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THE SOLUBILITY OF BISMUTH OXYCHLORIDE IN HYDROCHLORIC ACID AND ITS RELATION TO COMPLEX FORMATION.

BY ARTHUR A. NOYES, FRANK W. HALL AND JAMES A. BEATTIE.

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1. Introduction.

Although several investigations[1] have been made on the solubility of bismuth oxychloride in hydrochloric acid, no quantitatively verified explanation of the very large increase in solubility has been presented. Nor is any definite information available as to the form or forms in which bismuth chloride mainly exists when present in hydrochloric acid solutions. The purpose of this article is to offer a solution of these problems by presenting and discussing the results of measurements on the conductance of bismuth chloride dissolved in hydrochloric acid and on the solubility of bismuth oxychloride in that acid.

This investigation has been carried on with the aid of a grant made to A. A. Noyes by the Carnegie Institution of Washington, for which we wish to express our great indebtedness. We wish also to thank Mr. Roger Williams and Mr. A. W. Kenney for the valuable assistance which they gave us.

2. Conductance Measurements.

BY JAMES A. BEATTIE.

A study was made of the conductance of hydrochloric acid solutions of definite acid concentration to which varying quantities of bismuth chloride had been added.

The solutions were prepared by dissolving in a 1.9079 formal hydrochloric acid solution enough accurately weighed bismuth oxide to give in one case a solution 0.2544 formal[1] in bismuth trichloride and 1.1447 formal[2] in hydrochloric acid and in another case a solution 0.1272 formal in bismuth trichloride and 1.5263 formal in hydrochloric acid. These solutions were then diluted with multiple volumes of 1.1447 formal hydrochloric acid and 1.5263 formal hydrochloric acid, respectively. The bismuth oxide was prepared by igniting the carbonate precipitated by

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[1] Ostwald, *J. prakt. Chem.*, [2] **12**, 269 (1875); Herz and Bulla, *Z. anorg. allgem. Chem.*, **61**, 387; **63**, 59 (1909); Dubrisay, *Compt. rend.*, **148**, 830 (1909).

[2] That is, one containing 0.2544 formula weights of $BiCl_3$ and 1.1447 formula weights of HCl per liter of solution at 25°. The small expansion of the solution on dissolving the Bi_2O_3 in the HCl solution was taken into account.

ammonium carbonate out of a solution of the normal nitrate purified by recrystallization.

The conductance of these solutions at 25° was measured by the usual method, a closed cylindrical cell 11 cm. long and 1 cm. in bore with the electrodes at the two ends being employed.

The results are presented in the following table. The first and second columns show the concentration of the solution in formula weights of hydrochloric acid and of bismuth trichloride per liter, respectively; the third column gives the specific conductance of the solution at 25°; the fourth column contains the difference between the specific conductance of the solution and that of the solution containing hydrochloric acid at the same concentration but no bismuth trichloride; and the last column shows the percentage decrease in specific conductance per formula weight of bismuth trichloride per liter.

TABLE I.—CHANGE IN CONDUCTANCE PRODUCED BY DISSOLVING BISMUTH CHLORIDE IN HYDROCHLORIC ACID SOLUTIONS.

Mols HCl per liter solution.	Mols $BiCl_3$ per liter solution.	Specific conductance.	Decrease in conductance.	% decrease per mol $BiCl_3$.
1.1447	0.00000	0.3622	....	...
....	0.03180	0.3610	0.0012	10.4
....	0.06360	0.3593	0.0029	12.6
....	0.1272	0.3558	0.0064	13.8
....	0.2544	0.3503	0.0119	12.9
1.5263	0.00000	0.4500	....	...
....	0.03180	0.4477	0.0023	16.0
....	0.06360	0.4469	0.0031	10.8
....	0.1272	0.4445	0.0055	9.6

In considering the significance of these results it is to be noted that the conductance of the hydrochloric acid solution would be much increased if the bismuth chloride existed as Bi^{+++} and $3Cl^-$, or as $BiCl^{++}$ and $2Cl^-$, or as BiO^+, $2H^+$ and $3Cl^-$; that it would be little changed if it existed as un-ionized $BiCl_3$; and that it would be considerably decreased if it existed as $BiCl_4^-$ or $BiCl_5^=$, since these ions replace the doubtless faster moving Cl^- ion. The fact that a pronounced decrease in conductance takes place shows that complex anions are present in large proportion.

