THE HYDROLYSIS OF STANNIC CHLORIDE.¹

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MANY compounds when in aqueous solution are acted upon by the water, some of the atoms or radicals of the compounds being replaced by the hydroxyl (OH) group. This familiar phenomenon is termed *hydrolysis*. Such bodies as stannic chloride and ferric chloride belong to this class of compounds. The rate at which a body undergoes hydrolysis is largely regulated by the amount of water present in proportion to the compound, a large amount of water facilitating hydrolysis. Stannic chloride is one of the most instructive examples of this class of compounds, for the rate at which it suffers hydrolysis in solution of medium concentration is so gradual that the observer has ample time to determine the condition of the solution as the reaction progresses, and at the same time final equilibrium is reached without having to wait too long.

In determining the resistance of a freshly-prepared solution of half-normal SnCl_4 , I observed that the bridge-reading was not constant, but that it changed in such a manner as to indicate that the conductivity of the solution *increased*. As the change in the conductivity was so gradual, it at once suggested the idea of measuring the conductivity of a solution from time to time until it should become constant. A number of such measurements have thus been made.

It will be remembered that Loomis² found very large and surprising values for the molecular depression of the freezing-points of aqueous solutions of this salt. Thus while the maximum values found by him in other salts did not exceed 5.5, the value for SnCl_4 was found to be 12.61 for $m = 0.04$ ($m = 0.01$ according to Loomis).

¹ Part II. of thesis presented to the faculty of Princeton University for the degree of Doctor of Philosophy.

² PHYS. REV., Vol. IV., No. 22, 1897, pp. 278 and 294.

The *complete* dissociation of this salt as such could not account for this depression, and the present work was undertaken at the suggestion of Professor Loomis with the hope of finding some explanation of the phenomenon from the behavior of the compound as an electrolyte.

HISTORICAL.

Stannic chloride was known to the ancient chemists. It was mentioned by Libavius as far back as 1605, and it was early termed *Spiritus Fumans Libavii*. It has been known for some time that it is not stable in dilute aqueous solutions, but that it undergoes hydrolysis, forming a hydrate of tin.

It has also been thought for some time that tin forms at least two hydroxides. These are sometimes termed stannic and metastannic acid, or α - and β -stannic acids, respectively.

Berzelius, early in the present century, observed the difference between these bodies. He thought that the stannic acid was obtained by treating SnCl_4 with alkalies; and the metastannic acid, by treating tin with nitric acid.

The following are some of the very conflicting opinions held regarding the properties and composition of these bodies:

Stannic acid is transformed into metastannic acid by desiccation. It *cannot* be isolated in the dry state.¹ (Berzelius, Graham.) Stannic acid *can* be isolated without alteration. Its composition is the same as metastannic acid. (Neumann, Schiff, Lorenz.)²

The composition of metastannic acid dried in a vacuum is $(\text{SnO}_2)_5 \cdot 5\text{H}_2\text{O}$. (Fremy.)

The metastannates do not exist: they are stannates with excess of stannic acid. (Berzelius.) There exist between these bodies two or more acids. (Leó Vignon.)

There are two isomeric stannic hydrates, each of which behaves as an acid, yielding corresponding salts.

Both acids exist in all degrees of hydration between H_2SnO_3 and H_4SnO_4 ; no satisfactory explanation of their difference has been given. If SnCl_4 be treated with such compounds as NH_4NO_3 and

¹ R. Engel, Compt. Rend., 125, 651; 1897.

² Zeit. Anorg. Chem., 9, 376; 1895.

Na_2SO_4 ; it yields H_4SnO_4 when dried in the air; and H_2SnO_3 when dried over H_2SO_4 . Stannic hydrate is slightly soluble in water, and dissolves readily in dilute mineral acids. (Roscoe.)¹

Acid solutions of SnO_2 treated with alkalis, precipitate $\text{Sn}(\text{OH})_4$ (stannic hydrate), also known as stannic acid. It is a colloidal substance having several modifications which are identical in composition. The various hydroxides have also a different appearance and behave differently with reagents. There is a difference between ordinary stannic acid and metastannic acid. Stannic acid is precipitated from SnCl_4 by treating it with alkalis, and metastannic acid is obtained by treating tin with HNO_3 . Metastannic acid is insoluble in water in the presence of HCl . (Mendeleeff.)²

The cause of difference is due to polymerization.

