ACTA CHEMICA SCANDINAVICA 1 (1947) 631—655

On the Hydrolysis of the Bi^{3+} Ion

Repeated Oxygen Bridging: A new Type of Ionic Equilibrium

FREDRIK GRANÉR and LARS GUNNAR SILLÉN

Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden

It is well known that the ion Bi^{3+} easily reacts with water (is hydrolysed) in some way so that hydrogen ions are set free. On the nature of the reaction products, however, very little has been known with certainty.

PREVIOUS WORK

Smith[1] in 1923 studied

1. the conductivity of solutions of $Bi(NO_3)_3$ in excess of HNO_3,
2. the solubility of $Bi(OH)_2NO_3$ in HNO_3 of different concentrations,
3. the conductivity of solutions of $Bi(OH)_2ClO_4$ with different amounts of $HClO_4$ and
4. the emf of cells $Pt,H_2/HClO_4(NaClO_4)/Bi(ClO_4)_3,HClO_4(NaClO_4)/Bi$.

Smith concluded from 1. and 2. that bismuth is chiefly present as Bi^{3+} in solutions with excess of HNO_3. From 3. be concluded that the ion $Bi(OH)_2^+$ is rather stable but on addition of a large excess of $HClO_4$ is gradually transformed to $BiOH^{2+}$ and Bi^{3+}. He tried to evaluate 4. by assuming that all Bi is present either as BiO^+ only, or as $BiOH^{2+}$ only; no certain conclusions could however be drawn.

Swift[2] in the same year studied equilibria between Cu and Bi metals and Cu^{2+}, H^+ and bismuth (III) ions in perchlorate solutions. He assumed that Bi occurred either only as BiO^+ or only as $BiOH^+$; with the latter hypothesis the calculated molal potential of Bi came out slightly more constant.

Smith and Swift discussed only the formulae Bi^{3+}, $BiOH^{2+}$, BiO^+ (or Bi $(OH)_2^+$) and their complexes with NO_3^- or ClO_4^-. In 1936 Holmqvist[3] on one side and Prytz and Nagel[4] on the other, independently arrived at the conclusion that there must be *polynuclear* bismuth ions among the reaction products.

Prytz and Nagel concluded from measurements of the rate of diffusion of bismuth perchlorate that simple molecules prevail in solutions of high acidity. In less acid solutions the molecular weight is at first doubled and then increases further, although the latter process could not be followed for experimental reasons. On titration of Bi^{3+} with OH^- they found a number of small breaks in the curve (conductivity/added volume), which they explained in terms of the formation of $BiOH(ClO_4)_2$, $Bi(OH)_2ClO_4$, $Bi_2(OH)_2O(ClO_4)_2$, and $(BiOH)_4O_3(ClO_4)_2$. On titration of $Bi(OH)_2ClO_4$ with $HClO_4$, there was only one break in the curve (temperature/added volume) which was attributed to the formation of $BiOH(ClO_4)_2$ from $Bi(OH)_2ClO_4$. Measurements of the optical absorption of different solutions were explained in terms of the compounds mentioned. Emf titrations gave no useful results because of difficulties with the hydrogen and quinhydrone electrodes. Prytz and Nagel claim to have isolated, in addition to the previously known $Bi(OH)_2ClO_4$, the solid compounds $Bi_3(OH)_3O_2(ClO_4)_2$, $(BiO)_2OHClO_4$, and $Bi_2(OH)_3OClO_4$.

Holmqvist [3] measured the emf of different cells with Bi or quinhydrone electrodes in solutions containing bismuth perchlorate, $NaClO_4$, and $HClO_4$. From these measurements he concluded that bismuth is present almost exclusively as Bi^{3+} at $[H^+] > 0.5$ C, that there is no considerable complex formation between Bi^{3+} and ClO_4^- but strong complexes between Bi^{3+} and Cl^-, and that the bismuth ions formed in less acid solutions are chiefly binuclear. By assuming that only Bi^{3+}, $Bi_2(OH)_4^{2+}$ and $Bi_2(OH)_5^+$ are formed, and that the equilibrium constants (in 0.5 C $NaClO_4$) are: $[Bi^{3+}]^2 [Bi_2(OH)_4^{2+}]^{-1}[H^+]^{-4} = 0.025$, and $[Bi^{3+}]^2 [Bi_2(OH)_5^+]^{-1}[H^+]^{-5} = 0.000025$, Holmqvist could explain the measured emf:s with an accuracy of 1.5 mV, which he considered to be within the limits of experimental error. He has also prepared the solid compound $Bi_2(OH)_3OClO_4$.

Holmqvist is the only investigator, whose results have had enough accuracy for permitting him to try to apply the law of mass action to the equilibrium between different bismuth ions. His measurements are, however, rather few and did not allow a very elaborate theory. Otherwise it is difficult to understand, why the two complexes $Bi_2(OH)_4^{2+}$ and $Bi_2(OH)_5^+$ should predominate over all other conceivable formulae.

It thus seemed highly desirable to make new and accurate experiments on the hydrolysis of Bi^{3+}.

CHOICE OF EXPERIMENTAL CONDITIONS

We decided to work with solutions of constant ionic strength so that the activity factors of all ions could be assumed to be approximately constant. The anions that can be assumed to have the least tendency to form complexes with Bi^{3+} are NO_3^- and ClO_4^-; of these we preferred ClO_4^- since the hydroxynitrates of bismuth are known to be less soluble than the hydroxyperchlorates.

Our solutions were prepared so as always to contain 3 C ClO_4^- and Na^+, H^+ and Bi ions. Such a high ionic strength was desirable for two reasons: the H^+ concentration had to be rather high in some of our solutions, and it was necessary to counteract as much as possible the influence on the electrostatic forces in the solution by the polyvalent Bi ions which might be formed. The total bismuth concentration was kept at 10, 25, or 50 mC. At higher concentrations the changes in ionic strength caused by the reactions of bismuth would be too large and precipitation would occur inconveniently early; at lower concentrations the changes in $[H^+]$ could not be measured accurately enough.

In these solutions it was desired to measure the concentrations $[H^+] = h$ and $[Bi^{3+}] = b$. For measuring h, a hydrogen electrode cannot be used, since bismuth metal is then formed by reduction. A glass electrode might be used, but would not be expected to give very accurate results in solutions of such high H^+ and Na^+ concentrations. Happily enough the quinhydrone electrode proved to be accurate and not affected by the presence of Bi^{3+} (see below). For the measurements of $[Bi^{3+}]$ we preferred bismuth amalgam electrodes to the bismuth metal electrodes used by Holmqvist. They were found to function very well. The solutions were prepared by titration; in this way a considerable number of measurements could be obtained with a minimum of manipulation. We found it convenient to use as reference electrode:

$$\mathrm{CE}// = \mathrm{Hg,Hg_2Cl_2/4\ C\ NaCl/\ 4\ C\ NaClO_4/}$$

The cells used were of the following two types (Q=quinone):

$$-\ \mathrm{CE//H^+,QH_2,Q/Pt}\ +$$
$$E_Q = E_{0Q} + 59.16 \log h + E_d = E' + 59.16 \log h \qquad (1)$$

$$-\ \mathrm{CE//\ Bi^{3+}/Bi(in\ Hg)}\ +$$
$$E_{Bi} = E_{0Bi} + \frac{59.16}{3} \log [Bi^{3+}] + E_d = E' + (E_{0Bi} - E_{0Q}) + 19.72 \log b \qquad (2)$$

It is not required to determine separately the constant E_{0Q} or the variable diffusion potential E_d, whereas their sum E' is an accurately determinable quantity. As H^+ ions are always present in considerable amounts on the right hand side in our cells, and as their mobility by far exceeds that of the other ions present, we can confidently assume that *the diffusion potential and thus* E' *is a function of the hydrogen ion concentration* h *only.*

Then three types of measurements were needed:

1. Quinhydrone electrode with solutions of known h (h C $HClO_4$,(3-h) C $NaClO_4$). From these experiments the values of E' for different h were calcul-

ated, and E' could be plotted and tabulated as a function of h or, more conveniently, of E_Q.

