

Equilibrium Studies of Polyanions

8. On the First Equilibrium Steps in the Hydrolysis of Boric Acid, a Comparison between Equilibria in 0.1 M and 3.0 M NaClO₄

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The first equilibrium steps at 25°C for the hydrolysis of boric acid in 0.1 M and 3.0 M Na(ClO₄)₄ have been studied using a hydrogen electrode. In both media the data for *B* (the total boric acid concentration) ranging between 0.010 M and 0.200 M could be explained, as in our earlier study¹, by the formation of B(OH)₄⁻ and B₃O₃(OH)₄⁻. At higher *B* (*B* = 0.4 M and *B* = 0.6 M) the data could be explained by an additional polynuclear complex, either B₄O₅(OH)₄⁻ or B₅O₆(OH)₄⁻; a treatment with Letagrop ("pitmapping", a generalized least square treatment², see Table 2) favored B₅O₆(OH)₄⁻, which is also supported by structural work. The following set of constants is proposed: log *β₁ = -9.00 ± 0.02, log *β₁₃ = -6.91 ± 0.03, log *β₁₅ = -6.62 ± 0.16 (for 3.0 M NaClO₄); log *β₁ = -8.98 ± 0.01, log *β₁₃ = -7.29 ± 0.02, log *β₁₅ = -6.77 ± 0.10 (for 0.1 M NaClO₄).

In a previous emf investigation¹ of alkaline boric acid solutions we found that the first complexes formed when OH⁻ is added to B(OH)₃ are B(OH)₄⁻ and B₃O₃(OH)₄⁻. With more OH⁻ either B₄O₅(OH)₄²⁻ or B₃O₃(OH)₅²⁻ or both, seem also to be formed. Later, evidence⁷ in favour of B₄O₅(OH)₄²⁻ was obtained. When so much OH⁻ has been added that *z*, the mean charge of the complexes in solution reaches the value -1, all species are transformed to B(OH)₄⁻.

In the present work a number of new emf measurements in 0.1 M and 3.0 M Na(ClO₄)₄-media at high *B* and low *z* will be analysed. Our intention is to see whether our data indicate the formation of any more complexes than B, AB⁻, AB₃⁻ and A₂B₄²⁻ (A = OH⁻, B = B(OH)₃), for instance some of the complexes AB₂⁻, AB₄⁻, AB₅⁻, or AB₆⁻. One or more complexes of this type have been proposed by a number of previous workers³. The measurements

have been carried out in two different NaClO_4 -media, 3.0 M and 0.1 M. The aim with measurements in media of such a different total concentration is to see whether the suggestions made by Antikainen ³, that the borate equilibria should be displaced in such a manner, that the predominating polyborate in 3 M NaClO_4 should be AB_3 and in 0.1 M NaClO_4 , AB_4 , are also indicated by our emf technique. Antikainen ³ gives the following formation constants, $\log * \beta_{13} = -6.725$ (3.0 M NaClO_4) and $\log * \beta_{14} = -6.840$ (0.1 M NaClO_4). If the effect ascribed to larger complexes were really due to unexpected variations in the activity factors, then it was reasonable to expect that the effect would be very different in 0.1 and 3.0 M NaClO_4 ; as will be seen, however, the same conclusions could be drawn from data in these two media.

SYMBOLS AND FORMULAS

The symbols used in this work are the same as in Part 2¹ in this series; thus for the species we write in general $A_p B_q$: B for $\text{B}(\text{OH})_3$, A for OH^- , AB for $\text{B}(\text{OH})_4^-$, AB_3 for $\text{B}_3\text{O}_3(\text{OH})_4^-$, etc.: for concentrations, h for $[\text{H}^+]$, a for $[\text{OH}^-]$ and b for $[\text{B}(\text{OH})_3]$, B for the total boric acid concentration and H for the total analytical excess concentration of hydrogen ions assuming no hydrolysis; in most experiments H was negative. The notation BZ is used for the number of OH^- bound per boric acid. It can be calculated from the measured E -values (eqn. 2) and from the analytical composition of the solution using the formula

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

where K_w is the ionic product of water in 3 M NaClO_4 . In some cases BZ is divided into the contributions $B_1 Z_1, B_2 Z_2, \dots, B_q Z_q$ for the various "nuclearities" present.

