 0.461 | -0.029 | 0.068 | -2.371 | -1.030 | 93.4 | -0.013 | 0.958 | 95.8 | 2.8 | 0.8 |
| 7.20 | -0.018 | -0.031 | 0.461 | -0.020 | 0.040 | -2.343 | -1.017 | 96.1 | -0.013 | 0.971 | 97.1 | 3.9 | 1.3 |
| 7.00 | -0.013 | -0.024 | 0.461 | -0.020 | 0.040 | -2.343 | -1.017 | 96.1 | -0.013 | 0.971 | 97.1 | 3.9 | 1.3 |

Table 5. The values of \bar{q}_{poly} and \bar{p}_{poly}

| $-\log h$ | 0.100 M $-\log h$ calc. with E_{oh} | | 0.100 M $-\log h$ calc. with $E_{\text{oa}} + 59.15 \log K_w$ | | 0.200 M $-\log h$ calc. with E_{oh} | | 0.200 M $-\log h$ calc. with $E_{\text{oa}} + 59.15 \log K_w$ | | 0.400 M $-\log h$ calc. with E_{oh} | | 0.400 M $-\log h$ calc. with $E_{\text{oa}} + 59.15 \log K_w$ | |
|-----------|---|-------------------------|--|-------------------------|---|-------------------------|--|-------------------------|---|-------------------------|--|-------------------------|
| | \bar{q}_{poly} | \bar{p}_{poly} | \bar{q}_{poly} | \bar{p}_{poly} | \bar{q}_{poly} | \bar{p}_{poly} | \bar{q}_{poly} | \bar{p}_{poly} | \bar{q}_{poly} | \bar{p}_{poly} | \bar{q}_{poly} | \bar{p}_{poly} |
| 11.60 | 1.0 | 0.5 | 1.7 | 0.1 | 2.3 | 0.5 | 2.0 | 0.1 | 1.7 | 0.1 | 2.0 | 0.4 |
| 11.40 | 2.0 | 0.5 | 1.9 | 0.9 | 2.5 | 0.8 | 2.1 | 0.9 | 2.1 | 0.9 | 2.2 | 0.9 |
| 11.20 | 2.0 | 0.6 | 2.1 | 1.1 | 2.3 | 0.8 | 2.1 | 1.1 | 2.2 | 1.1 | 2.3 | 1.0 |
| 11.00 | 1.9 | 0.9 | 2.1 | 1.4 | 2.2 | 0.9 | 2.2 | 1.6 | 2.2 | 1.4 | 2.5 | 1.4 |
| 10.80 | 1.8 | 0.9 | 3.1 | 1.6 | 2.2 | 1.1 | 2.2 | 1.1 | 2.2 | 1.1 | 2.8 | 2.5 |
| 10.60 | 2.0 | 1.1 | 3.1 | 1.5 | 2.4 | 1.3 | 2.4 | 1.5 | 2.4 | 1.5 | 2.8 | 1.0 |
| 10.40 | 2.1 | 1.3 | 3.0 | 1.4 | 2.5 | 1.3 | 2.5 | 1.4 | 2.7 | 1.4 | 2.7 | 1.1 |
| 10.20 | 2.4 | 1.5 | 2.7 | 1.4 | 2.5 | 1.2 | 2.5 | 1.2 | 3.0 | 1.5 | 2.7 | 1.0 |
| 10.00 | 2.7 | 1.6 | 2.8 | 1.5 | 2.6 | 1.5 | 2.6 | 1.5 | 3.1 | 1.5 | 2.3 | 1.0 |
| 9.80 | 2.8 | 1.5 | 2.8 | 1.5 | 2.8 | 1.5 | 2.4 | 1.2 | 3.1 | 1.5 | 2.7 | 1.4 |
| 9.60 | 2.9 | 1.5 | 2.9 | 1.4 | 2.9 | 1.5 | 2.4 | 1.4 | 2.4 | 1.1 | 2.7 | 1.2 |
| 9.40 | 2.9 | 1.4 | 1.9 | 1.4 | 3.0 | 1.5 | 2.5 | 1.1 | 3.3 | 1.5 | 2.7 | 1.2 |
| 9.20 | 2.9 | 1.2 | 3.0 | 1.3 | 2.5 | 1.0 | 2.5 | 1.1 | 3.3 | 1.5 | 2.6 | 1.2 |
| 9.00 | 2.9 | 1.2 | 3.1 | 1.3 | 2.5 | 1.0 | 2.5 | 1.0 | 3.7 | 1.6 | 2.6 | 1.1 |
| 8.80 | 2.8 | 1.1 | 3.0 | 1.2 | 2.4 | 1.0 | 2.4 | 1.0 | 3.8 | 1.5 | 2.6 | 1.1 |
| 8.60 | 2.8 | 1.1 | 3.1 | 1.2 | 2.4 | 0.9 | 2.4 | 0.9 | 3.8 | 1.4 | 2.5 | 1.1 |
| 8.40 | 2.8 | 1.0 | 3.1 | 1.1 | 2.3 | 0.9 | 2.3 | 1.1 | 3.8 | 1.3 | 2.6 | 1.1 |
| 8.20 | 2.8 | 1.0 | 3.1 | 1.1 | 2.2 | 0.8 | 2.2 | 0.8 | 3.8 | 1.3 | 2.6 | 1.1 |
| 8.00 | 2.5 | 0.9 | 3.1 | 1.1 | 2.1 | 0.8 | 2.1 | 0.8 | 3.8 | 1.2 | 2.6 | 1.1 |
| 7.80 | 2.7 | 0.8 | 3.0 | 1.0 | 2.1 | 0.8 | 2.1 | 0.8 | 3.8 | 1.2 | 2.6 | 1.2 |
| 7.60 | 2.7 | 1.1 | 3.1 | 0.9 | 2.3 | 0.8 | 2.3 | 0.8 | 3.8 | 1.4 | 2.6 | 1.2 |
| 7.40 | 2.7 | 0.9 | 3.1 | 0.9 | 2.5 | 1.2 | 2.5 | 1.2 | 4.0 | 1.4 | 2.8 | 1.4 |
| 7.20 | 2.8 | 0.8 | 3.0 | 0.8 | 1.4 | 1.0 | 1.4 | 1.0 | 4.2 | 1.3 | 3.1 | 1.9 |
| 7.00 | 3.9 | 1.3 | 3.0 | 0.8 | 1.1 | 1.1 | 1.1 | 1.1 | 4.3 | 1.1 | 3.1 | 1.9 |