The ordinary acid corresponds to SnO_2 ; and the metastannic acid, to Sn_5O_{10} . (Fremy.)

The following opinions are entertained in regard to the change which SnCl_4 suffers in aqueous solution: Dilute HCl , especially when boiling, changes the ordinary hydrate which is first formed into metastannic acid. On this depends the formation of a white precipitate, stannic hydrate, in dilute aqueous solutions. (Mendeleeff.) When solutions of stannic acid in HCl (identical with solution obtained by the action of H_2O on SnCl_4) are allowed to stand, the stannic acid slowly undergoes conversion into metastannic acid, which usually separates out as an opalescent precipitate. (Roscoe.)

The dilute solution of SnCl_4 gradually decomposes, yielding HCl and metastannic acid. (Watts' Dict. of Chem.)

The solution of SnCl_4 diluted to a certain point yields *stannic hydrate* as well as metastannic acid. (Casselman.)

Stannic chloride boiled in water yields H_2SnO_3 and HCl , — $\text{SnCl}_4 + 3\text{H}_2\text{O} = \text{H}_2\text{SnO}_3 + 4\text{HCl}$.

Probably the following reaction takes place first:

$\text{Sn}(\text{OH})_4$ loses a molecule of H_2O and forms H_2SnO_3 , stannic acid. (Remsen.)

¹ Treatise on Chem., Vol. II., 1897.

² Treatise on Chem., Vol. II., London, 1897.

APPARATUS.

The apparatus employed in measuring the conductivity of solutions of SnCl_4 was the same as that described in Part I. of this thesis, with the addition of a thermostat.¹ The measurements in the thermostat were conducted at 28°C . It was easy to regulate the thermostat so that the temperature varied only a small fraction of a degree (usually much less than $\frac{1}{10}$) for hours at a time. Other measurements were made at 18° .

THE PREPARATION OF THE COMPOUND.²

To prepare SnCl_4 , c. p. tin was melted in a retort, and a strong, dry stream of chlorine was conducted into it, whereby SnCl_4 was formed. It is a strongly-fuming liquid; consequently a long condenser was connected with the retort, and the salt condensed in a pair of Woulf bottles surrounded by an ice bath. The liquid was transferred to a fractionation flask and some tin foil added to unite with the dissolved Cl. The SnCl_4 was distilled, treated with tin foil again, and the distillation repeated until the liquid became colorless and had a constant boiling-point.

The liquid was preserved in a well-stoppered flask to prevent access of aqueous vapor. The normal solution was prepared by first making up a solution of specific gravity 1.0927. This was analyzed, the Sn being determined as SnO_2 by precipitation as stannic hydrate by means of a strong solution of NH_4NO_3 , with the following results:

I.	5 c.c. of the solution gave	0.3551 g.	SnO_2
II.	" " " "	<u>0.3561</u>	" "
	mean value	0.3556	

This corresponds to 123.16 grams of SnCl_4 per liter. Accordingly, 288.23 grams of this solution were diluted to 500 c.c.

10 c.c. of this gave 0.3752 gm. SnO_2 , which corresponds to 65.07 grms. of SnCl_4 per liter. 64.975 grams are required for a normal solution. This indicated that the solution was 0.15% too

¹ Ostwald, Physiko-Chem. Messungen, Leipzig; 1893, p. 70.

² Chemische Präparatenkunde, Bender and Erdmann, Stuttgart.

strong, so it was diluted to normal strength. This solution was employed in preparing most of the dilute ones. For a few of the more concentrated solutions, the ordinary c. p. salt was employed. The strength of the solutions, other than those prepared by direct

Fig. 1.
Curves for SnCl_4 .

dilution from a solution of known strength, was determined by chemical analysis in some cases; and in others, by comparison of their sp. gr. with the sp. gr. of the solutions of known strength.

Fig. 2.

Curves for SnCl_4 .

THE MEASUREMENTS.

The Normal Solution.