The equilibrium concentration of hydrogen ions, h , has been calculated from the relation

$$E = E_{\text{oh}} - 59.15 \log h + E_j = E_{\text{oa}} + 59.15 \log K_w - 59.15 \log h + E_j \quad (2)$$

where E is the measured potential in mV and E_{oh} and E_{oa} constants. E_j is the liquid junction potential. The E_{oh} -value has been obtained from the range where the hydrolysis of $\text{B}(\text{OH})_3$ could be neglected and E_{oa} from the solutions of alkaline unhydrolysed $\text{B}(\text{OH})_4^-$ -solutions in a manner previously described in Part. 2¹. E_j has been neglected since $E_j \approx 17h - 8[\text{OH}^-]$.

In the cases where normalized curves and projection maps have been used the normalized quantities B , u and v corresponding to B , a and b have been introduced and defined. The other symbols which will be used are defined in the text.

In agreement with the notation in IUPAC, Tables of Stability constants ⁴, the notations β_{pq} and $*\beta_{pq}$ for the formation constants have been used. For formation of $\text{B}_3\text{O}_3(\text{OH})_4^-$ from $\text{B}(\text{OH})_3$; $*\beta_{13} = h[\text{B}_3\text{O}_3(\text{OH})_4^-][\text{B}(\text{OH})_3]^{-3}$ and $\beta_{13} = [\text{B}_3\text{O}_3(\text{OH})_4^-][\text{OH}^-]^{-1}[\text{B}(\text{OH})_3]^{-3}$. In the new edition of Stability constants, it is possible that $\text{B}(\text{OH})_4^-$ will be treated as a ligand, and H^+ as the "central group"; the corresponding changes are easily made. (Private communication from L. G. Sillén.)

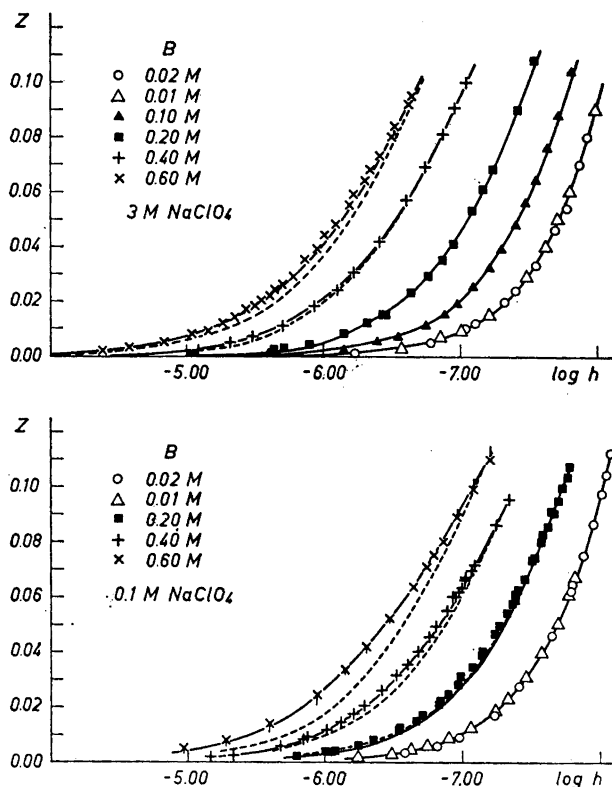


Fig. 1. Average number, Z , of $\text{OH}^- = \text{A}$ bound per $\text{B}(\text{OH})_3 = \text{B}$ as a function of $\log h$ with 3 M and 0.1 M $\text{Na}(\text{ClO}_4)$ as media. The full curves are calculated assuming the formation of AB^- , AB_2^- and AB_3^- . The curves calculated assuming AB_4^- instead of AB_3^- are practically the same as the full curves; the differences are indicated with vertical lines for $B = 0.60 \text{ M}$ and 0.1 M NaClO_4 . The dotted curves are calculated assuming only AB^- and AB_2^- . The equilibrium constants used are given in the text.