solution may also contain species with two or four boron atoms. In order to see which complexes occur, we have in the following tested various hypotheses with the aid of normalized graphs $^{30} B(\log u)_Z$.

The method of normalized $B(\log u)_Z$ graphs 30 .

It may be instructive to illustrate by an example the use of normalized graphs in the analysis of the experimental data. If we assume the four species B, AB, AB₃ and A₂B₃ — the combination that we finally have found the most likely one — the law of mass action gives the following equations:

$$[\text{AB}] = K_{11}bh^{-1} \quad (14)$$

$$[\text{AB}_3] = K_{13}b^3h^{-1} \quad (15)$$

$$[\text{A}_2\text{B}_3] = K_{23}b^3h^{-2} \quad (16)$$

where b is the concentration of free B

$$B = [\text{B}] + [\text{AB}] + 3[\text{AB}_3] + 3[\text{A}_2\text{B}_3] = b + K_{11}bh^{-1} + 3K_{13}b^3h^{-1} + 3K_{23}b^3h^{-2} \quad (17)$$

$$BZ = [\text{AB}] + [\text{AB}_3] + 2[\text{A}_2\text{B}_3] = K_{11}bh^{-1} + K_{13}b^3h^{-1} + 2K_{23}b^3h^{-2} \quad (18)$$

We wish to transform these expressions to the normalized form:

$$B = v(1 + u) + 3v^3u(1 + \alpha u) \quad (19)$$

$$BZ = uv + v^3u(1 + 2\alpha u) \quad (20)$$

$$\text{where } \alpha = \frac{K_{23}}{K_{11}K_{13}} \quad (21)$$

This is achieved by the substitutions:

$$u = K_{11}h^{-1}; \quad v = b(K_{13}K_{11}^{-1})^{\frac{1}{2}}; \quad B = B(K_{13}K_{11}^{-1})^{\frac{1}{2}} \quad (22)$$

From the normalized eqns. (19) and (20) we can get

$$2 \log B = 2 \log [1 - 2u(1 - \alpha) - \alpha u^2] + \log (2 + Zu - u) - 3 \log [(1 + 2\alpha u) - 3Z(1 + \alpha u)] - \log u \quad (23)$$

If the constant α is known one may calculate B as a function of Z and $\log u$.

Graphs $\log B(\log u)_Z$ were calculated for some values of α and compared with the experimental graph. From the graph which fitted best with the experimental data we obtained the constants K_{11} and K_{13} as differences along the coordinate axes.

$$\log B - \log B = \frac{1}{2} (\log K_{13} - \log K_{11}) \quad (24)$$

$$\log u - \log h = \log K_{11} \quad (25)$$

and the constant K_{23} from the value of α giving the best fit.

Survey of the projection map

The normalized $\log B(\log u)_Z$ graph calculated from (22) with $\alpha = 0.25$ is given in Fig. 3c, and the various complexes have been put down in the range where they dominate.