2. Quinhydrone electrode and the bismuth solution to be investigated. E' and h were obtained from the measured E_Q by means of the measurements 1/.

3. Bismuth amalgam electrode and the same bismuth solutions as in 2/. E' being known from the measurements 2/, one can calculate $E_{Bi}—E' = (E_{0Bi} — E_{0Q}) + 19.72 \log b$. If the total Bi concentration is kept constant at B, and h is increased, the hydrolysis is pressed back, and b tends to the value B. Happily enough, this seems to occur within the range of concentrations studied by us*: $E_{Bi} — E'$ tended to a limiting value, which according to (2) should be:

$$\lim_{h \to \infty} (E_{Bi} — E') = E_{0Bi} — E_{0Q} + 19.72 \log B \qquad (3)$$

When the constant $(E_{0Bi} — E_{0Q})$ had been obtained, $[Bi^{3+}] = b$ could be calculated for all solutions, by means of (2). E_{0Bi} can be expected to change with the composition of the amalgam, thus to be different for different batches of amalgam.

The following quantities were thus known for every solution:

From the analysis: $B =$ total bismuth concentration (in mC Bi)
$H =$ total hydrogen ion concentration (assuming all bismuth to be present as Bi^{3+})
From the emf: $b =$ actual concentration $[Bi^{3+}]$
$h =$ actual concentration $[H^+]$

In each series of experiments, B was kept constant. The results are conveniently given as graphs of bB^{-1} (the fraction of Bi present as Bi^{3+}) and $(h — H)B^{-1}$ (the number of H^+ set free per Bi atom) as functions of h.

EXPERIMENTAL

In all our measurements a solution T rich in H^+ was added to one S of low h and the same B. It was tried to add NaOH in order to study the equilibria at lower h, but then a precipitate was immediately formed. The apparatus used was the same as described by Sillén [5]. The bismuth amalgam electrodes consisted of a pool on the bottom of the titration vessel; the electrical connection was made by means of a Pt needle.

---

* In a few preliminary experiments with 1 C ClO_4^-, the limiting value could not be determined with certainty. This was one reason for our using 3 C ClO_4^- in all succeeding experiments.

Liquid bismuth amalgam containing about 1 % Bi was prepared by dissolving Bi in Hg at 90° under cover of boiled distilled water. It was stored under water. This procedure gave quite a satisfactory product and eliminated the necessity of using a N_2 atmosphere or vacuum.

The perchloric acid and sodium perchlorate were obtained and analysed as described by Sillén, the concentration of the perchloric acid being also determined by adding excess of NH_3, evaporating at 105° and weighing NH_4ClO_4 (*cf.* Holmqvist[3] p. 64). The results agreed with those of titration with NaOH within 0.2 %.

The bismuth perchlorate solutions were prepared by dissolving Bi_2O_3 (Merck pro analysi) in perchloric acid. Bismuth was precipitated with NH_3, ignited and weighed as Bi_2O_3; in the filtrate, the amount of ClO_4^- was determined by weighing as NH_4ClO_4 as above.

The E_Q and E_{Bi} measured were steady and very reproducible. Each titration was made at least twice and the difference between corresponding points seldom found to exceed 0.1 mV.

The glass electrode was a commercial one manufactured by Rudolph Grave AB. The glass electrode emf:s were measured by means of a Radiometer valve potentiometer.

COMPARISON OF GLASS AND QUINHYDRONE ELECTRODES

A number of titration experiments were made with cells

— CE//solution/glass electrode +

The emf obtained, E_{glass}, behaved in a very irregular way. In some pairs of titrations E_{glass} followed closely E_Q for the same solutions (*i. e.* $E_Q - E_{glass}$ kept almost constant) for a certain time, then suddenly E_{glass} would jump several mV, and then again follow E_Q. The quinhydrone electrode gave on the other hand very reproducible and steady potentials.

It might be feared that quinone or especially hydroquinone might form some sort of complex with Bi^{3+}; in this case E_Q could not be directly used for measuring h, and moreover all the bismuth equilibria would be displaced on addition of quinhydrone.

At high h almost all the Bi is assumed to be present as Bi^{3+} and it was found that, for a given h, almost the same E_Q was obtained whether the solution contained any Bi or not (see the discussion of δ below), and the variation of E_Q with h was identical within 0.1 mV. This seems to show that at high h no considerable error is caused by Bi-quinhydrone complexes. However, it was still desirable to make some sort of control at lower h.

Table 1. Comparison of quinhydrone and glass electrodes.

S = 2900 mC $NaClO_4$, 100 mC $HClO_4$, 100 ml
T = 2750 mC $NaClO_4$, 100 mC $HClO_4$, 50 mC $Bi(ClO_4)_3$, 0—50 ml

ml	E_Q	E_{glass}
0	413.0	61.2
5	413.5	61.8
10	414.2	62.1
15	414.8	62.8
20	415.3	63.2
25	415.9	63.7
30	416.5	64.0
35	417.0	64.6
40	417.4	65.0
45	417.9	65.4
50	418.3	65.9

In the experiments given in Table 1, the original solution S contained no Bi, whereas the added solution T contained 50 mC Bi. As seen from Table 1, E_Q and E_{glass} were parallel in the two titrations and there is no irregular behaviour of E_Q on the addition of Bi. During the entire titration, E_Q is changed by 5.3 mV and E_{glass} by 4.7 mV; this is normal, as the slope of E_{glass} against log h is, in such solutions, lower than 59.16 (see Dole[6] Chapter 8).

RESULTS

From our measurements of E_Q in solutions of known h every fourth of the points is given in Table 2. In Fig. 1, E' is plotted as a function of E_Q. It was necessary to add a small correction δ in order to make E_Q values measured at different times comparable. The correction δ was the same throughout each titration and was calculated so that $E_Q + \delta$ was the same for points of the same h in all titrations. One reason for the appearance of δ is that the calomel electrodes change slowly with time. If titrations with Bi solutions were made immediately before or after such without any Bi, δ was found to be 0.4 mV lower for $B = 25$ mC and 0.7 mV lower for $B = 50$ mC than for $B = 0$. The reason is probably the small changes in ionic strength on replacing 3 Na^+ by Bi^{3+}.

The measured E_Q and E_{Bi} in solutions containing bismuth are given in Tables 3—5. From these the quantities bB^{-1} (the part of the Bi present as

Table 2. Determination of E'. Only every fourth point is given.