EXPERIMENTAL

Reagents and analysis. All chemicals and apparatus used were the same as in Part 2¹ and the composition of the solutions has been determined as described in the same paper.

The titration procedure has also been the same except that in all solutions $[\text{Na}^+] + [\text{H}^+] = \text{constant} = 3 \text{ M}$. In Part 2 this sum was constant only in the alkaline solutions.

ASSUMPTIONS ON THE ACTIVITY FACTORS

In the following treatment of data, concentrations will always be used instead of activities. This is based on the assumption that the ratio of activity factors in the law of mass action expression for formation of $\text{B}(\text{OH})_3(\text{OH}^-)_p$ from $\text{B}(\text{OH})_3$ and OH^- stays constant, even though the individual activity factors vary. In the present case we shall see that it is a ratio of activity factors of

Table 1. Data with 0.1 M Na(ClO₄) medium. For the points used in LETAGROP, 10³ (Z_{calc} - Z) is given. For calculating Z_{calc}, log *β₁ = -8.98, log *β₁₃ = -7.29 and log *β₁₅ = -6.77 have been used.

B = 600 mM; Z, 10³ (Z_{calc} - Z), -log [H⁺]; 0.110, 2, 7.199; 0.099, 2, 7.082; 0.089, 2, 6.962; 0.080, 2, 6.858; 0.071, 6.743; 0.075, 1, 6.792; 0.063, 1, 6.640; 0.052, 1, 6.472; 0.042, 0, 6.300; 0.034, 0, 6.146; 0.024, 0, 5.936; 0.014, -1, 5.592; 0.008, -1, 5.279; 0.005, -1, 4.967;

B = 400 mM; Z, 10³ (Z_{calc} - Z), -log [H⁺]; 0.067, -1, 7.022; 0.060, 6.953; 0.055, 0, 6.891; 0.049, 6.809; 0.045, 0, 6.760; 0.040, 6.680; 0.035, 0, 6.600; 0.031, 6.522; 0.026, 0, 6.409; 0.020, 6.287; 0.017, 0, 6.207; 0.015, 0, 6.115; 0.012, 0, 6.006; 0.009, 5.868; 0.008, 0, 5.840; 0.006, 5.674; 0.003, 0, 5.328; 0.002, 0, 5.164; 0.095, 1, 7.338; 0.086, 1, 7.249; 0.072, 1, 7.092; 0.070, 7.071; 0.066, 7.018; 0.063, 1, 6.999; 0.062, 1, 6.979; 0.059, -1, 6.930;

B = 200 mM; Z, 10³ (Z_{calc} - Z), -log [H⁺]; 0.091, -2, 7.648; 0.083, 0, 7.580; 0.073, -2, 7.509; 0.062, -2, 7.408; 0.050, 7.270; 0.039, -2, 7.144; 0.031, -3, 6.993; 0.022, -2, 6.835; 0.015, -1, 6.658; 0.012, -1, 6.531; 0.008, -1, 6.354; 0.059, 6.235; 0.004, 0, 6.048; 0.002, 0, 5.792; 0.107, 1, 7.779; 0.104, 3, 7.772; 0.100, 0, 7.727; 0.095, 7.695; 0.091, -2, 7.648; 0.086, 0, 7.626; 0.080, 0, 7.580; 0.073, -2, 7.509; 0.067, 7.462; 0.060, 7.392; 0.059, 7.385; 0.057, -1, 7.371; 0.054, 7.332; 0.046, -2, 7.244; 0.039, -2, 7.144; 0.034, -1, 7.078; 0.028, 6.972; 0.024, -1, 6.896; 0.021, -1, 6.818; 0.017, -1, 6.707; 0.013, 6.542; 0.004, -1, 6.065; 0.004, 0, 5.997;

B = 10 mM; Z, 10³ (Z_{calc} - Z), -log [H⁺]; 0.062, 0, 7.797; 0.046, 7.659; 0.027, 0, 7.422; 0.017, 1, 7.238; 0.009, 1, 6.978; 0.006, 1, 6.817; 0.003, 1, 6.583; 0.112, 0, 8.078; 0.105, 1, 8.048; 0.098, 1, 8.014; 0.087, 7.956; 0.075, 7.886; 0.064, 0, 7.811;

