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THE CONDITION OF BISMUTH SALTS IN AQUEOUS SOLUTIONS AND THE MOLAL ELECTRODE-POTENTIAL OF BISMUTH

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Previous Investigations and Outline of this Research

Bismuth salts in aqueous solution are known to be subject to hydrolysis and complex formation. Thus Rutten[1] has shown that the solid phase in equilibrium with solutions of bismuth nitrate and nitric acid, when the latter is present in considerable excess over that needed to produce bismuth trinitrate, is the basic salt, $Bi(OH)_2NO_3$. Quartaroli's determinations[2] of the conductivity and of the hydrogen-ion concentration (by measurements of the catalysis of the methyl acetate hydrolysis) of solutions of bismuth nitrate indicate hydrolysis, especially in dilute solution. By experiments upon the conductivity and solubility of bismuth oxychloride in hydrochloric acid solutions, Noyes, Hall and Beattie[3] have shown the presence of complexes of the types, $HBiCl_4$ and H_2BiCl_5. The electromotive-force measurements of Noyes and Chow[4] have furnished a value for the molal electrode-potential of $Bi(s) + BiOCl(s), H^+Cl^-$.

The present investigation was undertaken for the purpose of determining the relative amounts of the different forms in which the bismuth exists in various nitrate and perchlorate solutions, and of evaluating the molal electrode-potential of bismuth.

Electrical-conductivity measurements were made upon a series of nitrate and perchlorate solutions; also upon solutions of nitric and perchloric acids, in order to enable the conductivities of the acids to be compared with those of the bismuth salt solutions.

A series of experiments was made on the solubility of bismuth oxynitrate ($BiONO_3.H_2O$ or $Bi(OH)_2NO_3$) in nitric acid solutions of various concentrations.

Electromotive-force measurements were made upon cells of the type, $H_2(g) \mid HClO_4 \mid HClO_4 + BiOClO_4 \mid Bi(s)$, in which the concentration of the acid in the hydrogen half-cell was such as to make the liquid potential as small as possible.

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[1] Rutten, *Z. anorg. Chem.*, **30,** 386 (1902).

[2] Quartaroli, *Gazz. chim. ital.*, **43,** 1, 97 (1913).

[3] Noyes, Hall and Beattie, THIS JOURNAL, **39,** 2526 (1917).

[4] Noyes and Chow, *ibid.*, **40,** 739 (1918).

to Professor Noyes for much valuable advice and assistance in the prosecution of this research and in the preparation of the data for publication.

Preparation of the Solutions and Materials

All bismuth solutions were directly made up from weighed amounts of pure bismuth oxide (Bi_2O_3) and of standardized acid. The oxide was prepared by dissolving the nitrate in conc. nitric acid, diluting to about 6 *N*, filtering, concentrating, precipitating by dilution with water, and igniting the precipitate to constant weight in an electric resistance furnace at 750° to 800°. The product was a light-yellow powder which gave no test for chlorides and left no residue when treated with acid. The nitric acid used was from a newly-opened bottle of chemically-pure reagent of commerce containing no chlorides or oxides of nitrogen and leaving no residue upon evaporation. The perchloric acid used was a pure commercial material which gave no test for chloric acid or for other oxidizing acids and only a slight test for chloride. The acids were standardized both against an imported sodium carbonate ("for analysis") and against an alkali solution previously titrated against a hydrochloric acid solution standardized gravimetrically by precipitation with silver nitrate, the two methods giving results differing by less than 0.1%. The atomic weights used throughout this research are: Bi, 208.0; N, 14.01; Ag, 107.88; Cl, 35.46.

The solid substance of the formula, $BiONO_3.H_2O$, used in the solubility determinations was prepared by adding a solution of bismuth nitrate in nitric acid to a moderately in large amount of boiling water. The fine white powder so obtained was rotated at 25° a thermostat for several days with *N* nitric acid, to assure its being the solid phase which is in equilibrium with acid solutions of the strength used in the solubility experiments.

