

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE  
UNIVERSITY OF PENNSYLVANIA]

## THE CONDUCTIVITY AND DEGREE OF HYDROLYSIS OF SODIUM BIGERMANATE AND THE PRIMARY DISSOCIATION CONSTANT OF GERMANIC ACID<sup>1</sup>

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The values obtained by the present authors for the conductivity of solutions of germanic oxide of a high degree of purity<sup>2</sup> tend to show that the probable value for the dissociation constant of germanic acid is approximately  $1.0 \times 10^{-9}$ , a value which is far removed from the values  $1.2 \times 10^{-7}$  and  $0.5 \times 10^{-7}$  obtained by Roth and O. Schwartz<sup>3</sup> and R. Schwarz and Huf<sup>4</sup> from similar conductivity measurements. Pugh,<sup>5</sup> whose value for the constant,  $2.5 \times 10^{-9}$ , is in good agreement with our own, attributes the very high value of Roth and Schwartz to the low grade of conductivity water used in their investigation. The specific conductivity of their water was  $1.5\text{--}1.7 \times 10^{-6}$  mhos per cm. at 18°, while that of the water used by Schwarz and Huf was  $1.8\text{--}2.0 \times 10^{-6}$  mhos per cm. at 20°; but, even though these values are much higher than that desirable for accurate measurements at these temperatures, they do not, alone, seem to be a sufficient explanation of the very wide discrepancy. The low conductivities found by us cannot be ascribed to colloidal dispersion because samples of the oxide which were definitely crystalline gave similar results. Furthermore, no matter from what source the germanic oxide was obtained, the results were always of the same order of magnitude. It seems, therefore, that either the results of other authors are subject to correction or that there exists in our own observations an undetected source of error of considerable magnitude. To remove the doubt that thus exists concerning the value for this constant, it was determined by two other methods, one conductimetric and the other colorimetric.

**Outline of Conductimetric Method.**—In order to secure some information concerning the behavior of germanic oxide in solution, conductimetric titrations were carried out. The titrations were performed in a closed conductivity cell, the air in which had been passed into it after purification through a line containing silver nitrate, concentrated sulfuric acid and solid sodium hydroxide. The carbonate-free caustic soda was prepared by

<sup>1</sup> From a thesis presented by C. E. Gulezian in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

<sup>2</sup> Gulezian and Müller, *THIS JOURNAL*, **54**, 3142 (1932).

<sup>3</sup> Roth and Schwartz, *Ber.*, **A59**, 338 (1926).

<sup>4</sup> Schwarz and Huf, *Z. anorg. allgem. Chem.*, **203**, 188 (1931).

<sup>5</sup> Pugh, *J. Chem. Soc.*, 1994 (1929).

Cornog's method.<sup>6</sup> Curves for several titrations are shown in Fig. 1. Curve A shows the results obtained when 25.0 cc. of 0.04453 *M* germanic oxide solution was titrated with 0.09287 *M* sodium hydroxide; curve B is for the titration of 25.0 cc. of 0.04632 *M* germanic oxide with the same caustic solution, while curve C gives the changes in specific conductivity when 100.0 cc. of 0.004453 *M* sodium hydroxide was titrated with 0.04453 *M* germanic oxide solution. In all these and similar cases, a definite break was obtained at a point corresponding to one equivalent of each substance.

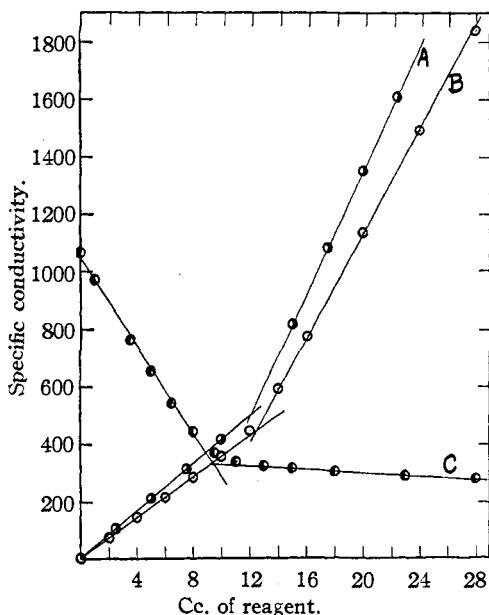


Fig. 1.—The conductimetric titration of germanic acid.

no appreciable formation of the normal meta salt. Obviously, accurate measurements of the concentration of germanic acid by conductimetric titrations is impossible due to the occurrence of considerable hydrolysis of the acid salt at the equivalent point—the evidence for this being especially noticeable in Curve C, Fig. 1; but the extent of this hydrolysis can be measured conductimetrically and from the degree of hydrolysis of the salt the dissociation constant of the parent acid can easily be calculated.