A. S = 3000 mC $NaClO_4$, 100 ml; T = 2800 mC $NaClO_4$, 200 mC $HClO_4$, 0—50 ml $\delta = +0.6$ mV.

ml	h mC	E	E'
1	1.98	300	(460)
5	9.52	337.2	457.4
9	16.51	351.2	457.2
13	23.01	359.6	457.1
20	33.33	369.0	457.0
30	46.15	377.0	456.6
45	62.07	384.4	456.5
50	66.67	386.2	456.3

B. S = 3000 mC $NaClO_4$, 100 ml; T = 1500 mC $NaClO_4$, 1500 mC $HClO_4$, 0—50 ml $\delta = 0.0$ mV.

ml	h mC	E	E'
1	14.9	349.5	(457.6)
5	71.4	388.2	456.0
9	123.9	400.9	454.6
16	207	412.4	452.9
25	300	420.2	451.1
35	389	425.4	449.7
45	465	428.8	448.4
50	500	430.2	448.0

C. S = 2700 mC $NaClO_4$, 300 mC $HClO_4$, 100 ml. T = 1500 mC $NaClO_4$, 1500 mC $HClO_4$, 0—50 ml. $\delta = 0.0$ mV.

ml	h mC	E	E'
0	300	420.2	451.1
10	409	426.5	449.5
20	500	430.3	448.1
30	577	432.9	447.0
40	643	434.8	446.2
50	700	436.1	445.3

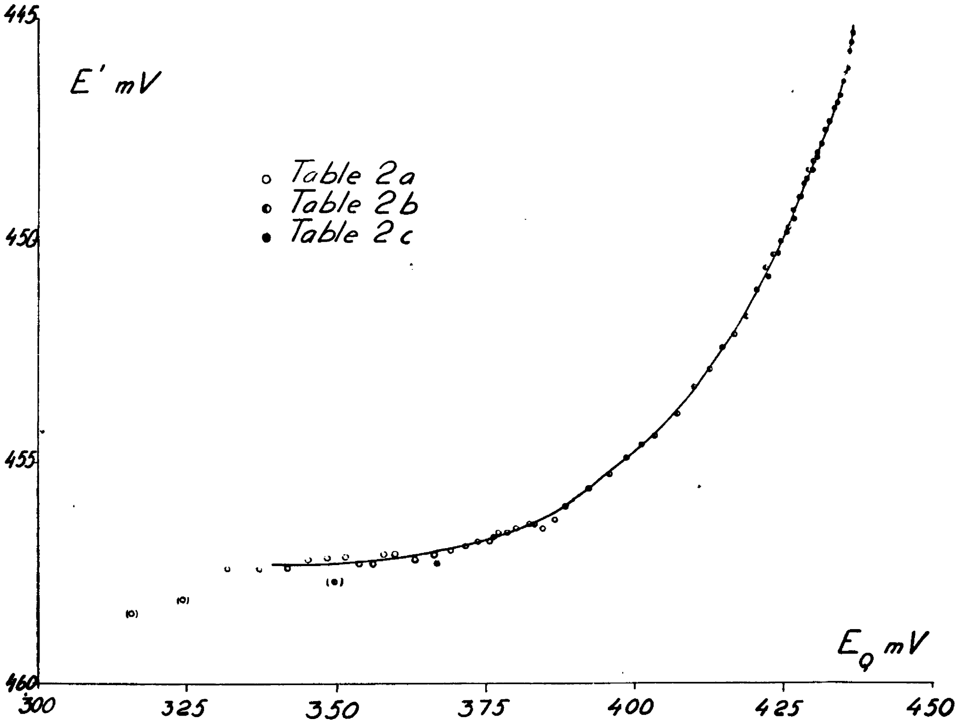


Fig. 1. E' as a function of E_Q (Tab. 1, eq. (1)).

Bi^{3+}) and $(h - H)B^{-1}$ (the number of H^+ ions set free per Bi atom) were computed by means of formulae (1), (2), and (3). They are plotted as functions of h in Figs. 2 and 3.

ON THE MECHANISM OF THE PROCESS

The simplest assumption that can be made is that, except Bi^{3+}, only mononuclear complexes $BiOH^{2+}$, $Bi(OH)_2^+$ (or BiO^+), and possibly uncharged $Bi(OH)_3$ are formed, thus

$$Bi^{3+} + H_2O \rightleftharpoons BiOH^{2+} + H^+; \; Bi^{3+} + 2H_2O \rightleftharpoons Bi(OH)_2^+ + 2H^+; Bi^{3+} + 3H_2O \rightleftharpoons Bi(OH)_3 + 3\,H^+$$

The equilibrium conditions would then be

$$[BiOH^{2+}] = \varkappa_1 \,[Bi^{3+}]\,[H^+]^{-1} = \varkappa_1 b h^{-1}; \; [Bi(OH)_2^+] = \varkappa_2 b h^{-2}; [Bi(OH)_3] = \varkappa_3 \, b h^{-3}$$

Table 3. Measurements with $B = 50$ mC.

$S = 2850$ mC $NaClO_4$, 50 mC $Bi(ClO_4)_3$
$T = 1350$ mC $NaClO_4$, 50 mC $Bi(ClO_4)_3$, 1500 mC $HClO_4$.
A. and B. Determination of h.
A. $S = 75$ ml; $T = 0$—65 ml; $\delta = -0.7$ mV.

ml	H mC	E_Q	E'	h mC	$h - H$
0	0	394.4	455.5	90.4	90.4
2	39.0	401.5	454.7	122.7	83.7
4	76.0	406.5	454.0	152.8	76.8
6	111.1	410.3	453.4	182.0	70.9
8	144.6	413.2	452.9	207.5	62.9
10	176.4	415.6	452.4	232.3	55.9
12	207	417.7	452.0	256	49
14	236	419.5	451.5	280	44
16	264	421.1	451.1	303	39
18	290	422.4	450.8	322	32
20	316	423.6	450.4	343	27
22.5	346	425.0	450.0	368	22
25	375	426.3	449.6	393	18
27.5	402	427.4	449.2	417	15
30	429	428.5	448.9	440	11
32.5	453	429.5	448.6	463	10
35	477	430.4	448.3	481	4
37.5	500	431.2	448.1	505	5
40	522	431.9	447.8	524	2
42.5	543	432.5	447.6	541	—2
45	563	433.2	447.3	562	—1
47.5	582	433.8	447.0	582	0
50	600	434.4	446.7	603	3
52.5	618	434.9	446.5	619	1
55	635	435.4	446.2	637	2
57.5	651	435.8	446.0	655	4
60	667	436.2	445.8	670	3
62.5	682	436.5	445.6	682	0
65	696	436.8	445.4	697	1

where $\varkappa_1$, $\varkappa_2$, and $\varkappa_3$ are constants. The total Bi concentration B and the amount of H^+ set free per litre would be

$$B = [Bi^{3+}] + [BiOH^{2+}] + [Bi(OH)_2^+] + [Bi(OH)_3] = b\,(1 + \varkappa_1 h^{-1} + \varkappa_2 h^{-2} + \varkappa_3 h^{-3})$$
$$h - H = [BiOH^{2+}] + 2[Bi(OH)_2^+] + 3[Bi(OH)_3] = b(\varkappa_1 h^{-1} + 2\,\varkappa_2 h^{-2} + 3\,\varkappa_3 h^{-3})$$

Table 3.

B. $S = 100$ ml, $T = 0$—50 ml, $\delta = -0.7$ mV.

ml	H mC	E_Q	E'	h mC	$h - H$
0	0	394.4	455.5	90.4	90.4
1	14.9	397.4	455.2	102.6	87.7
2	29.4	400.1	454.9	115.3	85.9
3	43.7	402.2	454.6	126.8	83.1
4	57.7	404.3	454.3	139.0	81.3
5	71.4	406.1	454.1	150.3	78.9
6	84.9	407.6	453.9	160.7	75.8
7	98.1	409.1	453.6	172.2	74.1
8	111.1	410.3	453.4	182	71
9	123.9	411.5	453.2	192	68
10	136.4	412.6	453.0	202	66
11	150.0	413.6	452.8	212	62
12	160.7	414.6	452.6	222	61
13	172.6	415.5	452.4	232	61
14	184.2	416.4	452.2	242	58
15	195.7	417.1	452.1	248	53
16	207	417.8	452.0	257	50
17	218	418.5	451.8	266	48
18	229	419.2	451.6	276	47
19	239	419.8	451.5	283	44
20	250	420.4	451.4	291	41
21	260	421.0	451.2	301	41
22.5	276	421.8	451.0	313	37
24	290	422.5	450.8	324	34
25	300	423.0	450.6	333	33
27.5	324	424.1	450.4	350	26
30	346	425.3	450.0	371	25
32.5	368	426.1	449.6	390	22
35	389	427.0	449.3	408	19
37.5	409	427.9	449.1	427	18
40	429	428.7	448.9	444	15
42.5	447	429.4	448.6	461	14
45	465	430.1	448.4	478	13
47.5	483	430.7	448.2	492	9
50	500	431.3	448.0	508	8

It is seen from the last two equations that in this case bB^{-1} and $(h—H)B^{-1}$ must be functions of h only, independent of the total bismuth concentration B. This is seen not to be true (Figs. 2 and 3). On the contrary for a given h,

Table 3.