A few points noticed in the preparation of the perchlorate solutions may be mentioned. It was found that 1 mole of bismuth oxide could be dissolved in a solution of 2 equivalents of perchloric acid, so that when the two pure constituents were weighed out in this proportion, the solution must have contained bismuth and perchlorate in the ratio required by the formula, $BiOClO_4$. Thus, when 1 mole of bismuth oxide is shaken with 2 of perchloric acid in about 9 *M* solution, the oxide slowly turns white and, upon being heated or upon the addition of water, dissolves. Such solutions do not precipitate, no matter how much they are diluted with water (although the slightest trace of chloride then comes out as the oxychloride). These results show that bismuth oxyperchlorate is a very soluble salt. If a considerable quantity of the oxide be dissolved in warm conc. perchloric acid and then be allowed to cool, large colorless crystals, presumably of the normal perchlorate, separate.

The Conductance Measurements

The electrical conductivity measurements were made with the usual decade resistance boxes, "buzzer," telephone receiver, and drum-type bridge wire. The solutions were made by dilution, either with water or standardized acid, of a standard bismuth solution made up from pure bismuth oxide and acid as previously described.

The solutions were contained in a closed conductivity cell of a type similar to that described by Washburn.[5] The cell-constant was determined by the use of two solutions of an imported potassium chloride ("for analysis") containing, respectively, 74.59 and 7.459 g. of potassium chloride per

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[5] Washburn, This Journal, **38**, 2450 (1916).

liter of solution at 18°, the assumed specific conductances at 25° being respectively 0.11180 and 0.012882 reciprocal ohms.[6]

The experimental values of the conductance at 25° are presented in Tables I–IV of which the headings are self-explanatory, except for the "calculated" conductances in Tables II and IV which are explained below.

TABLE I

CONDUCTANCE OF NITRIC ACID SOLUTIONS

Equiv. HNO_3 per liter of solution	Specific conductance	Equivalent conductance	Equiv. HNO_3 per liter of solution	Specific conductance	Equivalent conductance
0.3007	0.1112	369.8	0.9990	0.3302	330.5
0.3659	0.1336	365.1	1.0105	0.3335	330.0
0.4196	0.1520	362.2	1.3471	0.4223	313.5
0.5195	0.1850	356.1	1.7484	0.5148	294.4
0.5994	0.2108	351.7	2.5110	0.6541	260.5
0.8013	0.2729	340.6	3.3452	0.7585	226.7

TABLE II

CONDUCTANCE OF BISMUTH NITRATE SOLUTIONS

Assuming $BiOH^{++}(NO_3^-)_2$ formed

	At. wts. of Bi per liter of solution	Moles NO_3 per liter of of solution	Equivalents of		Specific conductance		
			Bi salt	HNO_3	Bi salt	Excess HNO_3	Mixture
1	0.0347	0.4180	0.0694	0.3486	0.0049	0.1264	0.1313
2	0.0503	0.4178	0.1006	0.3172	0.0071	0.1150	0.1221
3	0.0790	0.5926	0.1580	0.4346	0.0107	0.1530	0.1637
4	0.1600	0.9932	0.3200	0.6732	0.0200	0.223	0.243
5	0.2509	1.7384	0.5018	1.2366	....	0.365	....
6	0.2563	1.7400	0.5126	1.2274	....	0.362	....
7	0.3160	1.7337	0.6320	1.1017	....	0.325	....
8	0.5000	2.5088	1.0000	1.5088	....	0.394	....
9	0.6667	3.3451	1.3334	2.0117	....	0.456	....

Assuming $Bi^{+++}(NO_3^-)_3$ formed

	Spec. cond. obs.	Specific conductance			Equivalents of	
		Mixture	Bi salt	Excess HNO_3	Bi salt	HNO_3
1	*0.1141*	0.1198	0.0060	0.1138	0.1041	0.3139
2	*0.1046*	0.1056	0.0088	0.0968	0.1509	0.2669
3	*0.1366*	0.1365	0.0112	0.1253	0.2370	0.3556
4	*0.1860*	0.1833	0.0135	0.1698	0.4800	0.5132
5	*0.3082*	....	....	0.291	0.7527	0.9857
6	*0.3038*	....	....	0.286	0.7689	0.9711
7	*0.2551*	....	....	0.232	0.9480	0.7857
8	*0.2916*	....	....	0.263	1.5000	1.0088
9	*0.3348*	....	....	0.305	2.0001	1.3450

TABLE III

CONDUCTANCE OF PERCHLORIC ACID SOLUTIONS

Equiv. $HClO_4$ per liter of solution	Density in air at 25°	Specific conductance	Equivalent conductance
0.04967	0.9990	0.01944	391.4
0.0995	1.0017	0.03827	384.6
0.1993	1.0074	0.07491	375.9
0.3999	1.0185	0.1452	363.1

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[6] Landolt-Börnstein-Roth "Tabellen," Julius Springer, 1912–4, 1117.