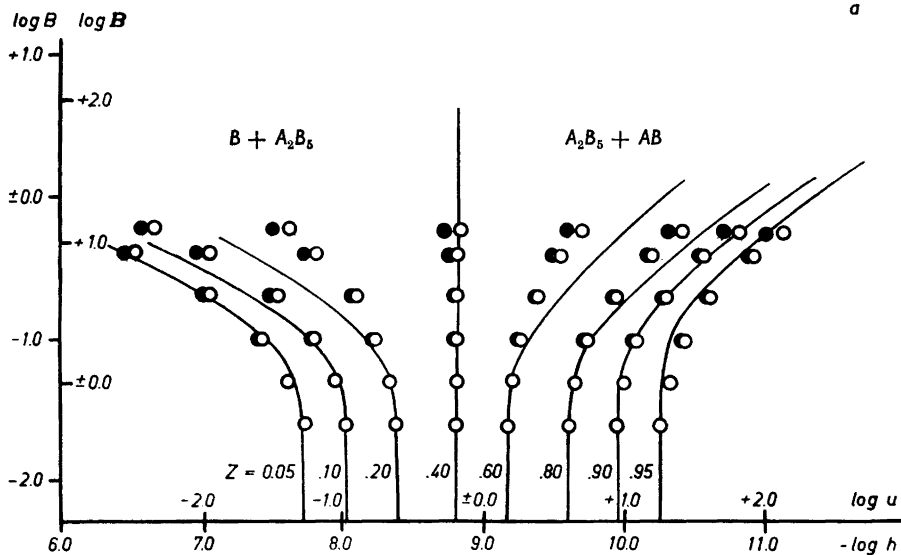


Fig. 3. "Surface-fitting" of the experimental data for the hydrolysis of boric acid and borate ion plotted as $\log B(\log h)_Z$ (open circles, experimental $-\log h$ calculated from E_{oh} and filled circles $-\log h$ calculated from $E_{ca} + 59.15 \log K_w$). The curves give the projection map $\log B(\log u)_Z$ in the best fit, calculated for the following species:

a) B, AB and A_2B_5 (the hypothesis of Carpéni²²)

$AB + B$. In the lower part of the graph the value of $(\log u)_Z$ does not change with B , and the vertical lines correspond to a system with two mononuclear species AB and B. The u values for different Z are given by

$$u \approx \frac{Z}{1-Z} \quad (26)$$

as may be derived from (19) and (20), with $v \ll 1$.

$$\begin{aligned} B + AB_3 \text{ From the eqns. (19) and (20) for } u \ll 1 \text{ and } \alpha u \ll 1 \text{ we get} \\ B = v + 3v^3u; \quad BZ = v^3u \end{aligned} \quad (27)$$

which means that practically only the complexes B and AB_3 are formed and

$$\log B = \frac{1}{2} \log \frac{Z}{(1-3Z)} - \frac{1}{2} \log u \quad (28)$$

Thus $\log B(\log u)_Z$ is the family of straight lines with the slope $-\frac{1}{2}$ in the left upper part of the graph.

$A_2B_5 + AB$. In a similar way the rectilinear curves to the right in the graph correspond to a range with practically only the complexes AB and A_2B_5 , and $\log B(\log u)_Z$ is given by

$$\log B = \frac{1}{2} \log \frac{Z-1}{(3Z-2)^3} - \frac{1}{2} \log \alpha + \frac{1}{2} \log u \quad (29)$$

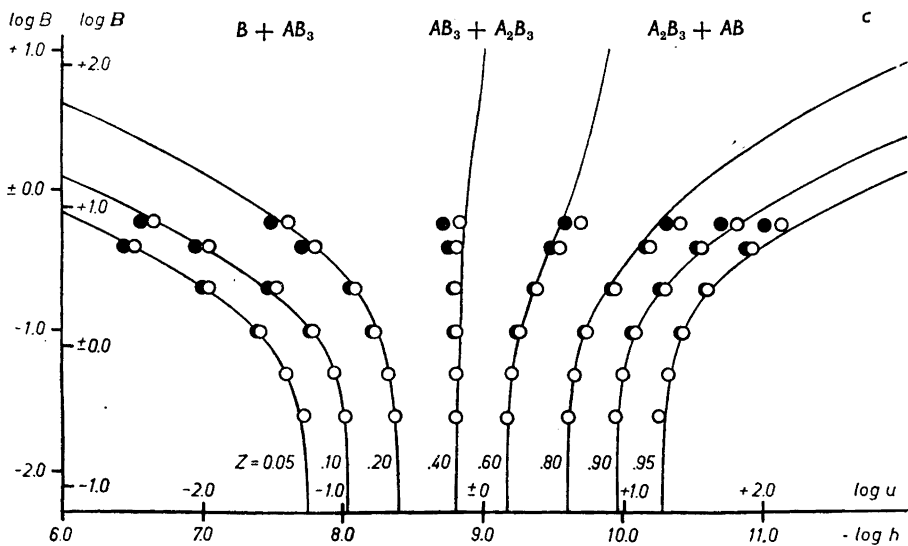
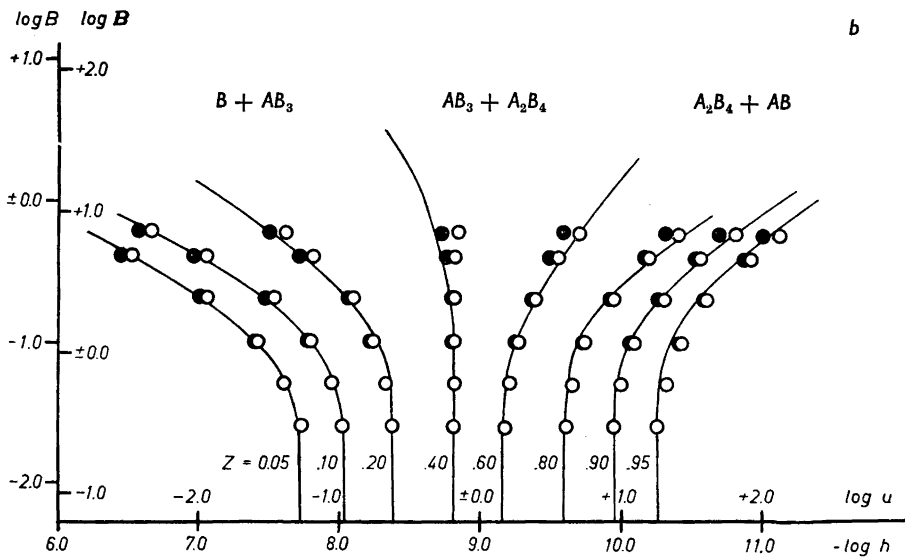


