

STUDIES ON SOLUTIONS OF TIN SALTS.

I. ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF STANNOUS CHLORIDE AND HYDROCHLORIC ACID.

BY S. W. YOUNG.

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THE following paper contains the first results of an investigation, which I hope soon to carry further, into the static conditions existing within solutions consisting of water, acid, and stannous salt, as well as the influence of other salts on such conditions. I hope by means of the knowledge thus acquired, to make some research into the velocity of reduction of various reagents by stannous chloride solutions, and thus, possibly, throw a little light on some of the existing anomalies in the field of chemical kinetics.

For example, there remains still unexplained the curious fact observed by Noyes¹ that in the reduction of ferric chloride by stannous chloride the order of the reaction is apparently displaced by addition of hydrochloric acid from one of the third order to one of the second.

It seems to me that up to the present, sufficient attention has not been directed toward the strict definition of the reagents in inorganic investigations. One has generally been contented with determining some one concentration in the solution; *e. g.*, hydrogen ions, or with working at great dilutions under the assumption that all of the reagent was dissociated, and that no other influences were present.

In many cases such procedure is wholly sufficient, but, as for example in the case of stannous chloride solutions where hydrolysis and complex molecule formation may (and do) enter in as complicating factors, a more accurate definition of the reagent is absolutely necessary. It was with this idea in mind that the following measurements of the electrical conductivity of solutions of stannous chloride and hydrochloric acid in water were made.

The method was the usual one of Kohlrausch with Wheatstone's bridge and telephone. The little apparatus shown in Fig. 1 served as the conductivity flask. Since the measurements ex-

¹ *Ztschr. phys. Chem.*, **16**, 546 (1895).

tended through a very considerable range of concentrations it was necessary to have three such flasks with different capacities, the capacities being varied simply by using different sized glass tubing for the U-shaped parts of the flasks. Measurements were made at 25° C. in an Ostwald thermostat, and at 0° C. in an ice thermostat. The conductivities are calculated as specific conductivities in reciprocal ohms.

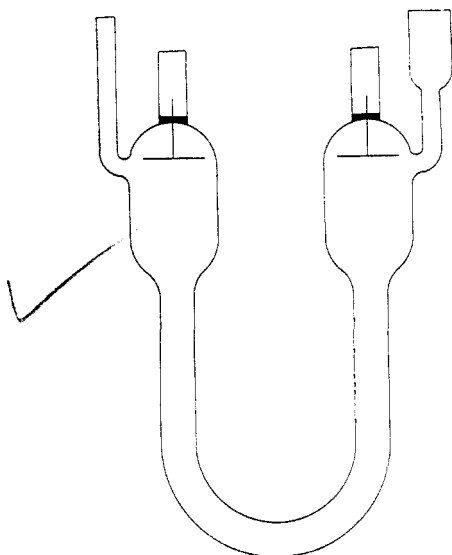


Fig. 1.

The solutions were prepared by taking a 100 cc. measuring flask, filling it to the mark with hydrochloric acid of accurately known strength. Roughly weighed amounts of pure crystallized stannous chloride were then added, brought into solution, and the liquid made up to 105 cc. The concentration of the hydrochloric acid in the solution was thus $\frac{100}{105}$ of that of the acid used.

The concentration of the stannous salt was readily determined by titration with standard bichromate, using potassium iodide and starch paste as indicator.

Hydrochloric acids of concentrations varying from 0.25 normal to nearly 8 normal were used. With each acid from six to eight different solutions were made, varying as to concentration of stannous chloride from zero to approximately normal. No attempt was made to prepare solutions that were exactly normal, 0.5 normal, etc., because of the somewhat uncertain composition of the crystallized stannous chloride used.¹ Following (Table I), are the tabulated results of the series of measurements at 25° C. The first columns contain the concentrations of stannous chloride in gram equivalents per liter, the second columns contain the val-

¹ A beautifully white, crystallized stannous chloride, which dissolved perfectly in pure water when the solution was not made too dilute, and whose hydrolyzed solutions cleared up immediately upon the addition of a few drops of acid, was obtained from Kahlbaum. The salt showed a distinct tendency to efflorescence, and from analyses showed itself to be nearly free from impurity.

ues of the specific conductivities in $\frac{I}{\text{ohms}} \times 10^4$; the third columns contain the values $\frac{\Delta K \times 10^4}{C_{\text{SnCl}_2}}$, *i. e.*, the change in the conductivity as a result of addition of stannous chloride, and calculated to the unit of concentration. A minus sign indicates a decrease of the conductivity, a plus sign an increase.