TABLE IV

CONDUCTANCE OF BISMUTH PERCHLORATE SOLUTIONS

Moles of $^1/_2Bi_2O_3$ per liter of solution	Moles of ClO_4 per liter of solution	Density in air at 25°	Specific Conductance Observed	Specific Conductance Increase	Of added acid, calc.
0.0500	0.0500	1.0096	0.00619		
				0.01587	0.01923
0.0500	0.1000	1.0126	0.02206		
				0.01622	0.01898
0.0500	0.1500	1.0151	0.03828		
				0.01522	0.01878
0.0500	0.2000	1.0180	0.05350		
0.1900	0.1900	1.0483	0.01753		
				0.0525	0.0675
0.1900	0.3800	1.0597	0.0700		
				0.0441	0.0654
0.1900	0.5700	1.0708	0.1141		
				0.0482	0.0635
0.1900	0.7600	1.0827	0.1623		

Discussion of the Conductance Results

The conductances of the bismuth nitrate solutions in Table II are calculated for two cases as indicated in the table. The first assumption made is that all of the bismuth exists as the partially ionized salt, $BiOH^{++}(NO_3^-)_2$, whose conductance is taken equal to that of the salt $Ca^{++}(NO_3^-)_2$, at the same total nitrate ion concentration, the values of the equivalent conductance used for the first 4 solutions being, respectively, 71, 71, 67.5, and 62.6. The second assumption made is that all the bismuth exists as the partially ionized salt, $Bi^{+++}(NO_3^-)_3$, whose conductance is calculated from that of the salt $La^{+++}(NO_3^-)_3$ at the same total nitrate ion concentration, the extrapolation required being made by use of the relation $\Lambda = B - Kc^{1/3}$, where Λ is the equivalent conductance at the concentration c, and B and K are constants, the Λ values so derived for the first 4 solutions being, respectively, 58, 58, 47, and 28. The conductance of the excess of nitric acid is calculated from the results in Table I, using Λ values for the total concentration of the nitrate radical. These calculations were made only for the most dilute 4 solutions, since the estimation of the partial conductances at the higher concentrations would be very uncertain.

The specific conductances thus calculated when compared with the observed values, correspond closely to the assumption of the normal salt, $Bi(NO_3)_3$. It will be observed that upon the first assumption ($BiOH(NO_3)_2$) the values for the conductance of the excess of nitric acid alone are greater than the observed values for the total conductance of the mixture. In the more concentrated solutions, although it was considered useless to attempt an evaluation of the bismuth salt conductances, it will be seen that the values under this assumption would be much too high, while the values under the second ($Bi(NO_3)_3$) assumption would be not far from correct if the salt were given a conductance amounting to 5 to 10% of that of the nitric acid.

In passing, mention may be made of the fact that while the values here given for the conductance of nitric acid solutions agree fairly well with those given by Quartaroli,[2] his values of the specific conductance of the bismuth solutions were much higher and led him to assume the presence in solution of basic bismuth salts. To confirm the correctness of the results here presented, a special solution identical in composition with one measured by Quartaroli (namely 0.2563 *M* in bismuth and 1.740 *M* in nitrate) was made up from pure bismuth oxide and the same nitric acid that was used for the conductivity measurements. Its specific conductance was found to be 0.3038, while Quartaroli found 0.3394. The bismuth content in the stock solution used for the measurements given in the table was verified by precipitation with ammonium carbonate, ignition of the precipitate, and weighing as the oxide.