Fig. 3. (Continued)

B + AB in all lower parts.

b) B, AB, AB₃ and A₂B₄ assuming $\frac{K_{24}}{K_{11} \cdot K_{13}} = 1.25$ c) B, AB, AB₃ and A₂B₃ assuming $\frac{K_{23}}{K_{11} \cdot K_{13}} = 0.25$

$AB_3 + A_2B_3$. The upper almost vertical lines in the graph correspond to the predominance of the two polynuclear complexes AB_3 and A_2B_3 , and the $\log u$ value for different Z is given by

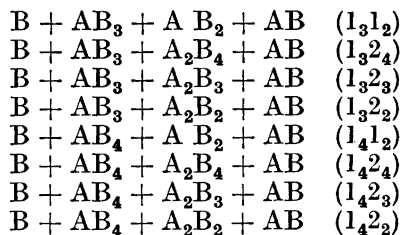
$$\log u = \log (1-3Z) - \log a - \log (3Z-2) \quad (30)$$

Hypotheses tested

We have tried to explain the experimental data with as few polynuclear complexes as possible. The value of \bar{p}_{poly} and \bar{q}_{poly} indicates that the number of boron atoms does not rise above four and the charge not above minus two in any complex.

If only *one polynuclear complex* exists, the Z value ≈ 0.40 of the intersection point of the curves would correspond to the formula of that complex. The only possible formula is then A_2B_5 which has been suggested by Carpéni^{20,21}. Although the value of \bar{q}_{poly} indicated that the complex A_2B_5 was not to be expected, normalized graphs were constructed with the function B , assuming B , AB and A_2B_5 to be the species present. For all values of Z the agreement was so poor (Fig 3a) that an explanation with only the complex A_2B_5 can be ruled out.

Next it was assumed that B , AB and *only two polynuclear complexes* exist and that these contain two, three or four boron and the charge minus one or two. All such combinations that can give an intersection at $Z \approx 0.40$ are as follows:



Normalized graphs $\log B (\log u)_Z$ were constructed for the combinations (1_31_2) , (1_32_4) , (1_32_3) and (1_42_4) .

The calculated graph with *the combination* (1_42_4) gave a fair fit in the range of A_2B_4 and AB , but did not fit at all at the low values of Z where B and AB_4 would predominate. We thus concluded that there is no range where B and AB_4 predominate *which rules out all the combinations containing* 1_4 (1_41_2 , 1_42_4 , 1_42_3 and 1_42_2).

In *the combination* 1_32_2 the intersection Z must vary between 0.33 and 1.00. Higher B increases the ratio $AB_3(A_2B_3)^{-1}$ and consequently decreases the intersection point. However, from the experimental $Z (\log h)_B$ we found a tendency of the intersection point to increase or to be constant; therefore *the combination* 1_32_2 has been ruled out as being unlikely.

The calculated graph for *the combination* 1_31_2 agreed too poorly with the experimental curves to explain them.

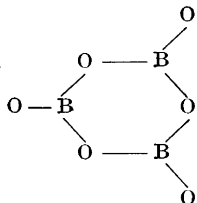
The normalized graph for the combination I_32_4 fitted fairly well with the experimental data (Fig. 3b) but not as well as the remaining combination I_32_3 (Fig. 3c).

Before a discussion of possible structures for the complexes found, it is necessary to survey some previous works on borate in crystals.

STRUCTURAL DATA

Structures of anhydrous borates. In such hydrogen-free compounds as may be obtained at high temperatures, isolated BO_3 triangles are very often encountered. For instance BO_3^{3-} triangles are found in LaBO_3 with the aragonite structure, in InBO_3 and ScBO_3 with the calcite structure (Wells³¹, p. 598), and in $\text{Co}_3(\text{BO}_3)_2$ and $\text{Mg}_3(\text{BO}_3)_2$ (Berger³²).