C. Determination of b.
$S = 75$ ml . $T = 0—65$ ml.
lim $(E' - E_{Bi}) = 413.7$; $E_{0Q} - E_{0Bi} = 447.2$.

ml	E_{Bi}	$E' - E_{Bi}$	b
0	16.8	438.7	2.70
1	19.4	435.7	3.84
2	21.4	433.1	5.20
3	23.0	431.3	6.41
4	24.5	429.5	7.91
5	25.6	428.1	9.31
6	26.7	426.7	10.96
7	27.6	425.5	12.62
8	28.3	424.6	14.00
9	29.0	423.6	15.7
10	29.7	422.7	17.5
11	30.3	421.9	19.2
12	30.8	421.2	20.8
13	31.3	420.5	22.6
14	31.6	420.0	24.0
15	32.0	419.4	25.7
16	32.2	419.0	26.9
17	32.5	418.5	28.6
18	32.8	418.0	30.3
20	33.3	417.1	33.7
22.5	33.7	416.3	36.9
25	33.9	415.7	39.6
27.5	34.1	415.1	42.5
30	34.1	414.8	44.5
32.5	34.0	414.6	45.0
35	33.8	414.5	45.5
37.5	33.7	414.4	46.1
40	33.5	414.3	46.7
42.5	33.2	414.4	46.1
45	33.3	414.0	48.3
47.5	33.2	413.8	49.4
50	32.9	413.8	49.4
52.5	32.7	413.8	49.4
55	32.5	413.7	50.0
57.5	32.3	413.7	50.0
60	32.1	413.7	50.0
62.5	32.0	413.6	50.6
65	31.7	413.7	50.0

Table 4. Measurements with B = 25 mC.

S = 2925 mC $NaClO_4$, 25 mC $Bi(ClO_4)_3$.
T = 1425 mC $NaClO_4$, 25 mC $Bi(ClO_4)_3$, 1500 mC $HClO_4$.
A. Determination of h.
S = 100 ml, T = 0—50 ml, δ = —0.4 mV.

ml	H mC	E_Q	E'	h mC	$h - H$
0	0	378.4	456.7	46.8	46.8
1	14.9	384.4	456.3	60.0	45.1
2	29.4	389.0	455.9	73.0	43.6
3	43.7	392.9	455.6	85.9	42.2
4	57.7	396.0	455.3	98.0	40.3
5	71.4	398.5	455.0	109.1	37.7
6	84.9	400.8	454.7	120.8	35.9
7	98.1	402.8	454.5	131.8	33.7
8	111.1	404.6	454.3	142.2	31.1
9	123.9	406.2	454.0	153.1	29.2
10	136.4	407.7	453.8	163.7	27.3
11	150.0	409.1	453.6	174	24
12	160.7	410.3	453.4	184	23
13	172.6	411.4	453.2	193	20
14	184.2	412.5	453.0	204	20
15	195.7	413.5	452.8	213	17
16	207	414.5	452.6	223	16
17	218	415.3	452.4	232	14
18	229	416.1	452.3	240	11
19	239	416.9	452.1	250	11
20	250	417.7	451.9	260	10
21	260	418.3	451.7	269	9
22.5	276	419.4	451.5	283	7
24	290	420.3	451.3	294	4
25	300	420.9	451.1	304	4
27.5	324	422.4	450.7	327	3
30	346	423.6	450.4	347	1
32.5	368	424.8	450.0	366	—2
35	389	425.8	449.7	388	—1
37.5	409	426.7	449.4	407	—2
40	429	427.7	449.1	429	0
42.5	447	428.5	448.8	447	0
45	465	429.3	448.6	460	—5
47.5	483	430.0	448.3	483	0
50	500	430.6	448.1	498	—2

Table 4.

B. Determination of b.
$S = 75$ ml, $T = 0$—50 ml.
$\lim\ (E' - E_{\mathrm{Bi}}) = 420.4$; $E_{0\mathrm{Q}} - E_{0\mathrm{Bi}} = 448.0$.

ml	E_{Bi}	$E' - E_{\mathrm{Bi}}$	b
0	5.4	451.3	0.68
1	10.3	445.9	1.27
2	14.2	441.5	2.13
3	16.7	438.6	2.98
4	18.8	436.1	3.99
5	20.7	433.9	5.18
6	22.1	432.2	6.31
7	23.3	430.7	7.53
8	24.3	429.4	8.75
9	25.3	428.1	10.20
10	26.1	427.0	11.55
12	27.3	425.3	14.15
14	28.1	424.0	16.40
16	28.7	423.0	18.45
18	29.0	422.3	20.0
20	29.2	421.7	21.5
22.5	29.2	421.2	22.8
25	29.0	420.9	23.6
27.5	28.7	420.8	23.9
30	28.4	420.7	24.2
32.5	28.1	420.6	24.4
35	28.0	420.4	25.0
37.5	27.6	420.5	24.7
40	27.3	420.5	24.7
42.5	27.1	420.5	24.7
45	26.8	420.5	24.7
47.5	26.7	420.3	25.3
50	26.5	420.2	25.6

the hydrolysis goes farther (bB^{-1} is smaller and $(h - H)B^{-1}$ larger) the larger is B. Thus it is clear that there must also be *polynuclear* complexes present. At first we tried to assume that the only ionic species present in considerable amounts are Bi^{3+} and one or two ions of the type $\mathrm{Bi}_n(\mathrm{OH})_m^{3n-m}$, where n and m were the unknowns sought for. Equilibrium conditions were set up assuming the combinations

$$\mathrm{BiOH}^{2+} + \mathrm{Bi}_n(\mathrm{OH})_m^{3n-m}$$

$$\mathrm{Bi(OH)}_2^{+} + \mathrm{Bi}_n(\mathrm{OH})_m^{3n-m}$$

$$Bi_n(OH)_m^{3n-m} + Bi_n(OH)_{m+1}^{3n-m-1}$$

among others, and an attempt was made to determine n and m. However, we could not explain, even approximately, our experimental data by any such assumption.

Considerations of several kinds led us to propose a new type of mechanism. As is well known, the acidity of Al^{3+} and Fe^{3+} was explained by Brönsted and Volqvartz [7] by the tendency of the coordinated water molecules to split off a proton; this process is favoured by the electrostatic repulsion of the central ion (Fig. 4a). For the »aquo» ions $Fe(H_2O)_6^{3+}$ and $Al(H_2O)_6^{3+}$ K_a seems to be about 10^{-3} and 10^{-5}. (As for Fe^{3+} see also Brosset [8] and Lindstrand [9].) For Bi^{3+} with its larger radius and thus lower Coulomb forces, the aquo acidity might be expected to be less; actually, however, the main part of the H^+

Table 5. Measurements with $B = 10$ mC.