Another more accurate series of conductance measurements at 25° was made, mainly to determine the relative conductances of the complex chlorobismuthic acid and of pure hydrochloric acid. In this series a conductance cell was used consisting of two ellipsoidal electrode compartments joined by a narrow vertical tube about 12 cm. in length and 0.8 mm. in bore.

The specific conductance of pure hydrochloric acid was first determined at a series of concentrations between 1.1226 and 2.2452 normal. The values found are given in the following table:

TABLE II.—SPECIFIC CONDUCTANCE OF HYDROCHLORIC ACID SOLUTIONS AT 25°.

Form. wts. HCl per liter	1.1226	1.4033	1.6839	1.9646	2.2452
Specific conductance	0.3650	0.4369	0.5000	0.5571	0.6054

The following table contains the results of the measurements with the bismuth solutions, and of the calculations based upon them. In the column headed ΣH is given the total concentration of the acid in equivalents per liter of solution at 25°; in that headed ΣBi is given the corresponding concentration of the bismuth in atomic weights per liter. The calculations are made on two bases, indicated by the letters A and B in the table, A being on the basis that all the bismuth is present as $H^+BiCl_4^-$ and B on the basis that it is all present as $H^+{}_2BiCl_5^=$. The "specific conductance of the free hydrochloric acid" in the mixture was found by plotting the above given specific conductances of hydrochloric acid, interpolating for the concentration ΣH, and multiplying this value by the ratio (A) of ΣH — ΣBi to ΣH, or (B) of ΣH — 2ΣBi to ΣH. This calculation is based on the assumption that the ionization of the HCl of the mixture is that which would prevail in a pure hydrochloric acid solution of a concentration equal to the sum of that of the hydrochloric acid and $HBiCl_4$ or H_2BiCl_5 in the mixture. The "specific conductance of the chlorobismuthic acid" in the mixture is found by subtracting that of the free hydrochloric acid from that of the mixture. And the equivalent conductances of hydrochloric acid and of the chlorobismuthic acid in the mixture are computed by dividing the two specific conductances by the concentration of the free hydrochloric acid and by (A) ΣBi or (B) 2ΣBi, respectively.

TABLE III.—EQUIVALENT CONDUCTANCE OF CHLOROBISMUTHIC ACID IN SOLUTIONS OF HYDROCHLORIC ACID AT 25°.

		Specific conductance of					Equivalent conductance of		
			Free HCl.		Chlorobismuthic acid.		Hydrochloric acid.	Chlorobismuthic acid.	
ΣH.	ΣBi.	Mixture.	(A).	(B).	(A).	(B).		(A).	(B).
1.1401	0.01754	0.3683	0.3640	0.3583	0.0043	0.0100	34	246	285
1.1577	0.03508	0.3716	0.3630	0.3516	0.0086	0.0200	323	245	285
1.1928	0.07016	0.3781	0.3611	0.3385	0.0170	0.0396	322	242	282
1.2629	0.1403	0.3906	0.3572	0.3126	0.0334	0.0780	318	238	278
1.4032	0.2806	0.4143	0.3495	0.2621	0.0648	0.1522	311	231	271
1.6839	0.5613	0.4540	0.3333	0.1667	0.1207	0.2873	297	215	256
2.2452	1.1226	0.5069	0.3027	0.00	0.2042	0.5069	270	182	226