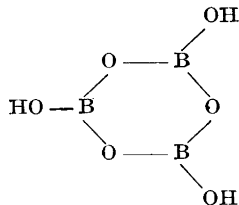
An almost planar group $\text{B}_2\text{O}_5^{4-}$, consisting of two BO_3 triangles sharing a corner, was found in $\text{Co}_2\text{B}_2\text{O}_5$ (Berger³³) and $\text{Mg}_2\text{B}_2\text{O}_5$ (Takéuchi³⁴). In CaB_2O_4 the BO_3 triangles form infinite chains, each BO_3 group sharing two of its O atoms with neighbors (Zachariassen and Ziegler³⁵). Finally, the BO_3 groups can also join to form planar rings $\text{B}_3\text{O}_6^{3-}$ in the salts $\text{K}_3\text{B}_3\text{O}_6$ and $\text{Na}_3\text{B}_3\text{O}_6$ previously written as KBO_2 and NaBO_2 (Zachariassen³⁶ and Fang³⁷).



Four-coordinated B (BO_4 tetrahedra) is found in B_2O_3 (Berger^{38,39}), in BPO_4 and BAsO_4 (Schulze⁴⁰), and in $\text{CaB}_2\text{Si}_2\text{O}_8$ (Machatschki and Stradner⁴¹). According to Ito, Morimoto and Sadanaga⁴², $\text{Mg}_3\text{B}_7\text{O}_{13}\text{Cl}$ (boracite) contains both BO_4 tetrahedra and flat BO_3 pyramids.

Structures of borates containing hydrogen. The crystal structure of boric acid is built up of layers with flat $\text{B}(\text{OH})_3$ triangles, joined by hydrogen bonds (Zachariassen^{43,44}). The metaboric acid, $\text{HBO}_2(\beta)$, contains chains with boron both in three- and four-coordination, according to a preliminary report by Zachariassen⁴⁵.

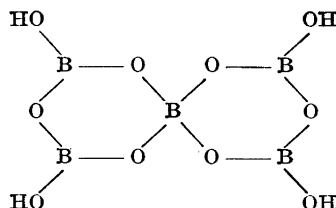
The α -form of metaboric acid has been investigated by Tazaki⁶⁴. According to him the structure is built up of ringshaped trimeric units:



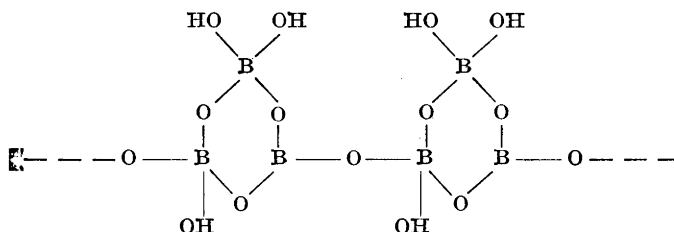
These units are bound together by hydrogen bridges to give a layer structure.

Tetrahedral ions $B(OH)_4^-$ have been found in the structures of the minerals teepelite, $Na_2B(OH)_4Cl$ (Formaseri ⁴⁶) and bandylite, $CuB(OH)_4Cl$ (Collin ⁴⁷). From the close similarity of the Raman spectra of teepelite and of concentrated potassium borate solutions, Edwards *et al.* ⁴⁸ concluded that the mononuclear borate ion in solution has the formula $B(OH)_4^-$.

Only two polyborates, to our knowledge, have been thoroughly studied. One is the salt " $KB_5O_8(H_2O)_4$ ", which is more properly written as $KH_4B_5O_{10}(H_2O)_2$. According to Zachariassen ⁴⁹, this salt contains the group B_5O_{10} , where two B_3O_3 rings have one B atom in common; this B has a tetrahedral configuration, whereas the others are triangular. From measurements of nuclear magnetic resonance, Smith and Richards ⁵⁰ concluded that there are four protons attached to this group, the remaining protons being bound in H_2O (Zachariassen originally proposed two H in the B_5O_{10} group, and two H_3O^+ ions). The formula of the group would thus be (the planes of the two rings form right angles)



The crystal structure of colemanite, $CaB_3O_4(OH)_3H_2O$ has been described as containing chains of three-boron rings:



where one B has triangular, two tetrahedral surroundings (Christ, Clark, and Evans ⁵¹).

A Spanish research group has proposed structures for some other polyborates, but according to the *Structure Reports* (1947—45, p. 428—432, 1949, p. 264) these cannot be considered as certain. If they are correct, the structures contain BO_3 and B_3O_6 rings, combined to form sheets.

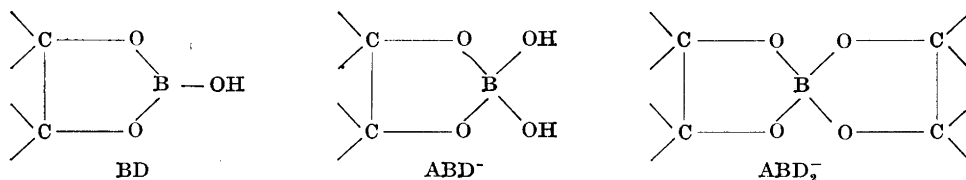
The fact that the mineral kernite, $Na_2B_4O_7(H_2O)_4$, has a fibrous structure indicates that it contains polyborate chains (Menzel and Schulz ⁵²). This is also indicated by a preliminary X-ray structure analysis (Berger ⁵³).