S = 2970 mC $NaClO_4$, 10 mC $Bi(ClO_4)_3$, 100 ml.
T = 1470 mC $NaClO_4$, 10 mC $Bi(ClO_4)_3$, 1500 mC $HClO_4$, 0—50 ml.
A. Determination of h.
$\delta = -1.6$ mV.

ml	H mC	E_Q	E'	h mC	$h - H$
0	0	358.4	457.3	20.0	20.0
1	14.9	371.5	457.1	33.6	18.7
2	29.4	379.9	456.7	47.3	17.9
3	43.7	385.8	456.3	60.5	16.8
4	57.7	390.4	456.0	73.1	15.4
5	71.4	394.2	455.6	86.1	14.7
6	84.9	397.3	455.3	98.4	13.5
8	111.1	402.2	454.7	121.9	10.8
10	136.4	406.0	454.2	143.9	7.5
12	160.7	409.1	453.8	165.2	4.5
14	184.2	411.9	453.3	187.5	3.3
16	207	414.3	452.9	209	2
18	229	416.4	452.5	231	2
20	250	418.3	452.1	252	2
25	300	421.9	451.2	301	1
30	346	424.7	450.4	343	—3
35	389	427.1	449.6	392	3
40	429	428.9	449.1	429	0
45	465	430.5	448.6	465	0
50	500	431.9	448.1	500	0

B. Determination of *b*

$\lim (E' - E_{\mathrm{Bi}}) = 428.1$ mV; $E_{0\mathrm{Q}} - E_{0\mathrm{Bi}} = 447.8$ mV

ml	E_{Bi}	$E' - E_{\mathrm{Bi}}$	b
0	—8.9	466.2	0.117
1	0.0	457.1	0.339
2	5.6	451.1	0.682
3	9.4	446.9	1.11
4	12.2	443.8	1.60
5	14.5	441.1	2.19
6	16.3	439.0	2.80
8	19.2	435.5	4.22
10	21.2	433.0	5.65
12	22.6	431.2	7.06
14	23.3	430.0	7.93
16	23.9	429.0	9.00
18	23.8	428.7	9.33
20	23.6	428.5	9.55
25	23.0	428.2	10.12
30	22.3	428.2	10.12
35	21.5	428.1	10.00
40	21.0	428.1	10.00
45	20.4	428.2	10.12
50	20.1	428.0	9.89

seems to be split off at about $h = 10^{-2}$ C. Thus it seems unlikely that the acidity of Bi^{3+} is mainly an aquo acidity.

If, as the experiments seems to indicate, there is a process which can couple Bi ions together to polynuclear complexes $\mathrm{Bi}_n(\mathrm{OH})_m$, it would be remarkable if complexes of some n were present and not of others; it seems more likely that all n: 1,2,3, . . . are possible. One would thus be inclined to search for a *general* process by which Bi atoms can be added one by one to the complex.

A closer study of the measurements revealed that at points of the same bB^{-1} but different B (10, 25, 50, mC), the quantity bh^{-2} had almost the same value (Fig. 2) and thus bB^{-1} seemed to be a function of the variable

$$y = bh^{-2} \tag{4}$$

The same is true for $(h\text{-}H)B^{-1}$. Moreover, y seemed to approach to a limiting value at low h. All this indicates that in the equation of the general reaction there is one Bi^{3+} on one side and two H^+ on the other. The following equation immediately suggests itself

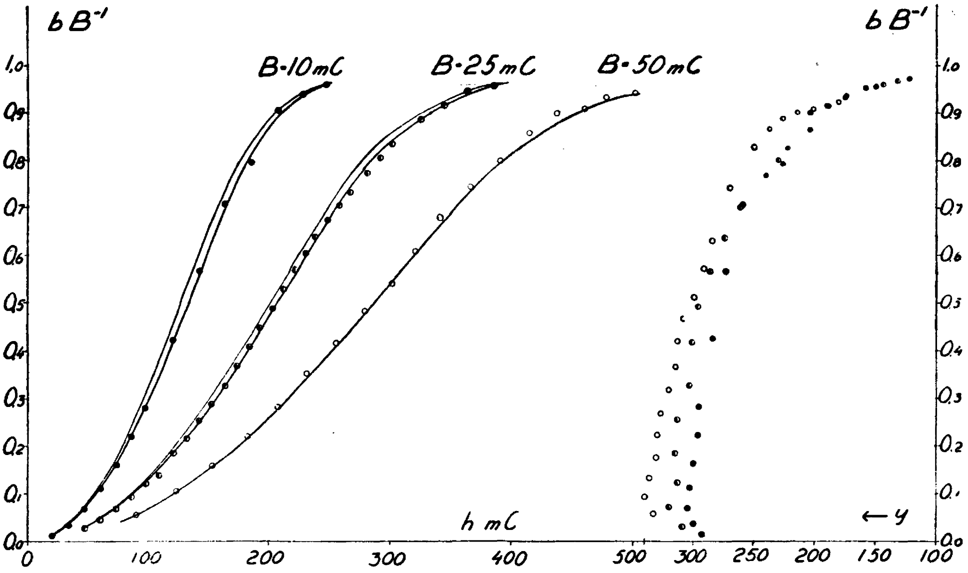


Fig. 2. $bB^{-1} = [Bi^{3+}]_{free}/[Bi]_{total}$ *as a function of* $h = [H^+]$ *and* $y = bh^{-2}$. *Circles = experimental values. Thick lines are calculated with eq. (11) and (4) and the constants: for* $B = 50$ *mC* $k_1 = 0{,}065$ *C* $k = 2.80$ *C; for* $B = 25$ *mC* $k_1 = 0{,}070$ *C* $k = 2.95$ *C; and for* $B = 10$ *mC* $k_1 = 0{,}060$ *C* $k = 3.15$ *C. Thin lines for 25 and 10 mC are calculated with the constants for* $B = 50$ *mC. The scale gives 1000 y.*

$$Bi^{3+} + H_2O + Complex^{q+} \rightarrow BiOComplex^{(q+1)} + 2H^+$$

The simplest reaction of this type would be

$$Bi^{3+} + H_2O + Bi^{3+} \rightarrow Bi_2O^{4+} + 2H^+$$

Thus a water molecule forms an *oxygen bridge* between two bismuth atoms, and at the same time two H^+ are set free (Fig. 4b). We shall see that a repetition of this process and a few simple assumptions gives a resonable explanation of the experimental data.

PROPOSED MECHANISM

We assume that the hydrolysis of Bi^{3+} takes part in the following steps:

	Equilibrium const.	
$Bi^{3+} + Bi^{3+} + H_2O \rightarrow Bi_2O^{4+} + 2H^+$	k_1	(5$_1$)
$Bi_2O^{4+} + Bi^{3+} + H_2O \rightarrow Bi_3O_2^{5+} + 2H^+$	k_2	
$Bi_3O_2^{5+} + Bi^{3+} + H_2O \rightarrow Bi_4O_3^{6+} + 2H^+$	k_3	