B = 20 mM; Z, 10³ (Z_{calc} - Z), -log [H⁺]; 0.067, 0, 7.823; 0.061, -1, 7.778; 0.050, 1, 7.703; 0.040, 0, 7.582; 0.031, 0, 7.470; 0.023, 0, 7.336; 0.018, 0, 7.238; 0.012, 0, 7.067; 0.009, 0, 6.902; 0.006, 0, 6.743; 0.004, 6.627; 0.003, 0, 6.482; 0.002, 6.235;

Data with 3 M Na(ClO₄) medium. For the points used in LETAGROP, 10³ (Z_{calc} - Z) is given. For calculating Z_{calc}, log *β₁ = -9.00, log *β₁₃ = -6.91 and log *β₁₅ = -6.62 have been used.

B = 600 mM; Z, 10³ (Z_{calc} - Z), -log [H⁺]; 0.004, 0, 4.840; 0.009, 0, 5.165; 0.014, 0, 5.360; 0.018, 1, 5.505; 0.022, 1, 5.617; 0.026, 1, 5.708; 0.029, 1, 5.784; 0.039, 0, 5.964; 0.047, 0, 6.099; 0.055, 0, 6.202; 0.063, 0, 6.313; 0.072, -1, 6.422; 0.080, -2, 6.511; 0.092, 6.630; 0.002, 0, 4.387; 0.003, 0, 4.582; 0.008, 0, 5.044; 0.012, -1, 5.272; 0.017, 0, 5.444; 0.020, 0, 5.553; 0.024, 0, 5.650; 0.035, 0, 5.875; 0.044, -1, 6.014; 0.059, -2, 6.229; 0.068, -3, 6.351; 0.084, -3, 6.531; 0.095, -4, 6.652;

B = 400 mM; Z, 10³ (Z_{calc} - Z), -log [H⁺]; 0.002, 1, 5.091; 0.004, 1, 5.320; 0.007, 0, 5.487; 0.011, 1, 5.665; 0.018, 1, 5.900; 0.024, 2, 6.072; 0.030, 2, 6.198; 0.043, 1, 6.385; 0.059, 1, 6.583; 0.073, 1, 6.725; 0.086, 1, 6.848; 0.095, 1, 6.928; 0.106, 1, 7.023;

B = 200 mM; Z, 10³ (Z_{calc} - Z), -log [H⁺]; 0.002, 1, 5.648; 0.004, 1, 5.903; 0.015, 1, 6.461; 0.035, 1, 6.878; 0.061, -1, 7.181; 0.000, 5.045; 0.003, 1, 5.720; 0.008, 1, 6.155; 0.011, 1, 6.323; 0.015, 1, 6.457; 0.023, 1, 6.644; 0.029, 1, 6.768; 0.041, 0, 6.958; 0.053, -1, 7.095; 0.068, -2, 7.246; 0.090, -4, 7.427; 0.108, -6, 7.555;

B = 100 mM; Z, 10³ (Z_{calc} - Z), -log [H⁺]; 0.000, 5.607; 0.002, 1, 6.153; 0.005, 1, 6.398; 0.007, 1, 6.554; 0.011, 1, 6.750; 0.015, 2, 6.885; 0.019, 1, 6.984; 0.025, 0, 7.101; 0.032, 0, 7.219; 0.039, 0, 7.309; 0.048, -1, 7.414; 0.056, -2, 7.489; 0.064, -2, 7.559; 0.076, -3, 7.646; 0.088, -4, 7.727; 0.104, -6, 7.821;

B = 20 mM; Z, 10³ (Z_{calc} - Z), -log [H⁺]; 0.003, 1, 6.575; 0.007, 0, 6.860; 0.009, 2, 7.009; 0.015, 1, 7.214; 0.029, 2, 7.492; 0.040, 2, 7.629; 0.050, 1, 7.720; 0.060, 2, 7.808; 0.090, 2, 7.999;