It seems very likely that the "sodium metaborate" $NaBO_2(H_2O)_2$ is really $Na^+B(OH)_4^-$. However, from the mere existence of salts like $Na_2B_4O_7(H_2O)_{10}$ and $NaB_5O_8(H_2O)_5$, it is not safe to conclude that ions $B_4O_7^-$ and $B_5O_8^-$ would exist as separate units, even in the crystal structures. The structures of silicate

minerals would give a warning against such conclusions; the structures may well contain infinite units (chains, sheets) or several different ionic species.

Complexes with polyols. Boric acid forms complexes with a number of polyols, *i.e.* organic compounds containing several OH groups. Such complexes are put to practical use, as for instance, when mannitol is added before titration of boric acid; the latter then behaves like a strong acid. Since these complexes may show analogies with the polyborate ions, we shall here try to summarize the main facts about them.

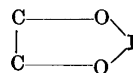
Most of the borate complexes prepared or proved to exist from equilibrium data may be written in one of the following three forms (see *e.g.* Böeseken ⁵⁴):



(D = diol). Compounds of type BD, when they have been prepared, have proved to be very weak acids, still weaker than boric acid (Hermans ⁵⁵). It has not been definitely proved whether the ions ABD^- formed with polyols have the four-coordinated configuration written above, or a three-coordinated configuration with a single O bound to B instead of 2 OH. However, considering the general weakness of the B—O—H acidity, it seems likely that negative ions which can exist where $\text{B}(\text{OH})_3$ would not be ionized are generally four-coordinated. For ions of the form ABD_2^- the tetrahedral configuration has been proved by the resolution of optical isomers.

The existence of complexes ABD^- and ABD_2^- has been proved in many instances by analysis of pH and conductance data (later work, *e.g.* Deutsch and Osoling ⁵⁶, mannitol; Ross and Catotti ⁵⁷, mannitol; Schäfer ⁵⁸, pyrocatechol, salicylic acid, and mannitol; Torsell ⁵⁹, mannitol and fructose). In all of the cases quoted only ABD^- and ABD_2^- were found. Occasionally there is evidence for uncharged BD (which has then probably the form above, Böeseken and Niks ⁶⁰) but never for uncharged BD_2 .


Boric acid is rather particular in the choice of diol (Schäfer ⁶¹, Isbell *et al.* ⁶², and especially Böeseken ⁵⁴). With glycol or glycerol it reacts only at high concentrations, whereas a strong reaction is observed with polyols like mannitol and erythritol. Considering aromatic diols, it reacts only with the ortho-compounds, but with *cyclopentane*-1,2-diol it reacts only with the *cis*form. It does not seem to react at all with any form of *cyclohexane*-diol. Steric explanations have been proposed (Böeseken ⁵⁴).

It seems essential that a five-membered-ring  is formed (a six-membered-ring with one more C has occasionally been obtained). Complexes where a carbonyl C—O may react like a $\text{C}(\text{OH})_2$ group are known; however, such OH groups do not seem to react with the same B atom forming a four-ring.

General rules for borate structures. From the equilibrium data, we may deduce the number of boron atoms and the charge for a certain polyborate ion

in solution. This still leaves us a number of possible formulas that differ by one or several H_2O , like $\text{B}_3\text{O}_3(\text{OH})_4^-$, $\text{B}_3\text{O}_4(\text{OH})_2^-$, B_3O_5^- etc; one cannot decide between them from equilibrium data alone. However, the structures of borate crystals and organic borate complexes may give some aid in proposing a formula and a reasonable structure.

BO_3 or BO_4 groups, as a rule, are joined by sharing an O atom, thus forming a B—O—B bridge. In B_2O_3 , some oxygen atoms are said to be shared

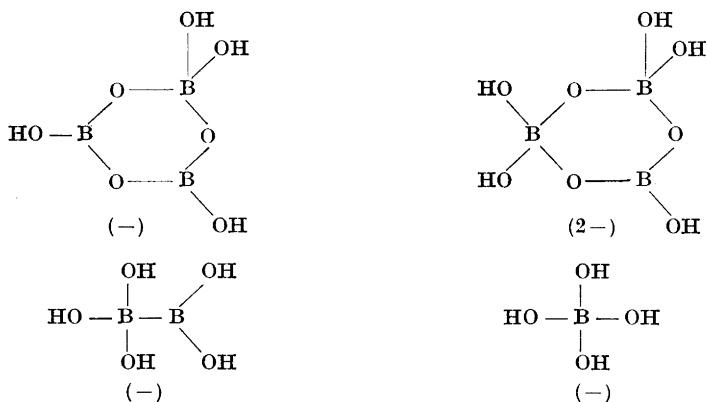
between three B atoms (Berger³⁰); however, no case with a four-ring  seems to be known. There is also no structure known with B—OH—B bridges.

The sharing of an oxygen between more than two B has not been proved in any other compound than B_2O_3 where there is a great shortage of oxygen. We shall assume that it does not occur in aqueous solutions, where a large number of oxygen atoms are available.

It seems very unlikely that polyborate ions in aqueous solution would be held together by hydrogen bonds between OH groups attached to different B, considering that solutions of pure boric acid show no association (Menzel⁷).