TABLE I.—CONDUCTIVITY OF SOLUTIONS OF STANNOUS CHLORIDE IN AQUEOUS HYDROCHLORIC ACID AT 25° C.

With $\frac{1}{2}$ normal HCl. ¹			With $\frac{1}{2}$ normal HCl.			With $\frac{2}{3}$ normal HCl.		
C	$\frac{\text{SnCl}_2}{2}$	$\frac{\Delta K \times 10^4}{C}$	C	$\frac{\text{SnCl}_2}{2}$	$\frac{\Delta K \times 10^4}{C}$	C	$\frac{\text{SnCl}_2}{2}$	$\frac{\Delta K \times 10^4}{C}$
	K × 10 ⁴ .			K × 10 ⁴ .			K × 10 ⁴ .	
0.000	900.3	0.000	1738	0.000	2045
0.0605	914.7	+238	0.061	1738	0.063	2045	00
0.1180	929.0	+243	0.122	1740	+16	0.111	2045	00
0.1810	946.4	+255	0.247	1746	+32	0.238	2045	00
0.2490	960.5	+242	0.366	1751	+36	0.391	2045	00
0.3125	977.4	+247	0.465	1756	+39	0.607	2040	-8
0.5830	1041.0	+243	0.575	1759	+37	0.920	2032	-14
1.1050	1123.0	+202	1.045	1794	+46
With $\frac{1}{2}$ normal HCl.			With normal HCl.			With $1\frac{1}{4}$ normal HCl.		
C	$\frac{\text{SnCl}_2}{2}$	$\frac{\Delta K \times 10^4}{C}$	C	$\frac{\text{SnCl}_2}{2}$	$\frac{\Delta K \times 10^4}{C}$	C	$\frac{\text{SnCl}_2}{2}$	$\frac{\Delta K \times 10^4}{C}$
	K × 10 ⁴ .			K × 10 ⁴ .			K × 10 ⁴ .	
0.000	2495	0.000	3205	0.000	3860
0.058	2493	-34.5	0.013	3202	-231	0.066	3848	-182
0.119	2489	-50.0	0.053	3190	-283	0.192	3827	-172
0.240	2479	-64.0	0.100	3187	-180	0.310	3805	-177
0.345	2473	-64.0	0.3125	3157	-157	0.475	3782	-164
0.475	2462	-70.0	0.4950	3128	-155	0.665	3748	-169
0.585	2457	-65.0	0.700	3107	-140	0.990	3700	-162
0.990	2425	-70.0	1.000	3093	-117
With $1\frac{1}{2}$ normal HCl.			With 2 normal HCl.			With $2\frac{1}{2}$ normal HCl.		
C	$\frac{\text{SnCl}_2}{2}$	$\frac{\Delta K \times 10^4}{C}$	C	$\frac{\text{SnCl}_2}{2}$	$\frac{\Delta K \times 10^4}{C}$	C	$\frac{\text{SnCl}_2}{2}$	$\frac{\Delta K \times 10^4}{C}$
	K × 10 ⁴ .			K × 10 ⁴ .			K × 10 ⁴ .	
0.000	4447	0.000	5478	0.000	6330
0.070	4429	-257	0.073	5456	-301	0.064	6305	-390
0.195	4408	-200	0.182	5434	-242	0.178	6262	-380
0.300	4389	-193	0.305	5401	-250	0.280	6244	-307
0.465	4357	-193	0.485	5352	-260	0.455	6205	-272
0.615	4332	-187	0.660	5316	-245	0.635	6152	-280
1.010	4249	-196	0.988	5226	-254	0.995	6053	-278

¹ These figures indicate the strength of the acid used in making the solutions and are to be multiplied by $\frac{1}{100}$ in order to get actual concentration in the solution as prepared.