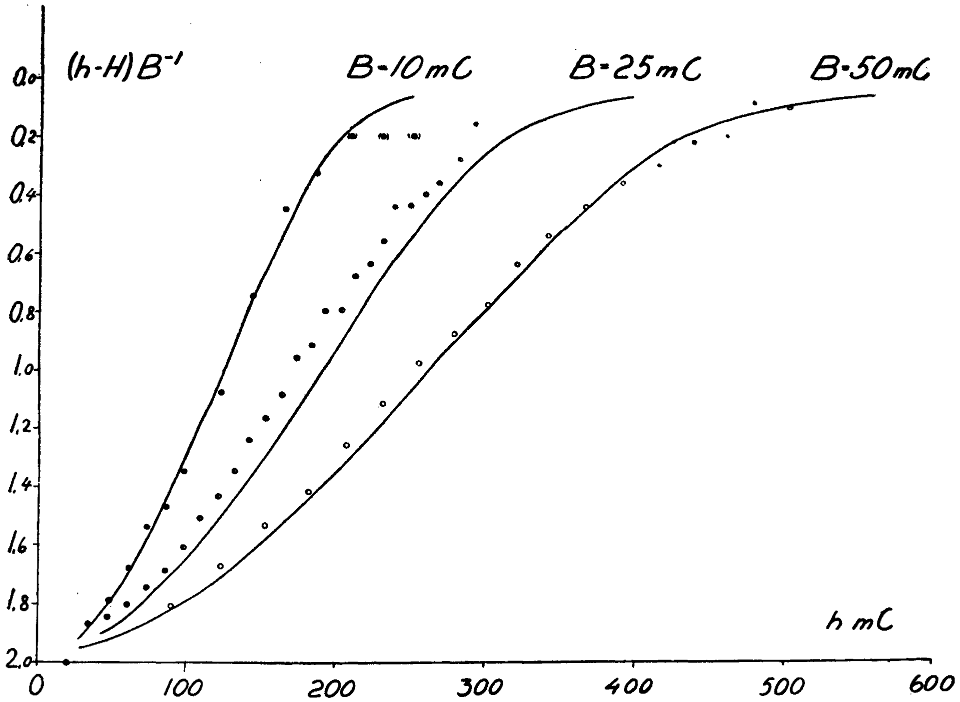


Fig. 3. $(h-H)B^{-1}$ (average number of H^+ set free per Bi atom) as a function of h. Circles = experimental values. The curves are calculated with eq. (11) and (12) and the constants: for $B = 50$ mC $k_1 = 0{,}065$ C $k = 2.80$ C; for $B = 25$ mC $k_1 = 0{,}070$ C $k = 2.95$ C and for $B = 10$ mC $k_1 = 0{,}060$ C $k = 3.15$ C.

or generally

$$\mathrm{Bi}_n\mathrm{O}_{n-1}^{(n+2)+} + \mathrm{Bi}^{3+} + \mathrm{H_2O} \rightarrow \mathrm{Bi}_{n+1}\mathrm{O}_n^{(n+3)+} + 2\mathrm{H}^+ \qquad k_n \qquad (5_n)$$

We shall moreover make the simplifying assumption *that except for k_1, all constants k_2, k_3 . . . . . k_n are assumed to be equal* and that there is no limit to *n:*

$$k_2 = k_3 = k_4 \ldots\ldots = k_n = \ldots\ldots = k \qquad (6)$$

With the notations

$$bh^{-2} = y \qquad (4)$$
$$ky = kbh^{-2} = z \qquad (7)$$

we find

$$c_1 = [\mathrm{Bi}^{3+}] = b \qquad (8_1)$$

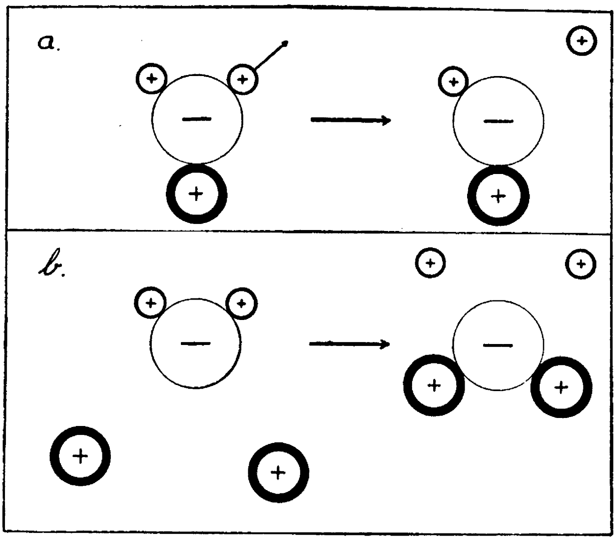


Fig. 4. Schematic picture of a) aquo acidity; a proton of a coordinated water molecule is repelled by the electrostatic forces from the central cation. b) oxygen bridging; a water molecule is split up so that an oxygen bridge is formed between two cations, and two protons are set free. — In the figure the other water molecules coordinated to the cation or to the protons have been left out.

$$
\begin{aligned}
c_2 &= [\mathrm{Bi_2O^{4+}}] = k_1 b^2 h^{-2} = k_1 b y \\
c_3 &= [\mathrm{Bi_3O_2^{5+}}] = k[\mathrm{Bi_2O^{4+}}] b h^{-2} = k_1 b y z \qquad (8_2) \\
c_4 &= [\mathrm{Bi_4O_3^{6+}}] = k[\mathrm{Bi_3O_2^{5+}}] b h^{-2} = k_1 b y z^2
\end{aligned}
$$

$$c_n = [\mathrm{Bi}_n\mathrm{O}_{n-1}^{(n+2)+}] = k_1 b y z^{n-2} \qquad (n > 1) \qquad (8_n)$$

For the total bismuth concentration B and the amount of $\mathrm{H^+}$ set free, $h—H$, we find

$$
\begin{aligned}
\mathrm{B} &= [\mathrm{Bi^{3+}}] + 2[\mathrm{Bi_2O^{4+}}] + 3[\mathrm{Bi_3O_2^{5+}}] + \ldots = \Sigma\, n c_n = \\
&= b + k_1 b y (2 + 3z + 4z^2 + \ldots) \qquad (9) \\
h - H &= 2[\mathrm{Bi_2O^{4+}}] + 4[\mathrm{Bi_3O_2^{5+}}] + 6[\mathrm{Bi_4O_3^{6+}}] + \ldots = \\
&= 2\,\Sigma\,(n - 1) c_n = 2 k_1 b y\,(1 + 2z + 3z^2 + \ldots) \qquad (10)
\end{aligned}
$$

If these expressions are summed to infinity we find

$$B = b + k_1 b y (2 - z)\,(1 - z)^{-2} \qquad (11)$$

$$h - H = 2 k_1 b y\,(1 - z)^{-2} \qquad (12)$$

In these equations, B, b, H, h and $y = bh^{-2}$ are directly measured variables, whereas k and k_1 are unknown constants and $z = ky$. The unknown constants can be found by a graphical method.
From (11) and (7) we find:

$$\log [(B-b)(by)^{-1}] = \log k_1 + \log [(2-z)(1-z)^{-2}] \quad (13)$$
$$\log y = \log z - \log k \quad (14)$$

On one graph one can construct the curve giving $\log [(2-z)(1-z)^{-2}]$ as a function of $\log z$ and on another plot to the same scale the experimental values of $\log [(B-b)(by)^{-1}]$ against $\log y$.

If our assumptions are permissible, it is possible, by horisontal and vertical translations, to make the experimental points coincide with the curve. Moreover, from the positions of the curves it is possible to obtain $\log k$ and $\log k_1$.

Finally, if k and k_1 are known, the measured quantities b, h and $h-H$ are conveniently calculated as follows:

$$b = B [1 + k_1 y (2-ky)(1-ky)^{-2}]^{-1} \quad (11)$$
$$h = \sqrt{by^{-1}} \quad (4)$$
$$h - H = 2k_1 by (1-ky)^{-2} \quad (12)$$

COMPARISON WITH THE MEASUREMENTS

In Fig. 5 the experimental values of $\log [(B-b)(by)^{-1}]$ are plotted against $\log y$. (In those points where only one of b and h had been measured, the other was found by graphical interpolation.) Within the limits of experimental error the points are seen to fit the theoretical curves. When the points for each value of B were regarded separately, the following constants were found:

$B = 50$ mC	$k_1 = 0.065 \pm 0.005$ C	$k = 2.80 \pm 0.05$ C
25 mC	$k_1 = 0.070 \pm 0.010$ C	$k = 2.95 \pm 0.10$ C
10 mC	$k_1 = 0.060 \pm 0.010$ C	$k = 3.15 \pm 0.20$ C

By means of these constants, b and $h-H$ were calculated as functions of h in the way indicated in the preceding section (cf. Tab. 6). In Fig. 2, the thin curves for $B = 25$ and 10 mC have been calculated by means of the constants 0.065 and 2.80, whereas the thick curves are in Figs. 2 and 3 are calculated by means of the »best values» given above.