The conductimetric method for the determination of the degree of hydrolysis of a salt was originally described by Walker<sup>7</sup> for salts of weak bases. Bredig<sup>8</sup> also applied the method to the determination of the dis-

<sup>6</sup> Cornog, *THIS JOURNAL*, **43**, 2573 (1921).

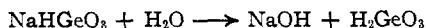
<sup>7</sup> Walker, *Z. physik. Chem.*, **4**, 319 (1889).

<sup>8</sup> Bredig, *ibid.*, **13**, 321 (1894).

The further addition of sodium hydroxide produced no change in the direction of the curve irrespective of the nature or source of the oxide in solution. Germanic acid, therefore, can behave toward sodium hydroxide as a monobasic acid with the formation of the salt sodium acid germanate (analogous to sodium bicarbonate), evidence for the existence of which has already been given by Pugh. Pugh has also shown that the salt sodium metagermanate,  $\text{Na}_2\text{GeO}_3$ , is hydrolyzed to an extent of 95% or more at concentrations approximately equal to those in our solutions, so that the addition of sodium hydroxide to sodium bigermanate produces

sociation constants of a number of weak organic bases; while, since then, it has been used to determine the degrees of hydrolysis of salts of weak acids as well as of weak bases. Examples of the application of the method for salts of weak acids are obtained in the work on cacodylic acid,<sup>9</sup> acetic acid,<sup>10</sup> cyanamide<sup>11</sup> and on certain oximes.<sup>12</sup>

In the present case, we have the reaction



taking place in a water solution of this salt. Direct measurement of the conductivity of the salt is, therefore, a measurement of the combined conductivity of the unhydrolyzed salt and of the sodium hydroxide formed. The conductivity of the free acid formed—exceedingly small as it is, even when present in water by itself at much higher concentrations—is here negligible, because of the very large excess of bigermanate ions from the salt. If, now, a buffer solution is formed having a considerable quantity of germanic acid present, hydrolysis of the salt can be prevented almost completely. The acid, again, will not contribute to the conductance of the solution, while complete dissociation of the salt can still be assumed. Measurement of the conductivity of such a solution will give a much more accurate value for the equivalent conductivity of the unhydrolyzed salt. From a knowledge of the equivalent conductivities in the two cases, it is possible to calculate the degree of hydrolysis from the expression.

$$\Lambda = x\Lambda'' + (1 - x)\Lambda'$$

where  $x$  is the degree of hydrolysis, and  $\Lambda$ ,  $\Lambda'$  and  $\Lambda''$  are the equivalent conductivities, at the same concentrations, of the hydrolyzed salt, the unhydrolyzed salt and sodium hydroxide, respectively. The value,  $\Lambda''$ , for the sodium hydroxide used at any concentration is assumed to be that which would be obtained if the salt were completely hydrolyzed.

### Experimental

The salt, sodium bigermanate, has never been isolated. Attempts to do so proved unsuccessful. It was, therefore, prepared in solution by adding exactly equivalent amounts of carbonate-free sodium hydroxide to known amounts of germanic oxide in solution. The figures in Table I show the method of preparation and composition of the various solutions used.

Twenty-five cubic centimeter portions of each of these solutions were transferred to the conductivity cell, dilutions made and the specific conductivity determined at each dilution. The apparatus was the same

<sup>9</sup> Zawidski, *Ber.*, **36**, 3325 (1903).

<sup>10</sup> Noyes, Kato and Sosman, *THIS JOURNAL*, **32**, 159 (1910).

<sup>11</sup> Kameyama, *Trans. Am. Electrochem. Soc.*, **40**, 131 (1921).

<sup>12</sup> Brady and Goldstein, *J. Chem. Soc.*, 1918 (1926).

TABLE I  
THE PREPARATION OF SODIUM BIGERMANATE SOLUTIONS

Solution	GeO <sub>2</sub> , solution, cc.	Concn. GeO <sub>2</sub> , mole/liter	NaOH 0.09287 <i>M</i> , cc.	Diluted to	Acid/salt ratio
(1)	100.0	0.04513	48.59	250.0	(Salt alone)
(2)	200.0	.04585	49.37	250.0	1.0
(3)	75.0	.05790	15.59	100.0	2.0
(4)	75.0	.05790	11.69	100.0	3.0

as that described in a previous paper.<sup>2</sup> Tables II, III, IV and V show the observations made on each of the solutions indicated in Table I. At the bottom of each table is included the specific conductivity of the water used in each case.