The specific gravity of the normal solution of SnCl_4 was found to be 1.0496 ($\frac{1.8^\circ}{4^\circ}$). The solution was prepared from the pure liquid salt on November 12, and the values of $\frac{K}{m}$ (equivalent-conductivity) at 18° are given below :

$$\frac{K}{m} \cdot 10^8 \text{ at } 18^\circ \text{C.}$$

November 14,	1805
“ 18,	2040
December 23,	2265
February 21,	2340

This solution remained *clear*, and stood in a room whose temperature averaged about 15° . It is thus seen that the normal solution changes more rapidly during the first few days after its preparation, and that it would be months in coming to its maximum con-

ductivity. Solutions from $m=0.0001$ to $m=0.01$ were prepared from the normal solution as in the first part of this work.¹ Two series of measurements were carried out. The results are given below. The concentration m in *gram-equivalents* is given in the first column; the specific conductivity at 18° (Hg at $0^\circ=1$) is given in column 2; and the equivalent-conductivity $\frac{K}{m}$ is found in column 3.

FIRST SERIES.			SECOND SERIES	
m	$K_{18} \times 10^{10}$	$\frac{K}{m} \cdot 10^8$	$K_{18} \cdot 10 \cdot 0$	$\frac{K}{m} \cdot 10^8$
Water.	(1.83)	—	(2.10)	—
0.0001017	37.06	3460	32.52	2990
0.0002032	71.08	3400	67.35	3210
0.0006077	205.07	3350	204.61	3320
0.001009	344.2	3390	342.40	3370
0.002015	683.7	3390	685.70	3390
0.006024	2010.5	3330	2010.5	3330
0.01000	3300.0	3300	3313.0	3310

The measurements of the first series were made as rapidly as possible, while more time was used in obtaining the second series. It is seen, then, in the *extremely dilute* solutions that the equivalent-conductivity *decreases*. The same phenomenon is characteristic of acids and bases.

When $m =$ about 0.001, the value of the two series come together, however, and solutions of such strength change very little with time. To ascertain just how much a solution in which $m = 0.001$ does change, or how much time it requires to come to final equilibrium, one was prepared directly from the normal solution, with the following result :

$m = 0.001$	$\frac{K}{m} \cdot 10^8$ at 18°
Feb. 6, 11 a. m.	3100
" " 2:30 p. m.	3440
" " 5 "	3440

It is thus seen that this solution reaches its maximum conductivity within two or three hours. It changes very rapidly at first.

¹ PHYSICAL REVIEW, May-June, 1899.

For $m = 0.01$, the freshly-prepared solution gave $\frac{K}{m} \cdot 10^8 = 3300$, and this soon reached a maximum value of 3475. Some interesting conclusions may be drawn from the facts now before us, namely:

1. The final conductivities of the solutions of SnCl_4 $m = 0.01$ and 0.001 are almost identical with those of HCl of the same concentrations.

m	SnCl_4	HCl
0.001	3440	3520
0.01	3475	3470
		$\frac{K}{m} \cdot 10^8$

For $m = 0.01$, these values are practically identical.

2. For the most dilute solutions of SnCl_4 , the values of $\frac{K}{m}$ become smaller. The same is true of HCl in dilute solutions.

3. The *dilute* solutions of SnCl_4 soon come to equilibrium, that is, the hydrolysis of the salt is soon completed.

It is worthy of note that these dilute solutions yield a white, amorphous precipitate. It is a well-established fact that many chlorides undergo hydrolysis to a greater or less extent, generating at the same time HCl ; and it has been known for some time that a large quantity of water, especially when heated, causes an aqueous solution of SnCl_4 to precipitate a compound variously termed "stannic hydrate," "stannic acid" and "metastannic acid."

From the data and facts given above, it would seem that the stannic compound formed by the action of the water, even before the separation is complete, is not dissociated to any considerable degree; but that the conductivity of the solution depends almost entirely upon the HCl that is generated.

The following reaction perhaps takes place:

$5\text{H}_2\text{SnO}_3 = \text{H}_{10}\text{Sn}_5\text{O}_{15}$ (insoluble metastannic acid).

It is here assumed that the SnCl_4 first decomposes, forming stannic hydroxide, and generating four molecules of HCl . The $\text{Sn}(\text{OH})_4$ then loses a molecule of water, forming stannic acid, and then the H_2SnO_3 molecule condenses to form $\text{H}_{10}\text{Sn}_5\text{O}_{15}$ (metastannic acid).

This is an insoluble, colloidal body which gradually settles down as a white precipitate.

100 c.c. of the $\frac{n}{100}$ SnCl_4 solution (*i. e.*, the clear supernatant liquid) was found to be in exact balance with 10 c.c. of $\frac{n}{10}$ NaOH , thus showing that an equivalent amount of HCl was in fact generated.