With $\frac{3}{4}$ normal HCl.			With 4.28 normal HCl.			With 7.7 normal HCl.		
C	$\frac{\text{SnCl}_2}{2}$	$\frac{\Delta K \times 10^4}{C}$	C	$\frac{\text{SnCl}_2}{2}$	$\frac{\Delta K \times 10^4}{C}$	C	$\frac{\text{SnCl}_2}{2}$	$\frac{\Delta K \times 10^4}{C}$
0.000	6985	0.000	8050	0.000	8250
0.065	6963	-336	0.060	8032	-300
0.192	6916	-360	0.151	7997	-351
0.300	6882	-343	0.236	7971	-336
0.420	6850	-321	0.415	7907	-340
0.580	6803	-314	0.560	7866	-327
0.995	6686	-300	0.885	7741	-349	0.985	7854	-402

In Table II are collected the results of an exactly similar set of measurements, carried out at 0° C. In this set of observations only four concentrations of stannous chloride for each concentration of hydrochloric acid were used, and some concentrations of hydrochloric acid measured at 25° C. were omitted from this set.

TABLE II.—CONDUCTIVITY OF SOLUTIONS OF STANNOUS CHLORIDE IN AQUEOUS HYDROCHLORIC ACID AT 0° C.

With $\frac{1}{4}$ normal HCl.			With $\frac{1}{2}$ normal HCl.			With normal HCl.		
C	$\frac{\text{SnCl}_2}{2}$	$\frac{\Delta K \times 10^4}{C}$	C	$\frac{\text{SnCl}_2}{2}$	$\frac{\Delta K \times 10^4}{C}$	C	$\frac{\text{SnCl}_2}{2}$	$\frac{\Delta K \times 10^4}{C}$
0.000	580.1	0.000	1117	0.000	2074
0.272	620.0	+147	0.295	1126	+30	0.449	2032	-93
0.655	664.9	+130	0.745	1134	+23	0.770	2009	-84
1.045	701.3	-115	1.165	1141	+21	1.090	1981	-76

With 2 normal HCl.			With 3 normal HCl.			With 4 normal HCl.		
C	$\frac{\text{SnCl}_2}{2}$	$\frac{\Delta K \times 10^4}{C}$	C	$\frac{\text{SnCl}_2}{2}$	$\frac{\Delta K \times 10^4}{C}$	C	$\frac{\text{SnCl}_2}{2}$	$\frac{\Delta K \times 10^4}{C}$
0.000	3545	0.000	4535	0.000	5160
0.290	3500	-155	0.327	4482	-160	0.293	5095	-222
0.690	3432	-164	0.710	4404	-184	0.670	5010	-224
1.005	3378	-166	1.035	4341	-188	0.965	4939	-229

With 5.79 normal HCl.		
C	$\frac{\text{SnCl}_2}{2}$	$\frac{\Delta K \times 10^4}{C}$
0.000	
0.290		-313
0.660		-290
1.025		-301

In Table IIIa, is given a summary of the results given in Table I for normal solutions of stannous chloride. In the first column are the concentrations of the hydrochloric acid used in making

up the solutions; in the second column the conductivities in $\frac{I}{\text{ohms}} \times 10^4$ for solutions containing no stannous chloride; in the third column the corresponding values for solutions whose concentrations in stannous chloride were approximately normal; in the fourth column the differences of the first two columns divided by the actual concentration of the stannous chloride (always very near to normal); *i. e.*, the *equivalent influence of stannous chloride upon the conductivity of hydrochloric acid solutions*; in the fifth columns the same values calculated in percentages of the conductivity of the pure hydrochloric acid solution.

Table III*b* contains the same results for the measurements at 0° C.

TABLE III*a*.—SUMMARY OF VALUES OF CHANGES IN CONDUCTIVITY OF HYDROCHLORIC ACID BY NORMAL STANNOUS CHLORIDE AT 25° C.