TABLE II  
SOLUTION (1)

$\sqrt{c}$	$k \times 10^6$	A
0.1344	1293.7	77.36
.0950	691.1	81.66
.07757	474.8	84.49
.06718	361.4	86.37
.05485	244.5	89.60
.04751	183.2	92.03
.03880	121.7	95.55

$$k(\text{H}_2\text{O}) = 0.90 \times 10^{-6}$$

TABLE III  
SOLUTION (2)

$\sqrt{c}$	$k \times 10^6$	A'
0.1354	1323.2	72.15
.09576	698.4	76.16
.06771	359.6	78.43
.03789	183.8	80.16
.03387	94.81	82.66
.02395	49.09	85.60
.01694	25.52	88.98

$$k(\text{H}_2\text{O}) = 0.90 \times 10^{-6}$$

TABLE IV  
SOLUTION (3)

$\sqrt{c}$	$k \times 10^6$	A'
0.1203	1060.5	73.24
.08509	557.3	76.98
.06948	372.8	77.23
.06015	281.1	77.66
.04912	189.8	78.66
.03805	115.7	79.91
.03216	83.55	80.80

$$k(\text{H}_2\text{O}) = 0.81 \times 10^{-6}$$

TABLE V  
SOLUTION (4)

$\sqrt{c}$	$k \times 10^6$	A'
0.1042	827.0	76.15
.07369	428.3	78.88
.06015	283.4	78.29
.05211	212.8	78.38
.04254	143.4	79.24
.03295	87.23	80.32
.02785	62.81	80.97

$$k(\text{H}_2\text{O}) = 0.97 \times 10^{-6}$$

**The Mobility of the Bigermanate Ion.**—When plotted against  $\sqrt{c}$ , the values for the equivalent conductivities for the salt in these four solutions give the results shown in Fig. 2. The points on curve A are for solution (1)—of the hydrolyzed salt. They fall on a smooth curve which rises very rapidly with dilution, indicating increasingly larger amounts of hydrolysis with decreasing concentration. The curve for the 1:1 buffer—curve C in the figure—shows that, in such a solution, hydrolysis is not completely repressed, since it becomes quite appreciable at low concentrations. Curve B is drawn through the points corresponding to the 3:1 buffer (Table V). The points for the 2:1 buffer, as shown, lie sufficiently close to this curve to warrant the conclusion that, in the case of the 3:1 buffer,

hydrolysis has been reduced almost to a minimum. As expected, curve B is asymptotic to curve A, since, in the more concentrated range, hydrolysis of the salt in water alone is very slight.

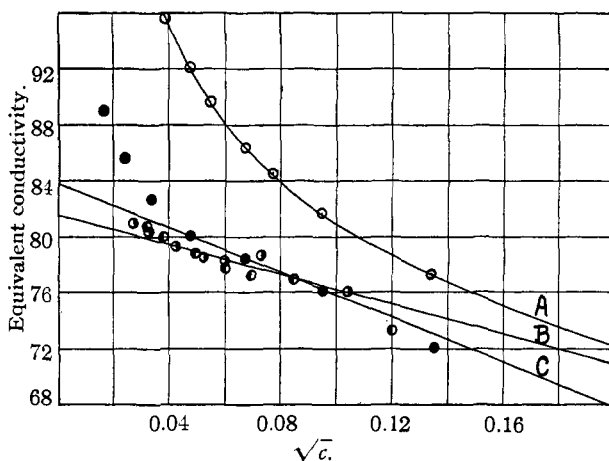


Fig. 2.—The equivalent conductivity of sodium bigermanate at 25°: ○, the salt in water alone; ●, 1:1 acid-salt ratio; ◐, 2:1 acid-salt ratio; ◑, 3:1 acid-salt ratio.