Measurements were now made on the $\frac{n}{10}$ solution of SnCl_4 , with the following results :

	$\frac{K}{m} \cdot 10^3$
Feb. 6, 9:30 a. m.	3125
“ “ 5:30 p. m.	3154
“ 7, 2:00 “	3159
“ 21,	3218

The last value remained constant from this time. The value of $\frac{n}{10}$ HCl is 3290.

The $\frac{n}{10}$ SnCl_4 (the clear supernatant liquid) was balanced against $\frac{n}{10}$ NaOH , and was found to be 1.6% weak.

Measurements were next made on a number of solutions at 28° with results as follows :

SOLUTION No. I. $m = 1.623$.

Some of the liquid SnCl_4 (about 10 c.c.) was quickly added to about 200 c.c. H_2O . The temperature was quickly brought to 28° , SnCl_4 and the resistance of the solution determined without delay. Time of bringing liquid SnCl_4 and H_2O together, 12 m.

Time.	Interval in min.	$K \cdot 10^8$ at 28°	$\frac{K}{m} \cdot 10^8$
Jan. 11, 12:05 p. m.	0	1485	915
12:10 "	5	1532	944
12:25 "	20	1608	991
1:45 "	100	1757	1083
2:45 "	160	1854	1142
3:45 "	220	1921	1183
5:00 "	295	1981	1221
6:05 "	360	2018	1243
7:05 "	420	2049	1262
Jan. 30.	19 days	2791	1719

II. $m = 0.802$.

Time of bringing SnCl_4 and H_2O together, 10.31 a. m.

Time.	Interval in Min.	$K \cdot 10^8$ at 28°	$\frac{K}{m} \cdot 10^8$
Jan. 13. 10:35 a. m.	0	1377	1717
10:40 "	5	1440	1796
11:00 "	25	1559	1944
11:30 "	55	1646	2052
12:01 p. m.	86	1706	2127
12:31 "	116	1748	2179
1:31 "	176	1806	2252
2:35 "	240	1857	2315
3:35 "	300	1892	2359
4:35 "	360	1922	2396
5:35 "	420	1948	2429
7:35 "	540	1989	2480
9:35 "	660	2021	2520
Jan. 30	17 days.	2251	2807
Feb. 21	39 days.	2293	2860

2860 at $28^\circ = 2460$ at 18° .

III. $m = 0.5065$.*SnCl₄ and H₂O came together at 1:50 p. m.*

Time.	Interval in min.	$K \cdot 10^8$ at 28°	$\frac{K}{m} \cdot 10^9$
Jan. 18. 1:45 p. m.	0	1183	2335
2:01 "	7	1246	2460
2:24 "	30	1321	2608
2:54 "	60	1362	2689
2:54 "	120	1405	2773
4:54 "	180	1434	2831
5:54 "	240	1451	2878
6:54 "	300	1466	2894
7:54 "	360	1475	2912
9:54 "	480	1488	2937
Jan. 19	1 day	1507	2975
" 30	12 days	1542	3044
Feb. 21	34 days	1562	3084

3084 at 28° = 2660 at 18°.

IV. $m = 0.2865$.*SnCl₄ and H₂O came together at 8:59 a. m.*

Time.	Interval in min.	$K \cdot 10^8$ at 28°	$\frac{K}{m} \cdot 10^9$
Jan. 17. 9:03 a. m.	0	841	2935
9:07 "	4	857	2957
9:30 "	27	887	3096
10:03 "	60	906	3162
11:03 "	120	921	3215
12:33 p. m.	210	930	3246
2:33 "	330	940	3281
6:30 "	567	946	3302
Jan. 30.	13 days.	957	3340

This solution on standing gave a white precipitate. Nos. I., II. and III. remained *perfectly clear*. The value of m in every case was determined at 15° C.

Four series of measurements were next made, starting with a very concentrated solution ($m = 5.048$). The c. p. SnCl₄ (crystalline) of Eimer and Amend was employed. It was analyzed at 15° C.

These solutions will be designated as A, B, C and D.

Solution A. $m = 5.048$.

Time.	Interval in min. min.	$K \cdot 10^8$ at 28°	$\frac{K}{m} \cdot 10^8$
Jan. 14. 9:50 a. m.	0	1272	252
11:32 "	102	1274	252
4:33 p. m.	260	1272	252
Jan. 30	16 days.	1281	256

252 at $28^\circ = 207$ at 18° .