The agreement for bB^{-1} is seen to be surprisingly good in view of the crude assumptions involved. For $(h-H)B^{-1}$ the deviations are somewhat larger, but it must be remembered that this quantity is the difference between two

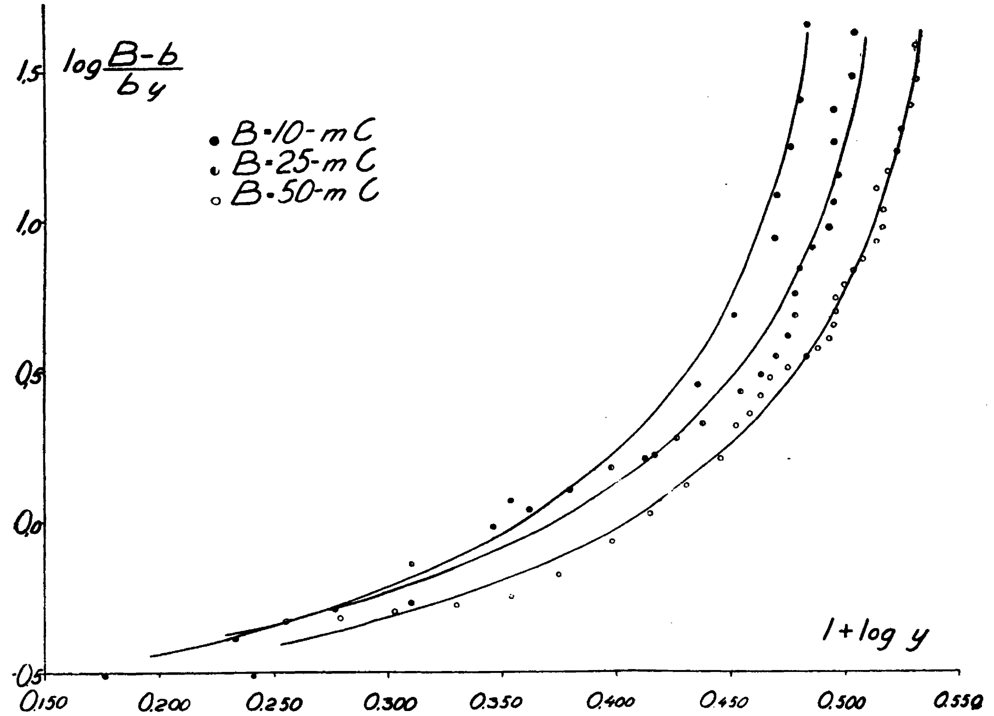


Fig. 5. Circles: experimental values of log (B—b) (by)$^{-1}$ as a function of log y. Curves: theoretical curves assuming, from right to left, k_1 = 0,065 C k = 2.80 C; k_1 = 0,070 C k = 2.95 C; k_1 = 0,060 C k = 3.15 C.

larger quantities and can therefore not be determined very accurately. In view of this fact the agreement must be said to be satisfactory.

The measurements give no indication of any systematic variation of k_1 with B; it may very well be constant at 0.065 in all the solutions studied. However, k seems to decrease somewhat with increasing B. This is not improbable since the ionic environment would be changed at higher B by the considerable concentration of polyions $\mathrm{Bi}_n\mathrm{O}_{n-1}^{(n+2)+}$ of large charge.

Our rather crude assumptions, involving only two equilibrium constants k_1 and k, give a good explanation of the experimental data. Actually, if it is desired to make the agreement still better by introducing a third constant, e. g. by assuming $k_2 \neq k$, or by assuming some different type of reaction (OH_2 acidity, formation of $(\mathrm{BiO})_n^{n+}$), it is hard to decide in which way to make the correction.

Table 6. Calculated values of b, h and h — H for round y values at B = 50 mC.

$k_1 = 0.065 \pm 0.01$ $k = 2.80 \pm 0.05$

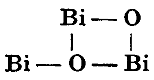
y	b	h	$h - H$
0.345	2.38	83	92
0.340	4.50	115	86.5
0.335	7.10	146	80.5
0.330	10.0	174	74.2
0.320	16.0	224	61.7
0.310	21.6	264	50.0
0.300	26.6	298	40.5
0.290	30.6	325	33.7
0.280	33.9	348	27.4
0.270	36.6	368	22.4
0.250	40.5	402	14.5
0.225	43.6	440	9.3
0.200	45.6	477	6.1
0.175	46.9	518	4.1
0.150	47.8	565	2.8

DISCUSSION

The general formula $(Bi_nO_{n-1})^{(n+2)+}$ may apply equally well to a straight or puckered chain.

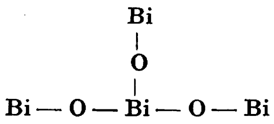
Bi — O — Bi — O — Bi — O — Bi

as to a branched one such as



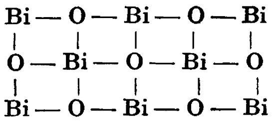
$$\begin{array}{lll} \mathrm{Bi} - \mathrm{O} & & \\ | \quad\;\; | & & \\ \mathrm{Bi} - \mathrm{O} - \mathrm{Bi} & & \end{array}$$

or



$$\begin{array}{ccccc} & & \mathrm{Bi} & & \\ & & | & & \\ & & \mathrm{O} & & \\ & & | & & \\ \mathrm{Bi} - \mathrm{O} & - & \mathrm{Bi} & - & \mathrm{O} - \mathrm{Bi} \end{array}$$

The first one can be formed for example by bending in of a straight chain Bi — O — Bi — O — Bi, a process which would be favoured by electrostatic attraction. By repetition of this process one can imagine complexes to be formed such as



$$\begin{array}{ccccccccc} \mathrm{Bi} & - & \mathrm{O} & - & \mathrm{Bi} & - & \mathrm{O} & - & \mathrm{Bi} \\ | & & | & & | & & | & & | \\ \mathrm{O} & - & \mathrm{Bi} & - & \mathrm{O} & - & \mathrm{Bi} & - & \mathrm{O} \\ | & & | & & | & & | & & | \\ \mathrm{Bi} & - & \mathrm{O} & - & \mathrm{Bi} & - & \mathrm{O} & - & \mathrm{Bi} \end{array}$$

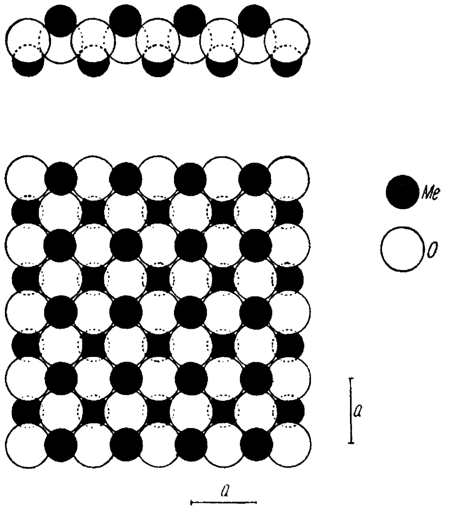
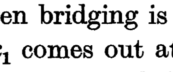


Fig. 6. Tetragonal metal-oxygen sheet in bismuth oxyhalides, viewed along a and c axes.

which can be considered as nuclei of the tetragonal $(MeO)_n$ sheets found in the crystal structures of many bismuth oxyhalides (Bannister and Hey [10]; Sillén [11, 12]) as well as in bismuth oxycarbonate (Lagercrantz and Sillén [13]) (Fig. 6). This is one reason why we prefer the formulation with oxygen bridges Bi — O — Bi to one with double hydroxyl bridges  $\mathrm{Bi}{<}^{\mathrm{OH}}_{\mathrm{OH}}{>}\mathrm{Bi}$. The latter would otherwise be equally consistent with the experimental data, which of course, give no means of distinguishing between two formulae differing by one or by several molecules of H_2O. (Our experiments, for similar reasons, give us no means of deciding whether or not there are ClO_4^- ions bound to the bismuth complexes.)