As for the *unshared oxygen* atoms bound to boron, it seems reasonable to assume as a working hypothesis that they are *always OH groups*. Thus Edwards *et al.*⁴⁸ suggest that $\text{B}(\text{OH})_3$ forms an ion not by splitting off H^+ to form $\text{BO}(\text{OH})_2^-$, but by addition of OH^- to boron $\text{B}(\text{OH})_4^-$. This also agrees with the crystal structures of $\text{KH}_4\text{B}_5\text{O}_{10}(\text{H}_2\text{O})_2$ and $\text{CaB}_3\text{O}_4(\text{OH})_3\text{H}_2\text{O}$ given above.

If these rules are general, we can easily see that in any borate ion there will be one negative charge for each four-coordinated boron atom, *e.g.*

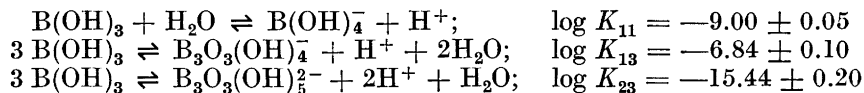


The ion $\text{H}_4\text{B}_5\text{O}_{10}^-$ agrees well with these principles.

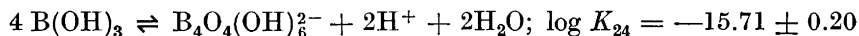
The ease with which boron can switch over between three- and four-coordination is probably one of the reasons why the polyborate equilibria are so rapidly achieved.

CONCLUSIONS

From the measurements made in this work, we have obtained the following equilibria:



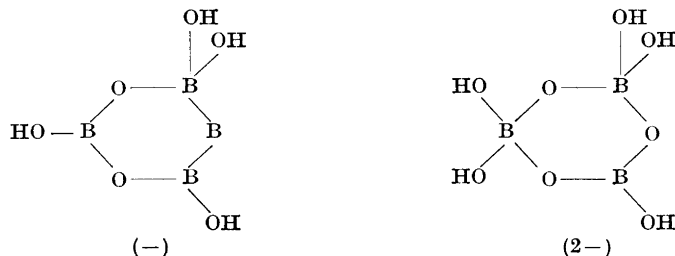
The experimental data may also be explained if the last equilibrium is replaced with



In both cases the agreement between the experimental and calculated data is satisfactory except for small deviations at high values of Z and B . These deviations may be explained as a variation in the activity factors. The agreement between the constant obtained in this investigation and in other investigations seems to be satisfactory — Owen¹¹ ($\log K_a^\circ = -9.236$), Thygesen¹³ ($\log K_{13} = -7.5$ at 18°C), Stetten¹⁴ ($\log K_{1,3,2} = -6.86$) and Edwards¹⁵ ($\log K_{13} = -7.5$).

From general chemical considerations, the polynuclear combination AB_3 and A_2B_4 seems to be very unlikely.

The possibility that AB_3 and A_2B_3 could be chains must be ruled out since it would be very hard to explain why a certain number should be preferred. It seems to be more likely that the complexes contain a six membered B—O—B ring



Note. When our work was completed a structure determination by Christ and Clark⁶³ appeared which corroborated our conception that the most likely two-charged polynuclear complex was to be $\text{B}_3\text{O}_3(\text{OH})_5^{2-}$. Christ and Clark⁶³ showed in a X-ray investigation of the mineral mayerhofferite, $2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$ that the crystal contains polyions consisting of two $\text{BO}_2(\text{OH})_2$ tetrahedra and a $\text{BO}_2(\text{OH})$ triangle linked to form a ring of the composition $\text{B}_3\text{O}_3(\text{OH})_6^{2-}$, which is the same complex that we have proposed above.

This work is part of a program financially supported by *Statens Naturvetenskapliga Forskningsråd* (Swedish Natural Science Research Council). It has also received much stimulation from research work supported by Columbia-Southern Chemical Corporation, in this laboratory.

REFERENCES

- Hietanen, S. and Sillén, L. G. *Acta Chem. Scand.* **8** (1954) 1607; Sillén, L. G. *Acta Chem. Scand.* **8** (1954) 299; Biedermann, G. and Sillén, L. G. *Acta Chem. Scand.* **10** (1956) 1011.
- Konopik, N. and Leberl, O. *Monatsh.* **80** (1949) 655.
- Carpéni, G. *Compt. rend.* **226** (1948) 807.
- Byé, J. *Bull. soc. chim. France* **1953** 390.
- Souchay, P. *Bull. soc. chim. France* **1953** 395.
- Kahlenberg, L. and Schreiner, O. *Z. physik. Chem.* **20** (1896) 547.
- Menzel, H. *Z. anorg. allgem. Chem.* **164** (1927) 1, 22.
- Menzel, H. and Schulz, H. *Z. anorg. allgem. Chem.* **251** (1943) 167.