It will be seen from Table III that the equivalent conductance of the chlorobismuthic acid under the assumption that it consists of $H^+BiCl_4^-$ is in the five most dilute mixtures about 75% of that of the hydrochloric acid, and in the most concentrated solution only 67% of it. Since transference experiments have shown that the conductance of the hydrogen ion in 1.2 *N* hydrochloric acid is 83% of the whole conductance, it would be necessary to assume that $H^+BiCl_4^-$ is a much less ionized acid than

H^+Cl^-. On the other hand, under the assumption that the acid is $H^+{}_2BiCl_5^-$, its equivalent conductance in the six most dilute solutions is 86 to 88% of that of the hydrochloric acid. This last result seems the more probable, and affords some evidence that the acid is $H^+{}_2BiCl_5^=$, so long as a considerable excess of free hydrochloric acid is present.

3. The Solubility Determinations.

By F. W. Hall.

The bismuth oxychloride used was prepared by precipitating with water a solution of bismuth nitrate in hydrochloric acid; and it was purified by successive reprecipitations from its solutions in hydrochloric acid. The hydrochloric acid used was purified by fractional distillation of the "chemically pure" commercial product.

Two series of solubility determinations were made. In one of these the equilibrium was approached from the undersaturated side, and in the other from the supersaturated side.

The equilibrium from the undersaturated side was attained by rotating in a thermostat at 25° solutions of various concentrations of hydrochloric acid with an excess of bismuth oxychloride and analyzing the resulting solutions for their chloride and bismuth content. To avoid possible variation in the condition of the solid salt, it was freshly prepared each time by precipitating the oxychloride from a concentrated solution of bismuth chloride in hydrochloric acid by adding water at a definite rate and at the same time stirring the solution at a fixed rate.

The equilibrium from the supersaturated side was attained as a follows: A 20% hydrochloric acid solution was nearly saturated with bismuth oxychloride, and the resulting solution was diluted with water until the acid was about 3 normal. This was then filtered; the filtrate was placed in a wide-mouth jar 5 cm. in diameter and 20 cm. high in a thermostat at 25°, and the bismuth oxychloride was precipitated by adding water (through a tube passing through the stopper of the jar) at the rate of 5 cc. per minute, at the same time stirring at a fixed rate by means of a motor-driven centrifugal stirrer. The resulting solution was then stirred until equilibrium was reached, this being determined by drawing off successive samples at definite intervals and determining the chloride content. Equilibrium was found to be established within twelve hours, but the solutions were in fact stirred twenty-four hours or more.

The samples were withdrawn through a tube provided with an expansion at its lower end containing asbestos-felt and glass-wool. Weighed portions were analyzed for their total chloride content by precipitating the bismuth as sulfide with hydrogen sulfide, filtering, heating the filtrate to expel the hydrogen sulfide, and titrating the acid in it with standard alkali solution. Separate weighed portions were analyzed for their bismuth content by evaporating them to dryness, moistening with nitric acid and evaporating repeatedly to convert the chloride into nitrate, dissolving in dilute nitric acid, precipitating with ammonium carbonate, igniting, and weighing as Bi_2O_3. The density of each sample was determined, in order to enable the concentration to be expressed on a volume basis, if this should prove advisable. The densities were measured in most cases with a Westphal balance, but in some cases (those to which a *p* is attached in the table below) by a 12 cc. pycnometer.

4. The Solubility Data.

The results of the solubility determinations are given in the following table. In the experiments to whose numbers asterisks are attached the equilibrium was approached from the oversaturated side; in all other experiments, from the supersaturated side. The densities, given in the second column, are those of the solutions at 25° referred to that of water at 4°. The directly determined chloride content (ΣCl) and bismuth