Extrapolation of curve B to zero concentration of salt then gives  $\Lambda_{\infty}$  for sodium bigermanate. This was done on a large scale plot and the value found to be 81.75. This value can then be inserted in the theoretical equation of Onsager<sup>13</sup> for strong electrolytes of the uni-univalent type

$$\Lambda = \Lambda_{\infty} - \alpha\sqrt{2\mu}$$

where  $\mu$  is the ionic strength (equal here to the concentration of the salt in moles per liter) and  $\alpha$  a constant varying with the electrolyte and equal at 25° to  $0.1605 \Lambda_{\infty} + 42.28$ . Evaluating this constant and introducing it as well as  $\Lambda_{\infty}$  into the above equation we get

$$\Lambda = 81.75 - 78.3\sqrt{\mu}$$

The experimental slope obtained from the curve was found on the large scale plot to be 79.2, which checks very favorably with the value indicated for  $\alpha$  in the above equation. We can, therefore, use the experimental curve and the extrapolated value of  $\Lambda_{\infty}$  for the salt to calculate the mobility of the bigermanate ion.

The mobility of the sodium ion at 25° was taken as 50.5, as calculated from the value at 18° and the temperature coefficient given in the "I. C. T."<sup>14</sup> Subtracting it from  $\Lambda_{\infty}$  for the salt, we obtain 31.25 for the value of the bigermanate ion at 25°. This is considerably less than the corresponding

<sup>13</sup> Onsager, *Physik. Z.*, **27**, 388 (1926); *ibid.*, **28**, 277 (1927).

<sup>14</sup> "International Critical Tables," Vol. VI, p. 230.

value for the bicarbonate ion, 46.6, calculated from Kendall's value<sup>15</sup> for  $\Lambda_{\infty}$  for sodium bicarbonate.

**The Dissociation Constant of Germanic Acid.**—In order to carry out the required calculations, it is necessary to have values for the equivalent conductivities of the hydrolyzed and unhydrolyzed salt as well as of sodium hydroxide at the same concentration. Inasmuch as the experimental concentrations for the different solutions from which the curves were drawn were not the same, the concentrations chosen for these calculations were those corresponding to the points on curve A for the hydrolyzed salt. The values for  $\Lambda'$  (for the unhydrolyzed salt) at these concentrations were then obtained by interpolation from curve B. Likewise, the values for sodium hydroxide were found by interpolation from a large scale plot of the values given for this substance in the "I. C. T."<sup>16</sup> In Table VI are shown the necessary values used in the calculations together with the values for  $\Lambda'$  calculated from the Onsager equation. Table VII gives the calculated values for the degree of hydrolysis and the hydrolysis constant of the salt and the dissociation constant of germanic acid.

TABLE VI

$\sqrt{c}$	$\Lambda$	$\Lambda'_{\text{curve}}$	$\Lambda'_{\text{calcd.}}$	$\Lambda''$
0.1344	77.36	74.05	71.23	230.7
.0950	81.66	76.25	74.31	235.0
.07757	84.49	77.25	75.67	236.4
.06718	86.37	77.85	76.49	237.7
.05485	89.60	78.52	77.45	239.2
.04751	92.03	78.95	78.03	240.1
.03880	95.55	79.48	78.71	241.2

In the fourth column of Table VII are given the values for the ionic product of water at these various concentrations, as interpolated from the values given by Harned<sup>17</sup> and by Harned and Swindells.<sup>18</sup> The value used for zero ionic strength was that determined by Roberts.<sup>19</sup>

TABLE VII

Concn	100x	$K_h \times 10^3$	$K_w \times 10^{14}$	$K_1 \times 10^6$
0.01805	2.11	0.823	1.35	1.64
.009025	3.41	1.09	1.19	1.10
.006017	4.55	1.31	1.16	0.89
.004513	5.33	1.35	1.13	.83
.003009	6.90	1.54	1.10	.72
.002257	8.12	1.62	1.08	.67
.001505	9.94	1.65	1.06	.64

<sup>15</sup> Kendall, *THIS JOURNAL*, **38**, 1480 (1916).

<sup>16</sup> "International Critical Tables," Vol. VI, p. 247.

<sup>17</sup> Harned, *THIS JOURNAL*, **47**, 930 (1925).

<sup>18</sup> Harned and Swindells, *ibid.*, **48**, 126 (1926).

<sup>19</sup> Roberts, *ibid.*, **52**, 3877 (1930).