B = 10 mM; Z, 10³ (Z_{calc} - Z), -log [H⁺]; 0.001, 1, 6.242; 0.005, 1, 6.790; 0.010, 1, 7.042; 0.012, 1, 7.117; 0.020, 1, 7.331; 0.024, 1, 7.412; 0.033, 2, 7.561; 0.046, 2, 7.699; 0.054, 3, 7.786; 0.070, 0, 7.878; 0.080, -1, 7.937;

monocharged ions, so that the approximation seems well founded. In addition to that we assumed that E_{ob} , obtained before every titration in the acid "unhydrolysed" boric acid solution is the same also in the hydrolysed solutions used ($Z \leq 0.1$).

ELIMINATION OF THE MONONUCLEAR SPECIES; MEAN COMPOSITION OF THE POLYNUCLEAR COMPLEXES

From our experimental data, $Z(\log h)_B$, given in Table 1 and Fig. 1, we wish to calculate R^{-1} , the average degree of condensation of $B(\text{OH})_3$, and b , the actual concentration of $B(\text{OH})_3$. For this calculation we use the following two general equations given by Sillén⁵

$$R = \text{const} + \int \left(\frac{d \ln a}{d \ln B} \right)_Z dZ \text{ at constant } B \quad (4)$$

$$\ln b = \text{const} + R - \int Z d(\ln a) \text{ at constant } B \quad (5)$$

Knowing the position of the mononuclear curve, the contributions, B_1 and B_1Z_1 , of the mononuclear species in B and BZ may be calculated

$$B_1 = b + \beta_1 ab \quad (6) \quad B_1Z_1 = \beta_1 ab \quad (7)$$

With these data the mean composition of the polynuclear complexes may be calculated from the relations

$$\bar{q}_{\text{poly}} = \frac{B - B_1}{BR - B_1} \quad (8) \quad \bar{p}_{\text{poly}} = \frac{BZ - B_1Z_1}{BR - B_1} \quad (9)$$

where \bar{q}_{poly} is the average number of boron atoms and \bar{p}_{poly} the average charge of every polynuclear complex.

Calculation of R . Through every set of experimental points, $Z(\log h)$, with a common B -value a smoothed curve was drawn. In the family of curves, $Z(\log h)_B$ so obtained, lines were drawn for a number of round values of Z , $Z = 0.01, 0.02, \dots, 0.1$; for each of these, $\log h$ was read off at the point of intersection with each of the various B -lines. Thus we obtained a set of values $\log h (\log B)_Z$, from which we calculated the derivative in eqn. (4). For this

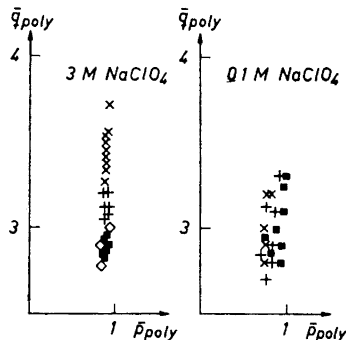


Fig. 2. The average charge, \bar{p} , and the average number of boron, \bar{q} , of polyborate ions in 3 M and 0.1 M $\text{Na}(\text{ClO}_4)$.

calculation we determined an approximating polynomial for every Z -value in such a way as to coincide with the function $\log h$ ($\log B$) at the points given. The desired derivative at a number of points could then be calculated from the derived polynomial. For every value of B , the derivatives were plotted against Z . These points fell approximately on a straight line and the value of the derivative at $Z = 0$ was obtained by linear extrapolation. The value of the integral in (4) was obtained by calculating the area between the straight line and the coordinate axes from $Z = 0$ up to an arbitrary Z -value. The integration constant was obtained from the lower limit of integration ($Z = 0$), at this limit only the mononuclear boric acid $B(OH)_3$ is present and $R = 1$.

Calculation of $\ln b$. The integral in (5) has been obtained by calculating the area between the $\log h$ -axes and the experimental $Z(\log h)_B$ -curves from $Z = 0$ up to an arbitrary Z -value and the constant was obtained from the lower limit of integration where $\ln b = \ln B$. The determination of the integral for $Z < 0.001$ using the experimental points is unsatisfactory and therefore this area has been estimated assuming the formation of one complex AB_3^- . (Ref.⁵, eqn. 20 ff.)