TABLE IV.—SOLUBILITY OF BISMUTH OXYCHLORIDE IN HYDROCHLORIC ACID AT 25°

						Mass action constants.		
No.	Density.	Chloride content ΣCl.	Bismuth content ΣBi.	Hydrogen content ΣH.	Activity coefficient α.	K.	K_1.	K_2.
1*	1.002 *p*	0.3477	0.00130	0.3438	0.800	0.228*	0.700*	2.48*
2	1.007	0.4350	0.00376	0.4237	0.794	0.294	0.712	2.21
3*	1.009 *p*	0.4414	0.00396	0.4295	0.795	0.291*	0.697*	2.14*
4	1.009	0.4892	0.00646	0.4698	0.793	0.335	0.744	2.14
5	1.010	0.5221	0.00869	0.4960	0.793	0.363	0.772	2.15
6*	1.011 *p*	0.5276	0.00899	0.5006	0.793	0.362*	0.763*	2.17*
7	1.012	0.5796	0.01323	0.5399	0.795	0.390	0.778	2.06
8	1.013	0.6244	0.01767	0.5714	0.797	0.412	0.790	2.04
9*	1.015 *p*	0.6299	0.01856	0.5742	0.797	0.423*	0.814*	2.10*
10	1.015	0.7038	0.02720	0.6222	0.802	0.439	0.806	2.04
11	1.018	0.7375	0.03138	0.6434	0.805	0.436	0.788	1.97
12*	1.020 *p*	0.7579	0.03473	0.6537	0.806	0.451*	0.812*	2.05*
13	1.025	0.8824	0.05338	0.7223	0.815	0.445	0.757	1.98
14*	1.028 *p*	0.9125	0.05936	0.7343	0.817	0.458*	0.804*	2.17*
15*	1.036 *p*	1.0760	0.08937	0.8079	0.828	0.446*	0.768*	2.25*
16	1.044	1.2277	0.1177	0.8746	0.836	0.412	0.727	2.26
17*	1.048 *p*	1.2724	0.1324	0.8752	0.839	0.455*	0.851*	2.99*
18	1.055	1.4348	0.1620	0.9488	0.849	0.385	0.711	2.69
19	1.061	1.5321	0.1810	0.9891	0.856	0.352	0.654	2.60
20	1.066	1.6235	0.2025	1.016	0.859	0.349	0.669	3.01
21*	1.066 *p*	1.6350	0.2050	1.020	0.861	0.345*	0.662*	3.01*
22	1.075	1.7706	0.2352	1.065	0.866	0.325	0.645	3.32
23	1.083	1.9021	0.2657	1.105	0.873	0.307	0.503	3.95
24	1.122	2.5578	0.4216	1.293	0.905	0.225	0.568	10.13
25	1.157	3.1865	0.5685	1.481	0.941	0.151	0.435	25.
26	1.185	3.6366	0.6792	1.599	0.970	0.117	0.386	92.
27	1.221 *p*	4.2552	0.8324	1.758	1.013	0.083	0.324	3375.
28	1.237 *p*	4.5056	0.9022	1.799	1.022	0.079	0.354	....
29	1.288 *p*	5.325	1.100	2.025	1.100	0.045	0.232	....
30	1.329 *p*	6.066	1.317	2.115	1.150	0.038	0.331	....

content (ΣBi), given in the third and fourth columns, are expressed in atomic weights per 1000 g. of water. The hydrogen content (ΣH), given in the fifth column, was calculated by subtracting 3(ΣBi) from (ΣCl); it therefore represents the total acid in the solution. The activity coefficients α, given in the sixth column, were obtained by interpolation at the concentration (ΣH) on a plot of the values given by Ellis[1] for hydrochloric acid at 18°. The values of K, K_1, and K_2, given in the last three columns, are those of the expression which correspond, as will be described below, to the mass-action equations, for the quantitative formation in the solution of un-ionized $BiCl_3$ and of the complex acids $H^+BiCl_4^-$ and $H^+_2BiCl_5^=$, respectively.