9. Doucet, Y. and Rollin, M. *Compt. rend.* **226** (1948) 1967.
10. Souchay, P. *Bull. soc. chim. France* **1951** 932.
11. Owen, B. D. *J. Am. Chem. Soc.* **56** (1934) 1695.
12. Kolthoff, I. M. *Rec. trav. chim.* **45** (1926) 501.
13. Thygesen, J. E. *Z. anorg. allgem. Chem.* **237** (1938) 101.
14. Stetten, D. Jr. *Anal. Chem.* **23** (1951) 1177.
15. Edwards, J. O. *J. Am. Chem. Soc.* **75** (1953) 6151.
16. Antikainen, P. *Ann. Acad. Sci. Fennicae, Ser A II*, No. 56.
17. Auerbach, F. *Z. anorg. Chem.* **37** (1903) 353.
18. Kolthoff, I. M. and Bosch, W. *Rec. trav. chim.* **46** (1927) 180.
19. Carpéni, G. and Souchay, P. *J. Chem. Phys.* **42** (1945) 149.
20. Carpéni, G. *Compt. rend.* **228** (1949) 89.
21. Carpéni, G. *Bull. soc. chim. France* **1952** 1010.
22. Carpéni, G. *Compt. rend.* **239** (1954) 1500.
23. Ågren, A. *Acta Chem. Scand.* **9** (1955) 49.
24. Biedermann, G. and Sillén, L. G. *Arkiv Kemi* **5** (1953) 425.
25. Lagerström, G. *To be published.*
26. Forsling, W., Hietanen, S. and Sillén, L. G. *Acta Chem. Scand.* **6** (1952) 901.
27. Bates, R. G. *Electrometric pH determinations*, John Wiley and Sons Inc. 1954.
28. Gran, G. *Analyst* **77** (1952) 661.
29. Sillén, L. G. *To be published.*
30. Sillén, L. G. *Acta Chem. Scand.* **10** (1956) 803.
31. Wells, A. F. *Structural inorganic chemistry*, Oxford 1950.
32. Berger, S. V. *Acta Chem. Scand.* **3** (1949) 660.
33. Berger, S. V. *Acta Chem. Scand.* **4** (1950) 1054.
34. Takéuchi, Y. *Acta Cryst.* **5** (1952) 574.
35. Zachariasen, W. H. and Ziegler, G. E. *Z. Krist.* **83** (1932) 354.
36. Zachariasen, W. H. *J. Chem. Phys.* **5** (1937 a) 919.
37. Fang, S. M. *Z. Krist.* **99** (1938) 1.
38. Berger, S. V. *Acta Cryst.* **5** (1952) 389.
39. Berger, S. V. *Acta Chem. Scand.* **7** (1953) 611.
40. Schulze, G. E. R. *Z. physik. Chem.* **B24** (1934) 215.
41. Machatschki, F. and Stradner, E. *Österr. Akad. Wiss. Math-naturw. Kl. Anz* **2** (1953) 26.
42. Ito, T., Morimoto, N. and Sadanaga, R. *Acta Cryst.* **4** (1951) 310.
43. Zachariasen, W. H. *Z. Krist.* **88** (1943) 150.
44. Zachariasen, W. H. *Acta Cryst.* **7** (1954) 305.
45. Zachariasen, W. H. *Acta Cryst.* **5** (1952) 68.
46. Fornaseri, M. *Periodico mineral. Rome* **18** (1949) 103. (*Structure Reports* **12**, 263).
47. Collin, R. L. *Acta Cryst.* **4** (1951) 204.
48. Edwards, J. O., Morrison, G. C., Ross, V. F. and Schultz, J. W. *J. Am. Chem. Soc.* **77** (1955) 266.
49. Zachariasen, W. H. *Z. Krist.* **98** (1937 b) 266.
50. Smith, J. B. S. and Richards, R. E. *Trans. Faraday Soc.* **48** (1952) 307.
51. Christ, C. L., Clark, J. R. and Evans, H. T. Jr. *Acta Cryst.* **7** (1954) 149.
52. Menzel, H. and Schulz, H. *Z. anorg. allgem. Chem.* **245** (1940) 157.
53. Berger, S. V. *Private communication* (1955).
54. Böeseken, J. *Advances in Carbohydrate Chem.* **4** (1949) 189.
55. Hermans, P. H. *Z. anorg. allgem. Chem.* **142** (1925) 83.
56. Deutsch, A. and Osoling, S. *J. Am. Chem. Soc.* **71** (1949) 1637.
57. Ross, S. D. and Catotti, A. J. *J. Am. Chem. Soc.* **71** (1949) 3563.
58. Schäfer, H. *FIAT Rev. Ger. Sci.* 1939—1946 (1948), *Inorg. Chem.* **III**, 225.
59. Torssell, K. *Arkiv Kemi* **3** (1952) 571.
60. Böeseken, J. and Niks, A. *Rec trav. chim.* **59** (1940) 1062.
61. Schäfer, H. *Z. anorg. allgem. Chem.* **247** (1941) 96.
62. Isbell, H. S., Brewster, J. F., Holt, N. B. and Frush, H. L. *J. Research Natl. Bur. Standards* **40** (1948) 129.
63. Christ, C. L. and Clark, J. R. *Acta Cryst.* **9** (1956) 830.
64. Tazaki, H. *J. Sci. Hiroshima Univ. Ser A*, **10** (1940) 55—61.

Received March 25, 1957.