Table IV shows the results of the measurements upon the bismuth perchlorate solutions. It will be seen that the solution of bismuth oxyperchlorate at the lower concentration has the conductance of a normal uni-univalent salt, like potassium nitrate. By comparing the calculated with the actual increase in the specific conductance of the solutions of bismuth oxyperchlorate as additional equivalents of acids are added, it will be seen that only a small proportion of the added acid is used up in the conversion of the oxyperchlorate into less basic salts such as the hydroxy perchlorate, $BiOH(ClO_4)_2$, or the normal salt, $Bi(ClO_4)_3$. A quantitative estimate may be made by comparing the first and fourth solutions. If the bismuth salt were considered to remain unchanged except for the reduction in its conductance due to the higher concentration of perchlorate radical, the conductance of the bismuth oxyperchlorate in the fourth solution would be, from the data of the fifth solution, approximately $0.01753 \times 20/4 \times 19$ or 0.00461. The remaining conductivity, 0.0489, would then be due to the excess acid. The concentration of perchloric acid which at the total concentration of 0.20 would have this conductivity would be $0.0489/0.3755 = 0.1302$ *M*. Thus, of the 0.15 equivalents of acid added there have been used up 0.0198 equivalents, or 39.6% of the bismuth has been converted into the less basic salt, $BiOH^{++}(NO_3^-)_2$. However, due to the increased conductance of the bismuth when the less basic salt is formed, the actual amount of conversion would be more than this—perhaps 50% altogether.

The difference in the behavior of the bismuth in the nitrate and in the perchlorate solutions is doubtless partly due to the much greater excess of acid in the former case; but it indicates also that there is some marked difference in the ionization or complex formation of the nitrates and perchlorates. Thus, the more complete conversion of the nitrate into the neutral salt might arise from normal bismuth nitrate being a much less ionized compound than the normal perchlorate. It may be recalled that aluminum nitrate, even though it is the salt of a very weak base, is hydrolyzed only 2.4% in 0.03 *M* solution.[7]

The Solubility Determinations

In order to make sure that the solid phase used in the solubility determinations has the basicity of the salt, $BiONO_3.H_2O$, as shown by the work of Rutten previously referred to, 2 nitric acid solutions of the same concentration were shaken for 48 hours, one with a small excess of the solid and the other with thrice this amount of solid. The final bismuth content of the 2 solutions was found to be the same within 0.5%, showing that none of the nitric acid was used in changing the basicity of the solid phase.

The solid, prepared as previously described, was always kept under nitric acid, and before being introduced into a solution was first washed with the solution three or four times and never allowed to dry. Undersaturated solutions were prepared merely by adding the solid to the nitric acid which had been brought to a temperature of 25°. Supersaturated solutions were prepared by dissolving an excess of the solid in conc. acid and then diluting with water at 25° to the proper concentration. The solubility values from the undersaturated and supersaturated solutions always agreed to within 1.0%.

The bismuth content of the solutions was determined by precipitating with ammonium carbonate reagent, igniting to constant weight in an electric furnace at 750° to 800°, and weighing as bismuth oxide (Bi_2O_3). From the original concentration of the nitric acid and from the amount of nitrate radical brought into solution by the $BiONO_3.H_2O$, the total amount of nitrate radical in the saturated solutions was calculated.

The solid, prepared as previously described, dissolved to saturation in about 48 hours, although the solid prepared by the usual methods did not

TABLE V

SOLUBILITY OF BISMUTH OXYNITRATE IN NITRIC ACID SOLUTIONS AT 25°

Density in air at 25°	Mols in 1 liter of solution							
	Bi	NO_3	K_1	K_2	K_3	K_4	K_5	K_6
1.0005	0.002713	0.1027	390	0.031	33.8	0.003	0.286	0.019
1.0067	0.01449	0.2168	120	0.105	16.1	0.017	0.409	0.048
1.0228	0.04944	0.4485	35	0.246	6.1	0.063	0.403	0.074
1.0422	0.09956	0.6969	24	0.438	4.0	0.140	0.402	0.086
1.0643	0.1592	0.9537	22	0.670	3.1	0.239	0.393	0.082
1.0912	0.2354	1.2547	25	0.980	2.6	0.376	0.381	0.064

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[7] Bruner, *Z. physik. Chem.*, **32**, 134 (1900).

bring the solution within 10% of the saturation value in this length of time.

Experimental Values of the Solubility

The solubility results, the average from one undersaturated and one supersaturated solution at each concentration being taken, are given in the first 3 columns of Table V.

Discussion of the Solubility Data

Various possible reactions for the solution of the solid substance, $Bi(OH)_2NO_3$, in nitric acid, and the corresponding mass-action expressions (assuming the constituents to exist entirely in the forms shown in the equations) are as follows.