The \bar{q}_{poly} - and \bar{p}_{poly} -values obtained are collected in Fig. 3 and indicate both in 0.1 M and 3.0 M $\text{Na}(\text{ClO}_4)$

- that at least two polynuclear complexes must be formed
- that the anions formed all have the charge minus one
- that the average number, \bar{q}_{poly} , of boron atoms in the polynuclear complexes varies between 2.7 (≈ 3) and 3.7.

ANALYSIS USING NORMALIZED PROJECTION MAPS

On the basis of the results given in the previous section we constructed a number of normalized curves, $\log \mathbf{B}$ ($\log u$) $_{Z,l}$ and compared them with the

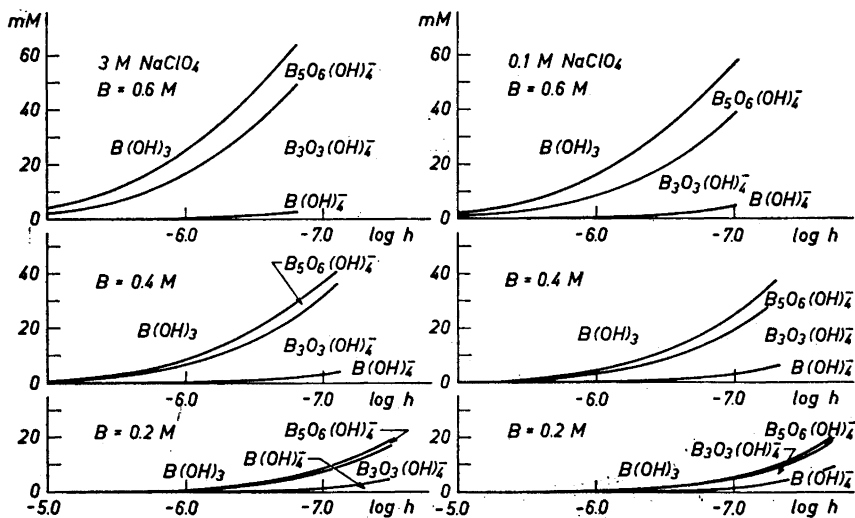


Fig. 3. Distribution of complexes as a function of $\log h$ for the total boron concentrations, $B = 0.6$ M, $B = 0.4$ M and $B = 0.2$ M.

corresponding experimental ones. We tried to explain our data with as few complexes as possible. With the data available we do not pretend to be able to determine more than three formation constants at the same time; thus every normalized projection map was constructed assuming not more than two polynuclear complexes AB_q and $AB_{q'}$ besides $B = B(OH)_3$ and $AB = B(OH)_4^-$. On the basis of the deduced \bar{q}_{poly} -values we also assumed $\bar{q}_{poly} \leq 6$.

Our analysis started with testing only one polynuclear complex besides B. Of these combinations, that one containing the polynuclear complex AB_3 , $B_3O_3(OH)_4^-$, could explain our experimental data over the broadest B - and Z -range. The explanation was satisfactory only at low B -values ($B \leq 0.2$ M). In the range of agreement between experimental and calculated points the following equilibrium constants could be deduced:

$$\log^* \beta_1 = -8.99, \log^* \beta_{13} = -6.85 \text{ (3 M NaClO}_4\text{)} \text{ and } \log^* \beta_1 = -8.98, \log^* \beta_{13} = -7.28 \text{ (0.1 M NaClO}_4\text{)}.$$

The agreement between calculated and experimental points is illustrated in Fig. 1 (the calculated curve is dotted).