5. Discussion of the Solubility Values.

The increase in the solubility of bismuth oxychloride caused by hydrochloric acid will depend on the form in which the bismuth exists mainly in the solution. We need consider only the three reactions expressed by the following equations:

$$BiOCl(\text{solid}) + 2H^+Cl^- = H_2O + BiCl_3$$
$$BiOCl(\text{solid}) + 3H^+Cl^- = H_2O + H^+BiCl_4^-$$
$$BiOCl(\text{solid}) + 4H^+Cl^- = H_2O + H_2{}^+BiCl_5^=$$

The mass-action expressions for these reactions are evidently

$$\frac{(BiCl_3)}{(H^+)^2(Cl^-)^2} = K;\ \frac{(BiCl_4^-)}{(H^+)^2(Cl^-)^3} = K_1;\ \text{and}\ \frac{(BiCl_5^=)}{(H^+)^2(Cl^-)^4} = K_2.$$

If we assume now that substantially all the bismuth in the solution is in the form indicated by one of the above given equations and that the complex acids $H^+BiCl_4^-$ and $H^+_2BiCl_5^=$ have in any mixture the same ionization γ as the HCl, these mass-action equations may be expressed in terms of the total bismuth content ΣBi and total hydrogen content ΣH, as follows:

$$\frac{\Sigma Bi}{(\Sigma H)^4\gamma^4} = K;\ \frac{\Sigma Bi}{(\Sigma H)^2(\Sigma H - \Sigma Bi)^3\gamma^4} = K_1;\ \text{and}$$

$$\frac{\Sigma Bi}{(\Sigma H)^2(\Sigma H - 2\Sigma Bi)^4\gamma^5} = K_2$$

These expressions may probably be made more exact by substituting for the ionization γ the activity coefficient α which has recently been determined by Ellis in this laboratory. This was done in calculating the values of K, K_1 and K_2, given in Table IV.

It will be seen from the table that the values of K increase rapidly, pass through a maximum value, and then rapidly decrease; that the values of K_1 show a variation similar in direction, but much smaller in magnitude; and that the values of K_2 show a behavior exactly opposite to that

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[1] THIS JOURNAL, 38, 759 (1916).

of K_1, in that they first decrease slowly, pass through a minimum, and then increase rapidly. This result shows that the actual conditions are intermediate between those assumed in computing the constant K_1 and the constant K_2, and makes it probable that the two complex acids $H^+BiCl_4^-$ and $H^+_2BiCl_5^=$ are both present in the solution. The H_2BiCl_5 doubtless predominates in the more dilute solutions where there is a large excess of free hydrochloric acid,[1] and the $HBiCl_4$ in the more concentrated solutions, where ultimately (in the last three solutions) there is not even enough chloride present to convert all the bismuth into the $BiCl_5^=$ ion (since ΣCl is less than $5\Sigma Bi$). Alkali salts of both of these complex acids have previously been separated from their solutions.[2]

6. Summary.

In this article have been presented measurements on the electrical conductance at 25° of solutions of bismuth chloride in aqueous hydrochloric acid. The results show that the conductance of this acid is considerably reduced by dissolving bismuth chloride in it, and indicate the formation of a complex acid of the form $HBiCl_4$ or H_2BiCl_5.

Experiments on the solubility at 25° of bismuth oxychloride in hydrochloric acid through a wide range of concentration have also been presented. The results considered from the mass-action standpoint are shown to be intermediate between those required by the assumption that the complex acid is $HBiCl_4$ and the assumption that it is H_2BiCl_5. The latter doubtless predominates in solutions containing a considerable excess of hydrochloric acid; and the former, in those in which this is not the case.

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THE FREE ENERGY OF HYDROCHLORIC ACID IN AQUEOUS SOLUTION. II.

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1. Introduction.

In a previous article[3] were presented the results of measurements

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[1] It will be noted that, while ΣBi increases from 0.0038 to 0.053, the constant K_2 decreases only 10%, a decrease that might be accounted for by ionization effects.

[2] Abegg, "Handbuch d. anorg. Chem.," 3, III, 653.

[3] Ellis, THIS JOURNAL, 38, 737–762 (1916).