1. $Bi(OH)_2NO_3(s) + 3H^+ + 3NO_3^- = H^+ + Bi(NO_3)_4^- + 2H_2O.$

$$K_1 = \frac{\Sigma Bi}{(\Sigma NO_3 - 3\Sigma Bi)^2\,(\Sigma NO_3 - 4\Sigma Bi)^3}$$

2. $Bi(OH)_2NO_3(s) + 2H^+ + 2NO_3^- = Bi^{+++} + 3NO_3^- + 2H_2O.$

$$K_2 = \frac{(\Sigma Bi)(\Sigma NO_3)}{(\Sigma NO_3 - 3\Sigma Bi)^2}$$

3. $Bi(OH)_2NO_3(s) + 2H^+ + 2NO_3^- = Bi(NO_3)_3 + 2H_2O.$

$$K_3 = \frac{\Sigma Bi}{(\Sigma NO_3 - 3\Sigma Bi)^4}$$

4. $Bi(OH)_2NO_3(s) + H^+ + NO_3^- = BiOH^{++} + 2NO_3^- + H_2O.$

$$K_4 = \frac{(\Sigma Bi)\,(\Sigma NO_3)}{(\Sigma NO_3 - 2\Sigma Bi)}$$

5. $Bi(OH)_2NO_3(s) + H^+ + NO_3^- = BiOH(NO_3)_2 + H_2O.$

$$K_5 = \frac{\Sigma Bi}{(\Sigma NO_3 - 2\Sigma Bi^2)}$$

The values of these "equilibrium-constants" in terms of moles per liter are given in Table V.

It will be seen that the only one of these five expressions giving a constant is K_5, corresponding to un-ionized bismuth hydroxy nitrate $BiOH(NO_3)_2$; but, as the conductivity data have clearly shown that the bismuth is mainly converted into the neutral non-hydrolyzed salt, this result is to be regarded as a coincidence. It will be further seen that, in accordance with the assumption that the bismuth is present in the non-basic form, the values of K_2 and K_3 progress in opposite directions, corresponding to a condition between completely ionized and completely un-ionized bismuth trinitrate.

In fact, a fairly close correspondence with the observed solubility values can be secured by estimating the ionization of the bismuth salt and substituting the corresponding bismuth-ion concentration in the above equation for K_2, in place of the value of the total bismuth (ΣBi), at the same time correcting the total nitrate (ΣNO_3) by subtracting from it the un-ionized bismuth nitrate, thus calculating a new constant K_6 by the expression

$$K_6 = \frac{\gamma(\Sigma \mathrm{Bi})\ (\Sigma \mathrm{NO_3} - \mathrm{Bi(NO_3)_3})}{(\Sigma \mathrm{NO_3} - 3\Sigma \mathrm{Bi})^2}.$$

The ionization, γ, of the bismuth salt was calculated from the conductance ratios found for normal lanthanum nitrate by Noyes and Johnston[8] and extrapolated by means of the cube-root equation, $\Lambda = B - Kc^{1/3}$, the concentration c being taken equal to that of ΣNO_3, and the nitric acid being assumed to be completely ionized. The calculated values of K_6, which are given in the last column of Table V, are seen to give an approximate constant. The variations between 0.2 and 1.25 N concentrations are from 0.0485 to 0.0862, and this may well be due to inaccuracy in the estimated ionization values. We may, therefore, conclude that the assumption of partially ionized normal bismuth nitrate is in accord with the solubility results.

Apparatus and Method Used for the Electromotive-force Measurements

The electromotive-force measurements were made with the usual type of hydrogen half-cell containing 2 platinized platinum electrodes and a bismuth half-cell containing 2 platinum spirals plated electrolytically with a gray crystalline deposit of bismuth. The cell was arranged so that the liquid junction could be easily renewed. Air was carefully excluded from the apparatus, and the acid was boiled before use to remove dissolved air. The hydrogen was made by electrolysis of a solution of potassium acid sulfate contained in a U-tube the platinum electrodes of which were placed well up in the tube so that the oxygen would not diffuse over to

TABLE VI

CONSTANCY OF THE BISMUTH ELECTRODES

Time H. m.	E.m.f. of 1st Bi against 1st H_2 electrode	E.m.f. of 2nd Bi against 1st H_2 electrode	E.m.f. of 2nd Bi against 2nd H_2 electrode	Barometer
1:15	0.30661	0.30688	0.30708	...
2:15	0.30961	0.30961	0.30967	...
3:15	0.31128	0.31128	0.31126	...
4:10	0.31168	0.31166	0.31166	74.27
4:10	0.31168	.....	.....	...
5:30	0.31176	0.31175	0.31175	...
6:25	0.31176	0.31174	.....	74.27
6:25	.....	0.31172	0.31171	...
7:35	0.31175	0.31172	.....	...
7:35	0.31175	0.31171	.....	...
8:40	0.31173	0.31170	.....	74.33
8:40	0.31172	0.31169	.....	...
10:00	0.31172	0.31169	.....	74.34
10:00	0.31172	0.31169	.....	...