In order to explain the deviation at higher B , we constructed normalized curves for various combinations of two q -values between 2 and 6 which makes $\bar{q}_{poly} \approx 3-4$ and $\bar{p}_{poly} = 1$, and compared them with the experimental data. For these cases the conditions for the concentrations together with the law of mass action gives

$$B = b + * \beta_1 h^{-1} b + q' * \beta_{1q} h^{-1} b^{q'} + q'' * \beta_{1q} h^{-1} b^{q''} \quad (10)$$

$$BZ = * \beta_1 h^{-1} b + * \beta_{1q} h^{-1} b^{q'} + * \beta_{1q} h^{-1} b^{q''} \quad (11)$$

and by the substitutions

$$u = * \beta_1 h^{-1}; v = b(* \beta_{1q} * \beta_1^{-1})^{1/(q'-1)}; B = B(* \beta_{1q} * \beta_1^{-1})^{1/(q'-1)} \quad (12)$$

(10) and (11) may be rewritten in the normalized form

$$B = v + uv + q' uv^{q'} + q'' l uv^{q''} \quad (13)$$

$$BZ = uv + uv^{q'} + l uv^{q''} \quad (14)$$

$$\text{where } \log l = \log \beta_{1q} + \frac{(q'' - q')}{(q' - 1)} \log \beta_1 - \frac{\{(q'' - 1)\}}{(q' - 1)} \log \beta_{1q} \quad (15)$$

With a known value of l one may calculate $\log B$ as a function of $\log u$ at constant Z -values. In order to decide whether a combination is possible or not it is necessary to calculate a number of projection maps with different l -values. In the present work about 5-8 l -values have been tested for every combination. The calculation of these projection maps has been carried out using the Ferranti Mercury high speed digital computer, "MATIMA", and an autocode program called PROKA^{2c}. Some of the maps have also been calculated on the Swedish computer "BESK" using a program written up for calculation of maps $\log B$ ($\log u$)_Z.

We found from these calculations that the two complex-combinations, $B + AB + AB_3 + AB_4$ and $B + AB + AB_3 + AB_5$ well explained our experi-

mental data. The projection maps which were calculated assuming polynuclear complexes, $AB_2 + AB_4$ and $AB_2 + AB_5$ as well as the mononuclear species, could be ruled out as they explained the experimental data only at high B -values and not at all at low B (0.01 M and 0.02 M); neither did the combination $B + AB + AB_3 + AB_6$ explain our data.

For the two possible combinations the following preliminary equilibrium constants were calculated:

in 3 M $NaClO_4$: $\log * \beta_1 = -8.98$, $\log * \beta_{13} = -6.86$, $\log * \beta_{15} = -6.70$,
 $\log * \beta_1 = -8.98$, $\log * \beta_{13} = -6.90$, $\log * \beta_{14} = -6.87$

in 0.1 M $NaClO_4$: $\log * \beta_1 = -8.96$, $\log * \beta_{13} = -7.35$, $\log * \beta_{15} = -6.70$,
 $\log * \beta_1 = -8.96$, $\log * \beta_{13} = -7.28$, $\log * \beta_{14} = -7.20$

The use of normalized projection maps and the computer program PROKA^{2c} has thus made possible the first assessment of the different complex-combinations. For the final choice and for the refinement of the equilibrium constants it was desirable to compare all experimental data directly with calculated curves. For this purpose the methods of LETAGROP^{2c} and KUSKA^{2c} seemed to be promising.

REFINEMENT OF THE EQUILIBRIUM CONSTANTS

In the present work we started the refinement of the equilibrium constants for the two possible complex-combinations by calculating a number of maps $Z(\log h)_B$ for different sets of equilibrium constants and compared these ones with the experimental points. For this calculation we used "MATIMA" and the autocode program KUSKA^{2c}. This refinement gave the following set of equilibrium constants:

in 3 M $NaClO_4$: $\log * \beta_1 = -9.00 \pm 0.05$, $\log * \beta_{13} = -6.90 \pm 0.1$, $\log * \beta_{15} = -6.65 \pm 0.20$;
 $\log * \beta_1 = -9.00 \pm 0.05$, $\log * \beta_{13} = -6.94 \pm 0.1$, $\log * \beta_{14} = -6.95 \pm 0.20$;

in 0.1 M $NaClO_4$: $\log * \beta_1 = -8.98 \pm 0.05$, $\log * \beta_{13} = -7.29 \pm 0.1$, $\log * \beta_{15} = -6.77 \pm 0.20$;
 $\log * \beta_1 = -8.98 \pm 0.05$, $\log * \beta_{13} = -7.36 \pm 0.1$, $\log * \beta_{14} = -7.14 \pm 0.20$;