CHCl.	K × 10 ⁴ . SnCl ₂ = 0.	K × 10 ⁴ . SnCl ₂ = N.	$\frac{\Delta K \times 10^4}{CN}$	Per cent.
0.25 N	900.3	1123	+202	+22.44
0.50	1738	1794	+46	+2.17
0.60	2045	2032	-13	-0.60
0.75	2495	2425	-70	-2.81
1.00	3205	3093	-117	-3.64
1.25	3860	3700	-162	-4.20
1.50	4447	4249	-196	-4.41
2.00	5478	5226	-254	-4.50
2.50	6330	6053	-278	-4.40
3.00	6985	6686	-300	-4.35
4.28	8050	7741	-349	-4.02
7.70	8250	7854	-402	-4.81

TABLE III*b*. CORRESPONDING VALUES AT 0° C.

CHCl.	K × 10 ⁴ . SnCl ₂ = 0.	K × 10 ⁴ . SnCl ₂ = N.	$\frac{\Delta K \times 10^4}{CN}$	Per cent.
0.25 N	580.1	701.3	-115	+19.82
0.50	1117	1141	+21	+1.85
1.00	2074	1981	-76	-3.67
2.00	3545	3378	-166	-4.68
3.00	4535	4341	-188	-4.14
4.00	5160	4939	-229	-4.44
5.79	5600	5293	-301	-5.38

The following curves will make the relationships between the values given in the tables, somewhat more readily comprehensible. In the set of curves, Fig. 2, are plotted as abscissas, the concen-

trations of hydrochloric acid, and as ordinates the changes in the conductivity, brought about by the addition of stannous chloride. The curve with continuous line is for normality in stannous chloride, at 25°C. ; the curve with dotted line is for normality in stannous chloride at 0°C. In the set of curves, Fig. 3, are the same values calculated to percentages.

DISCUSSION OF THE RESULTS.

The method of determining variations in the electrolytic conductivity of mixed electrolytes as a test for the formation of molecular complexes in such solutions, is by no means new. Thus, Peters¹ measured the conductivities of solutions of ferrous and ferric salts, and the influence of sodium fluoride upon the same. From the results of his work, he concludes that complex molecules are formed in the case mentioned, and the conclusion is supported by measurements of freezing-points, transference numbers, and electromotive forces.

Also the idea, that solutions of stannous salts containing excess of acid were prone to form complex molecules in solution, is not new. From the great increase in the solubility of stannous chloride, in solutions of increasing concentration of hydrochloric acid, Engel² concluded that in such solutions, the formation of complex molecules occurred. In previous papers by me,³ a similar condition was shown to exist for stannous iodide and hydriodic acid, and it was further shown that at moderately low temperatures, a compound, probably SnI_2HI , crystallizes out from solutions not too dilute in hydriodic acid.

That a reduction of the total conductivity of the solution to a point far beyond what is to be expected from any theory of mixed electrolytes, occurs upon the addition of stannous chloride to moderately concentrated hydrochloric acid solutions, is very definitely proved by the above measurements. By reference to Table IIIa, it will be seen that the addition of stannous chloride, to normality, to a 0.25 normal solution of hydrochloric acid, conditions an increase of conductivity of 202 units.⁴ Neglecting the

¹ *Zeit. phys. Chem.*, **26**, 193 (1895).

² *Ann. chim. phys.*, **17**, 338 (1889).

³ *This Journal*, **19**, 845 and 851 (1897).

⁴ It is quite possible that this number is too low from some experimental error (*c.f.* Table I). It may be mentioned here, in passing, that what little evidence is at hand, seems to indicate that the hydrolysis constant of stannous chloride, is a fairly large one,

influence of this concentration, of hydrolysis, molecular complex formation, and of variations from the fact that the solutions are not isohydric, we can get a very rough idea of the magnitude of the conductivity of stannous chloride in normal solution, the value being 202, a number of a magnitude comparable with the corresponding value for cadmium bromide (about 200), or cadmium chloride (about 230). When 0.5 normal hydrochloric acid is used, the increase is only 46 units. With 0.6 normal acid there occurs a small reduction $\left(-13\frac{1}{2} \times 10^4 \text{ or } 0.6 \text{ per cent.}\right)$. With stron-