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[8] Noyes and Johnston, THIS JOURNAL, **31**, 987 (1909).

the hydrogen side. The measurements were made with a potentiometer of the latest type against a Weston standard cell.

Table VI serves to show the typical constancy and reproducibility of the cells. The headings are self-explanatory except that the lower figures under the same hour represent the potentials measured after renewal of the liquid junction.

Experimental Values of the Electromotive Forces

The final results of the electromotive-force measurements are given in Table VII, whose headings are for the most part self-explanatory. The concentrations are expressed in formula-weights per liter of solution at 25°. The electrode-potential of the hydrogen half-cell was calculated with the help of Lewis and Randall's[9] values of the activity coefficient for hydrochloric acid, under the assumption that the hydrogen-ion activity is substantially the same in the perchloric acid solutions. Since there was always a large excess of acid in the bismuth cell, and since the transference numbers of the bismuth ion-constituent and the perchlorate ion-constituent must be nearly the same, there should be no considerable liquid potential due to salts such as the oxyperchlorate, $BiOClO_4$. Also since the acid in the 2 half-cells was at very nearly the same concentration, the acid should cause no appreciable liquid potential. Moreover, the extreme reproducibility of the liquid junction, which was noticed in all

TABLE VII

FINAL VALUES OF THE ELECTROMOTIVE FORCE OF HYDROGEN–BISMUTH-PERCHLORATE CELLS AT 25°

Cell no.	1	2	3	4	5	6
Bismuth half-cell:						
ClO_4	0.1000	0.2000	0.2000	0.2000	0.2000	0.1500
Na	0.0	0.0	0.0	0.1000	0.0700	0.0
Bi	0.0200	0.0200	0.0500	0.0200	0.0500	0.0300
g./cc. in air	1.0059	1.0118	1.0184	1.0140	1.0199	1.0112
Hydrogen half-cell:						
ClO_4	0.08103	0.1803	0.1505	0.1800	0.1500	0.1208
Na	0.0	0.0	0.0	0.1000	0.0700	0.0
H_2 pressure	72.24	72.00	72.36	72.14	71.96	71.91
g./cc. in air	1.0050	1.0058	1.0043	1.0084	1.0061	1.0026
Activity of H^+	0.0673	0.1418	0.1198	0.0629	0.0636	0.0976
E.m.f. of cell	0.3118	0.3020	0.3054	0.3101	0.3119	0.3082
Electrode-potential of $H_2(g)$, H^+	0.0693	0.0502	0.0545	0.0710	0.0708	0.0598
Electrode-potential of $Bi(s)$, Bi^{+++}	−0.2425	−0.2518	−0.2509	−0.2391	−0.2411	−0.2484
Relative activities of Bi^{+++}	1.00	2.96	2.67	0.672	0.849	1.99

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[9] Lewis and Randall, THIS JOURNAL, 43, 1112 (1921).

the cells, seems to indicate that there was no appreciable liquid potential. Consequently no correction was made for it.

Derivation of the Electrode Potential of Bismuth from the Electromotive-force Data

Comparing Cells 1 and 4 in which the total concentration of bismuth is the same and that of hydrogen ion is nearly the same, but that of the total perchlorate is doubled, the activity of the bismuth ion is seen to be reduced by about $^1/_3$ of its value, doubtless owing largely to diminution of the ionization of the bismuth salt. Comparing Cells 3 and 5 in which the total perchlorate and total bismuth are the same, but in which the hydrogen-ion concentrations are considerably different, the activity of bismuth ion is seen to be approximately trebled when the hydrogen-ion activity is doubled. Cells 2 and 4 again show the great effect of increased hydrogen-ion concentration when other factors are approximately the same. This effect clearly shows that the bismuth exists mainly as basic salt and not as normal bismuth perchlorate.