B. $m = 2.524$.

Time.	min.	$K \cdot 10^8$ at 28°	$\frac{K}{m} \cdot 10^8$
Jan. 15. 4:05 p. m.	0	1461	579
4:45 "	40	1468	582
5:45 "	100	1479	586
7:30 "	205	1501	594

C. $m = 1.262$.

Time.	min.	$K \cdot 10^8$ at 28°	$\frac{K}{m} \cdot 10^8$
Jan. 16. 9:29 a. m.	0	1409	1116
9:33 "	4	1458	1155
10:00	31	1598	1266
11:00 "	91	1727	1369
12:00 m.	151	1815	1438
2:00 p. m.	271	1913	1516
3:45 "	376	1971	1562
5:30 "	481	2025	1605
8:30 "	661	2103	1666

D. $m = 0.1231$.

Time.	Min.	$K \cdot 10^8$ at 28°	$\frac{K}{m} \cdot 10^8$
Jan. 19. 10 a. m.	0	426	3461
10:20 "	20	435	3534
12:20 p. m.	140	446	3623
2:20 "	260	450	3655, Sol. opalescent
4:20 "	380	451	3664, Ppt. forming
7:00 "	540	453	3680
Jan. 30.	11 days.	454	3688 Ppt. all settled down.

GRAPHIC REPRESENTATION OF THE RESULTS.

Fig. 1 shows the change, with time, in specific-conductivity at 28° C. (Hg at 0 = 1.)

The ordinates represent the specific-conductivity, and the abscissas represent the time in hours; m , as before, represents the *gram-equivalent* concentration.

In Fig. 2 the equivalent-conductivity $\left(\frac{K}{m}\right)$ is represented by ordinates and the abscissas represent the time in hours.

The solution $m = 1.623$, as shown in Fig. 1, conducts better than any other solution studied, although m ranges from 0.1231 to 5.048.

Fig. 2 shows (1) the familiar fact, that the equivalent-conductivity is always greater as the dilution is increased; (2) that for solutions from $m = 2.524$ to 0.1231, the equivalent-conductivity increases with time, soon reaching a maximum value in the more dilute solutions. It is also true that the rate of the increase in the equivalent-conductivity is more rapid and pronounced in proportion as the solution is diluted, but the curves for the more dilute solutions do not show this from the fact that most of the salt suffers hydrolysis before the first measurement can be made.

In summing up the work, the following facts and inferences may be enunciated:

(1) The dilute solutions of SnCl_4 are hydrolyzed more rapidly than those of medium concentration, while the very concentrated solutions come to equilibrium at once.

(2) The extent to which hydrolysis takes place is no doubt regulated by the law of mass action as set forth by Guldberg and Waage, and we are dealing with a state of chemical equilibrium or balanced action which may be represented thus:

$\text{SnCl}_4 + 4\text{HOH} \rightleftharpoons \text{Sn}(\text{OH})_4 + 4\text{HCl}$. One cannot measure the extent to which hydrolysis takes place, however, by simply determining the electrical conductivity of the solution, for the problem is a complicated one. The water goes on supplying OH and H ions and HCl is generated. An inventory of the solution as the reaction progresses would show something like the following:

1. Some dissociated SnCl_4 , giving Sn and Cl ions.
2. Some dissociated HCl giving H and Cl ions.

3. The stannic compound resulting from hydrolysis, not dissociated (say).

4. H_2O , very slightly dissociated, giving H and OH ions.

5. Non-dissociated SnCl_4 .

6. Non-dissociated HCl (very small amount). Only 1 and 2, or the dissociated SnCl_4 and HCl, take any appreciable part in determining the conductivity of the solution.

We have, therefore, two variables in the problem, that is, the SnCl_4 is growing less as hydrolysis goes on, and thus more completely dissociated, while the HCl is gradually increasing and hence not so completely dissociated. The ultimate state of things would seem to be this: as the SnCl_4 is transformed the specific-conductivity of the solution is decreased (as far as it depends upon the SnCl_4) but as the SnCl_4 becomes less its dissociation is more complete, and its conductivity therefore increased. These tend to balance each other. As the HCl increases the conductivity of the solution increases; but as the solution becomes more concentrated with reference to HCl, the acid will not be so completely dissociated. Likewise these tend to balance each other.