Our calculations suggest that the first oxygen bridging is much less easily brought about than the following steps since k_1 comes out at about 40 times smaller than k. Maybe the forces withstanding an attack by $(Bi^{3+} + H_2O)$ are much weaker in Bi_2O^{4+} than in Bi^{3+}, even if the formation of a straight chain $(Bi\text{-}O\text{-}Bi\text{-}O\text{-}Bi)^{5+}$ is the result; at any rate the »bending in» of the complexes must greatly stabilize the larger complexes from $Bi_3O_2^{5+}$ on.

In Fig. 7 is given the distribution of bismuth (in weight fractions nc_nB^{-1}) over complexes of different n with four different h for $B = 50$ ml. The average n by number has been computed from the formula

$$\bar{n}_n = \frac{\Sigma n c_n}{\Sigma c_n} = \frac{B}{b\,(1 + k_1\,y\,(1 - z)^{-1})} = 1 + k_1\,y\,(1 - ky)^{-1}\,(1 - k + k_1 y)^{-1} \quad (15)$$

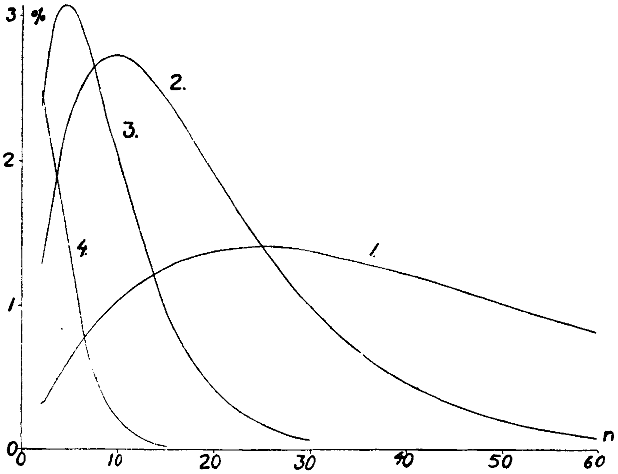


Fig. 7. Distribution of bismuth over complexes $(Bi_nO_{n-1})^{n+2}$ *of varying n in four differen solutions with B = 50 mC, calculated from eq. (15) assuming* k_1 *= 0,065 C, k = 2.80 C*

No.	z	y C^{-1}	b mC	h mC	H mC	$\overline{n}_w$	$\overline{n}_n$
1	.960	.3429	3.23	97.0	7.1	46.0	9.95
2	.900	.3214	15.16	207.4	144.1	13.7	2.73
3	.800	.2857	32.11	287.7	305.5	3.98	1.42
4	.600	.2143	44.57	457.0	449.2	1.39	1.08

The »average n by weight» was calculated from

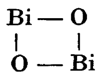
$$\overline{n}_w = \frac{\Sigma n^2 c_n}{\Sigma n c_n} = \frac{b\,[1 + k_1\, y\,(z^2 - 3\,z + 4)\,(1 - z)^{-3}]}{B} =$$

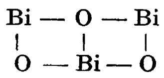
$$= 1 + \frac{2\, k_1\, y\, (1 - z)^{-1}}{(1 - z)^2 + k_1\, y\, (2 - z)} \qquad (16)$$

For the special case of ky close to 1, we have

$$\overline{n}_n \approx (1 - ky)^{-1}; \; \overline{n}_w \approx 2\,(1 - ky)^{-1}$$

A possible type of complex not included in our formulae is that containing rings of formula $(BiO)_n^{n+}$ such as





At lower h, which we have not been able to investigate because of precipitations, the aquo acidity of Bi — OH_2 may begin to appear. When this happens, one Bi may set free more than $2H^+$, the highest value obtained by the mechanism of oxygen-bridging proposed here.

It would be interesting to study the spatial arrangement of the Bi (and O) atoms by means of the X-ray diffraction of Bi solutions. If the three atoms Bi — O — Bi form a straight line, the Bi — Bi distance would be about 4.6 Å. On the other hand, in the crystal structures referred to, every O is surrounded by an almost regular tetrahedron of Bi atoms, as is seen *e. g.* from the Bi — Bi distances tabulated by Sillén[11] (p. 73). If, as we find probable, the angles Bi — O — Bi are »tetrahedral» in solution also, the smallest distance Bi — Bi would be about 3.9 Å. It should not be very difficult to decide between these alternatives.

SUMMARY

The hydrolysis of the Bi^{3+} ion has been studied by measuring the concentrations $[H^+] = h$ and $[Bi^{3+}] = b$ in solutions with $[ClO_4^-] = 3$ C, and Na^+ as the only foreign cation. The total bismuth concentrations used were $B = 50$, 25 and 10 mC.

The results cannot be explained by assuming that only mononuclear complexes $BiOH^{2+}$ and BiO^+ are formed, nor by assuming that one or two polynuclear complexes $Bi_x(OH)_y$ predominate.

However, a surprisingly good agreement with the experimental data is obtained by assuming the main process to be a chain of reactions:

$$Bi^{3+} + Bi^{3+} + H_2O \rightleftharpoons Bi_2O^{4+} + 2H^+$$
$$Bi_2O^{4+} + Bi^{3+} + H_2O \rightleftharpoons Bi_3O_2^{5+} + 2H^+$$
$$Bi_3O_2^{5+} + Bi^{3+} + H_2O \rightleftharpoons Bi_4O_3^{6+} + 2H^+$$
$$Bi_nO_{n-1}^{(n+2)+} + Bi^{3+} + H_2O \rightleftharpoons Bi_{n+1}O_n^{(n+3)+} + 2H^+$$

and the equilibrium constant of all reactions except the first to have the same value k.

At 25° C and in the ionic medium used the first constant is found to be $k_1 = 0.065 \pm 0.005$ C. The constant k seems to decrease slowly with increasing B from 3.15 ± 0.20 C at $B = 10$ mC and 2.95 ± 0.10 at $B = 25$ mC to 2.80 ± 0.05 at $B = 50$ mC.

The more facile formation of the higher complexes (from $Bi_3O_2^{4+}$ on) can be explained by a »bending in» of these complexes; by this process sheets can be formed which may be nuclei of the $(BiO)_n$ sheets found in the crystal structures of many bismuth oxyhalides.

Our thanks are due to fil. mag. Börje Andersson, who prepared our Bi stock solutions and made a series of preliminary measurements which aided us greatly in choosing suitable experimental conditions.

REFERENCES

1. Smith, D. F. *J. Am. Chem. Soc.* **45** (1923) 360.
2. Swift, E. H. *J. Am. Chem. Soc.* **45** (1923) 371.
3. Holmqvist, A. Dissertation. Lund 1936; *Svensk Kem. Tid.* **48** (1936) 106.
4. Prytz, M., and Nagel, P. *Z. anorg. allgem. Chem.* **227** (1936) 65.
5. Sillén, L. G. *Svensk Kem. Tid.* **58** (1946) 52.
6. Dole, M. *The Glass Electrode.* New York (1941).
7. Brönsted, J. N., and Volqvartz, K. *Z. physik. Chem.* **134** (1928) 97.
8. Brosset, C. Dissertation. Stockholm (1942) 32.
9. Lindstrand, F. Dissertation. Lund (1939) (Part III).
10. Bannister, F. A., and Hey, M. H. *Mineralog. Mag.* **24** (1935) 49.
11. Sillén, L. G. Dissertation. Stockholm (1940).
12. Sillén, L. G. *Naturwissenschaften* **30** (1942) 318.
13. Lagercrantz, Å., and Sillén, L. G. *Arkiv Kemi, Mineral. Geol.* **25 A** (1947) no **20.**

Received August 1, 1947.