Recalling now that the conductance data indicate that in solutions containing this moderate excess of acid the bismuth is present mainly as largely ionized $\mathrm{BiO^+ClO_4^-}$ and $\mathrm{BiOH^{++}(ClO_4^-)_2}$, we have calculated by the usual logarithmic expressions[10] from the six actual bismuth potentials given in the next to the last row of Table VII the values of the molal potential of Bi(s), $\left\{\begin{matrix}\mathrm{BiO^+}\ (1\ M)\\ \mathrm{H^+}\ (1\ M)\end{matrix}\right.$ and of Bi(s), $\left\{\begin{matrix}\mathrm{BiOH^{++}}\ (1\ M)\\ \mathrm{H^+}\ (1\ M)\end{matrix}\right.$, regarding the free perchloric acid as completely ionized and making the two limiting assumptions that all the bismuth is in the form of $\mathrm{BiO^+}$ and of $\mathrm{BiOH^{++}}$, respectively. The potentials thus calculated referred to the molal hydrogen electrode are given in the upper and lower halves of Table VIII. The concentrations are in moles per liter; but, if they were expressed in moles per 1000 g. of water, as is the usual practice, the potential values would not be changed by as much as 1 millivolt.

TABLE VIII

MOLAL ELECTRODE-POTENTIAL OF BISMUTH AT 25° CALCULATED UNDER TWO ASSUMPTIONS

$(\mathrm{BiO^+})$	0.02	0.02	0.05	0.02	0.05	0.03	
$(\mathrm{H^+})$	0.08	0.18	0.15	0.08	0.08	0.12	
Potential	−0.319	−0.315	−0.309	−0.316	−0.310	−0.315	Av. −0.314
$(\mathrm{BiOH^{++}})$	0.02	0.02	0.05	0.02	0.05	0.03	
$(\mathrm{H^+})$	0.06	0.16	0.10	0.06	0.03	0.09	
Potential	−0.300	−0.301	−0.296	−0.297	−0.297	−0.299	Av. −0.298

It will be seen that the two assumptions lead to values of the molal electrode-potential which vary by only a few millivolts at the different

[10] $E = \mathrm{E} + \frac{RT}{3\mathrm{F}}\, ln\ (\mathrm{BiO^+})\ (\mathrm{H^+})^2$; and $\mathrm{E} = E + \frac{RT}{3\mathrm{F}}\, ln\ (\mathrm{BiOH^{++}})\ (\mathrm{H^+})$.

concentrations, and that the average values of the two series differ by only 0.016 volt. These results are doubtless due in part to the fact that the logarithmic function expressing the relation between electrode potential and concentration is not very sensitive to changes in concentration, and in part to the fact that the bismuth actually exists in the solution partially in each of the forms corresponding to the two assumptions.

Experiments upon the equilibrium in perchloric acid solution of the reaction $3Cu(s) + 2Bi(ClO_4)_3 = 2Bi(s) + 3Cu(ClO_4)_2$, made in this Laboratory by Mr. E. H. Swift, the results of which are published in the following article, show that by use of the molal potentials derived above either for BiO^+ or for $BiOH^{++}$, it is possible to calculate the values of the equilibrium potentials within a few millivolts.

Summary

1. Electrical conductance and solubility measurements have been made upon solutions of bismuth nitrate containing various quantities of nitric acid. The results indicate that in solutions containing considerable excess of nitric acid the bismuth exists mainly in the form of the partially ionized salt, $Bi^{+++}(NO_3^-)_3$.

2. Conductivity measurements with bismuth perchlorate show that the very soluble basic salt $Bi(OH)_2^+ClO_4^-$ has the conductivity of an unhydrolyzed uni-univalent salt like potassium nitrate, and that it is converted into less basic salts such as $BiOH^{++}(ClO_4^-)_2$ and $Bi^{+++}(ClO_4^-)_3$ only slowly upon the addition of an excess of acid. Even when the ratio of perchlorate to bismuth is as much as 4:1, not more than 40–50% of the bismuth oxyperchlorate is converted even into the hydroxy salt, $BiOH(ClO_4)_2$.

3. Electromotive-force measurements upon solutions of bismuth perchlorate confirm the conclusions from the conductance measurements. They lead to the following values for the molal electrode-potential of bismuth, which were calculated under the two assumptions that the bismuth exists wholly in the form of the ion BiO^+ and the ion $BiOH^{++}$, respectively: $Bi(s), BiO^+ + H^+$: —0.314 volt; $Bi(s), BiOH^{++} + H^+$: —0.298 volt.

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