(3) The *dilute* solutions of SnCl_4 hydrolyze with great rapidity; and when equilibrium is reached, they behave in every respect like dilute solutions of HCl, and in fact an equivalent amount of this acid is generated in the process of hydrolysis.

4. The conductivity of solutions of SnCl_4 of medium concentration increases slowly with time and *tends* toward a maximum value, namely, *the conductivity of a solution of HCl of the same equivalent strength*.

5. In the very concentrated solutions, the conductivity does not change with time. This does not show that the solution has not undergone any hydrolysis, for it gives a strongly acid reaction.

6. The stannic compound formed by hydrolysis *does not separate out in the more concentrated solutions*, and the hydrolysis of dilute solutions of SnCl_4 is practically complete long before the precipitation of the insoluble compound begins. At no time in the reaction does the stannic hydrate seem to take any part in determining the conductivity of the solution.

This compound is no doubt a colloid in dilute solutions, es-

pecially when first formed. We may look upon a colloid as a body in pseudo-solution, that is, a step between a true solution and an emulsion. It is known that the diffusion of colloids takes place slowly, the osmotic pressure is small and there is only a slight lowering of the freezing-point or raising of the boiling-point. With these facts and the fact that colloids do not conduct electricity, we conclude that they are not only larger than ordinary molecules, but that they are not dissociated into ions.

7. Attention was called in the first part of this paper to the abnormally large values of the depressions of the freezing-point as found by Loomis. For $m = 0.04$ ($m = 0.01$ according to Loomis)

$\frac{\Delta}{m}$ was found to be 12.61. Considering that one molecule of SnCl_4 will give 4 HCl molecules (see reaction above) and that the HCl is completely dissociated in *very dilute* solutions, we shall have eight ions for every molecule of SnCl_4 . These ions would take part in the conduction of the electricity and also act to lower the freezing-point. The maximum value of $\frac{\Delta}{m}$ would therefore be

$(1.86 \times 8) = 14.88$. As stated above, Loomis found $\frac{\Delta}{m} = 12.61$ for a solution which he supposed to be 0.04 normal. He prepared this solution from a more concentrated solution made up according to Gerlach's table. According to this table the *gram-equivalent* solution of SnCl_4 has a sp. gr. of 1.0486 $\left(\frac{15^\circ}{4^\circ}\right)$. This was the strength of the solution used by Loomis. The writer found the sp. gr. of a gram-equivalent solution to be 1.0496 $\left(\frac{18^\circ}{4^\circ}\right)$, as may be seen in the first part of this paper.

Reducing Loomis' solution as prepared from Gerlach's table to $\frac{18^\circ}{4^\circ}$, it will be seen that our solutions differ by about two points in the third place of decimals. With these facts before us, Loomis prepared a solution with sp. gr. 1.0486 $\left(\frac{15^\circ}{4^\circ}\right)$, and according to my analysis it was found to be 11.5% *weaker* than a gram-equiva-

lent solution. Loomis' value for $\frac{\Delta}{m}$ (12.61) is therefore 11.5% too small. Its corrected value is 14.25.

A 0.04 gram-equivalent solution of HCl is 94.5% dissociated $\left(\frac{\mu_x}{\mu_\infty} = \frac{3400}{3600}\right)$. From this it follows that the theoretical value of $\frac{\Delta}{m}$ is $14.88 \times \frac{94.5}{100} = 14.06$. It is thus seen that this value corresponds well with the corrected value, 14.25, as found by Loomis.

8. Stannic chloride does not furnish an exception to the "dissociation theory"; for when account is taken of its hydrolysis, the phenomena manifested in its aqueous solution in connection with the electrical conductivity and the depression of the freezing-point are explained in accordance with this theory. On the other hand, however, it furnishes direct evidence against the "hydrate theory," *for the hydrate formed takes no appreciable part in the conduction of electricity*. Moreover, it is not probable that water sets HCl free, and then unites with the acid to form a second hydrate. We must still look upon the theory of electrolytes as founded by Arrhenius and others on van't Hoff's view of the nature of solution, as the one nearest in accord with the experimental data.

Finally, I wish to express my gratitude to Professor Loomis whose kindness and assistance have made it possible to carry out this investigation.

PHYSICAL LABORATORY, PRINCETON UNIVERSITY, March, 1899.