**Colorimetric Determination of the Dissociation Constant.**—Buffer solutions were prepared, as before, containing germanic acid and sodium bigermanate, except that, before the final dilution, the indicator thymol blue was added to the solution. Determinations were carried out with two different samples of indicator of ordinary purity (Hynson, Westcott and Dunning) with no differences in the results. The indicator stock solution was prepared according to the directions given by Clark.<sup>20</sup> Throughout the measurements the concentration of the indicator in the buffers and comparison solutions was kept at  $2 \times 10^{-5}$  mole per liter; while the fully transformed acid and basic forms of the indicator were prepared as described by Kolthoff<sup>21</sup> for the alkaline range of thymol blue. A Gillespie colorimeter was used to determine the acid–base ratio of the indicator in the buffer solutions. From this value and the relationship  $[H^+] = K_{\text{Ind. acid/base}}$  are obtained the hydrogen-ion concentrations in the various solutions. As the ratios of the salt to the free acid are known for each buffer, simple calculation with the aid of the mass action law gives the dissociation constant of the acid. The observations and calculated results are shown in Table VIII. The values in the third column for the dissociation constants of thymol blue at different ionic strengths were obtained by interpolation from a large scale plot of corrected values for this indicator which were very kindly supplied by Dr. Martin Kilpatrick, Jr.

TABLE VIII

	Concn. of salt	Buffer ratio (acid/salt)	$K \times 10^9$ (T. B.)	Ind. ratio (acid/base)	$[H^+] \times 10^9$	$K_1 \times 10^9$
1	0.01180	1.0	0.980	0.332	0.326	0.326
2	.00944	1.5	.950	.612	.581	.388
3	.00787	2.0	.925	.989	.915	.458
4	.00674	2.5	.900	1.41	1.27	.506
5	.00592	3.0	.880	1.87	1.64	.547
6	.00157	2.0	.700	0.988	0.692	.346

### Discussion

The values found for  $K_1$  by the conductimetric method decrease with ionic concentration, as is to be expected on the basis of our present concepts on electrolytic solutions. The reverse seems to be the case for the values obtained colorimetrically. This apparent discrepancy is probably due to the fact that in the solutions studied by the latter method—with the exception of the one numbered 6—the buffer ratio is getting larger from solution to solution, even though the salt concentration is decreasing. In the case of two solutions—for example, 3 and 6—in which the ratio of molecular acid to dissociated salt is the same, the hydrogen-ion concentra-

<sup>20</sup> Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Md., 3d ed., 1929, p. 91.

<sup>21</sup> Kolthoff, "The Colorimetric and Potentiometric Determination of  $pH$ ," John Wiley and Sons, New York, 1931, p. 45.

tion as well as the dissociation constant of the acid are found to decrease with decreasing ionic strength. On comparing the values  $0.55 \times 10^{-9}$  obtained colorimetrically with the value  $0.89 \times 10^{-9}$  obtained conductimetrically on a similar 3 : 1 buffer at approximately the same ionic strength, the agreement is found to be fair. The magnitude of the values is, again, of the same order, while the results themselves agree very well with the values close to  $1.0 \times 10^{-9}$  obtained previously by us from conductimetric measurements on solutions of the free acid. The colorimetric method is, of course, limited in its accuracy, but it serves as a very good check on the values obtained by the other and more accurate methods. The fact that the hydrogen-ion concentrations in the buffer solutions studied lie within the range of applicability of this indicator is good indication that the dissociation constants of thymol blue and germanic acid are of the same order of magnitude.

Three methods, independent of each other, were thus used and all gave values in good agreement. The average value of all the determinations—about  $1.5 \times 10^{-9}$ —though somewhat smaller than the value  $2.5 \times 10^{-9}$  reported by Pugh from potentiometric measurements, points rather definitely to the conclusion that values in the neighborhood of  $1.0 \times 10^{-7}$  are considerably in error. We attribute our lower values to a higher degree of purity of the germanic oxide used.

**Acknowledgment.**—Grateful acknowledgment is made by C. E. Gulezian to the George Leib Harrison Foundation for the fellowship grant which made it possible to carry out this investigation.

### Summary

1. Conductimetric titrations of germanic acid with sodium hydroxide have been carried out and indicate the existence in solution of the salt sodium bigermanate.

2. The degree of hydrolysis of this salt at different concentrations has been measured by a conductimetric method, and the dissociation constant of germanic acid calculated from the observations made.

3. The mobility of the bigermanate ion was determined and found to be 31.3 at 25°.

4. Thymol blue was used, in buffer solutions, for the colorimetric determination of the dissociation constant of germanic acid.

5. The average value—approximately  $1.5 \times 10^{-9}$  at 25°—found for the constant by the use of three different methods was compared with the values of other investigators and found to agree with that of Pugh.