The choice of this set of constants as the "best" one is based on a visual comparison between experimental data and a number of calculated maps, $Z(\log h)_B$. The limits of the errors given are those within which the constants may be varied before "fitting is lost". This treatment is satisfactory considering the reproducibility of analyses and emf measurements. A more quick treatment may be given by using the method of last squares. A suitable form for this calculation has been given by Sillén^{2b} and also, a program, LETAGROP, for calculations using a high speed computer has been worked out^{2c}. The information obtained by using LETAGROP on data of the present work is collected in Table 2.

Table 2. Equilibrium constants, ${}^*\beta_{pq}$, with the errors, 3σ , obtained by using the least squares program LETAGROP on data for equilibria in borate solutions. The complexes $AB^-({}^*\beta_1)$, $AB_3^-({}^*\beta_{13})$, $AB_5^-({}^*\beta_{15})$ or $AB_4^-({}^*\beta_{14})$ are formed from boric acid, B. The experimental points, which have been used in the calculation are denoted in Table 1 and all points have been given the weight, $w = 1$. B stands for $B(OH)_3$.

Reaction	3 M Na(ClO ₄)		0.1 M Na(ClO ₄)	
	$\sim AB_4^-$	$\sim AB_5^-$	$\sim AB_4^-$	$\sim AB_5^-$
$B + H_2O \rightleftharpoons B(OH)^- + H^+$ $-\log {}^*\beta_1 \pm 3\sigma =$	9.00 ± 0.018	9.00 ± 0.015	8.98 ± 0.009	8.98 ± 0.006
$3B + H_2O \rightleftharpoons B_3(OH)^- + H^+$ $-\log {}^*\beta_{13} \pm 3\sigma =$	6.94 ± 0.051	6.91 ± 0.028	7.36 ± 0.042	7.29 ± 0.015
$4B + H_2O \rightleftharpoons B_4(OH)^- + H^+$ $-\log {}^*\beta_{14} \pm 3\sigma =$	6.96 ± 0.180	—	7.14 ± 0.108	—
$5B + H_2O \rightleftharpoons B_5(OH)^- + H^+$ $-\log {}^*\beta_{15} \pm 3\sigma =$	—	6.62 ± 0.156	—	6.77 ± 0.102
Standard deviation in Z , $\sigma(Z) =$	± 0.0024	± 0.0021	± 0.0016	± 0.0011

In the calculation using LETAGROP only random errors are considered. Our emf measurements are not better than ± 0.1 mV and the reproducibility of our chemical analysis, 0.3 %.

CONCLUSIONS

Consequently our data for the hydrolysis of boric acid in 3.0 M NaClO₄ and 0.1 M NaClO₄ could be explained, assuming constant activity factors in each medium, with the species $B(OH)_3$, $B(OH)_4^-$, $B_3O_3(OH)_4^-$ and either $B_5O_6(OH)_4^-$ (best fit) or $B_4O_5(OH)_3^-$. Due to the low solubility of boric acid, B_5 could not be as high as would be desirable for making a choice between $B_4O_5(OH)_3^-$ and $B_5O_6(OH)_4^-$. We are, however, inclined to favour the formula $B_5O_6(OH)_4^-$; it gives a somewhat better agreement with the data, and moreover this ion (but not $B_4O_5(OH)_3^-$) has been found as a separate unit in crystals⁶.

One may ask whether it is possible to explain the present data with $B(OH)_3$, $B(OH)_4^-$ and $B_3O_3(OH)_4^-$ only, by analysing each curve, $Z(\log h)_B$, independent of the others, and get a new set of equilibrium constants for every B. Such an analysis has also been made and we found that this treatment also explained the data tolerably. However in this case the fit between the experimental and calculated curves was not as good as by assuming, *e.g.*, $B_5O_6(OH)_4^-$ and therefore we preferred an explanation using the law of mass action. This explanation may also to some extent be supported by the fact that both media give the same answer.

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