ger acids a reduction in the conductivity always occurs which becomes larger as the strength of the acid increases. The conduct at 0° C. (Table III*b*) is wholly analogous to that at 25° C. A curious thing is to be noticed in Fig. 3. The percentage influence of normal stannous chloride on hydrochloric acid solutions of increasing concentration shows a maximum at about double normal hydrochloric acid. From this point on, the percentage influence decreases to a minimum at about 4 normal hydrochloric acid at 25° C., and at about 3 normal hydrochloric acid at 0° C. From these minimum points on, the percentage influence again increases with increasing concentration of hydrochloric acid. The counterpart of this peculiarity is to be distinctly seen in Fig. 2. In the curve for 25° C., it appears as a mere flattening of the curve, while in the curve for 0° C., an actual change in the direction of curvature is to be seen. As to the physical significance of these peculiarities, perhaps the

and that a very considerable degree of hydrolysis occur even in moderately acid solutions of the salt. It is further quite probable that the hydrolysis is a reaction requiring a very considerable amount of time for its completion. Both of these statements are rendered likely from the results of the following experiment: A 0.2 normal solution of hydrochloric acid was taken, and to it, some stannous chloride was added. The solution was then placed in the conductivity flask (Fig. 1), and placed in the thermostat at 25° C. The conductivity measured immediately, was 843.7. After twenty-five minutes it was 850, after sixty-five minutes 852; and after 1100 minutes, 870.4. This increasing conductivity can easily be explained, as due to progressing hydrolysis. The solution remained clear throughout the whole time. That the phenomenon was not due to oxidation, is indicated by the fact that a similar experiment with stronger acid (0.5 normal) gave constant readings for twenty-four hours. It was also observed that rather concentrated solutions of stannous chloride have the power of dissolving very considerable quantities of hydrolyzed stannous chloride (oxychloride). Thus it appears probable that stannous chloride may become hydrolyzed to a very considerable extent without separation in an insoluble form of oxychloride. This probability is rendered greater by evidence derived from a study of the oxidation of stannous chloride to be published in a subsequent paper. If true, the fact would have an important bearing on the work of Noyes, "On the Reduction of Ferric Chloride with Stannous Chloride" (*q.v.*). The whole matter of hydrolysis will be made the subject of a special investigation.

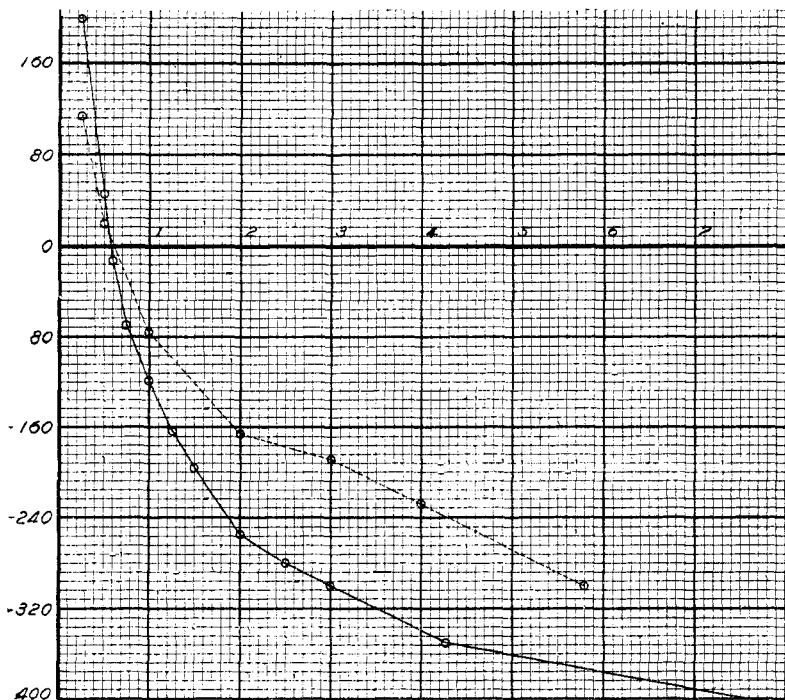


Fig. 2.

simplest and most satisfactory explanation would be to assume that in stannous chloride and hydrochloric acid solutions, there are two distinct kinds of molecular complexes formed. For example, at low concentrations, we may assume that the equilibrium, $\text{SnCl}_2 + \text{HCl} \rightleftharpoons \text{HSnCl}_3$, plays the chief rôle, while at high concentrations, the equilibrium $\text{H.SnCl}_3 + \text{HCl} \rightleftharpoons \text{H}_2\text{SnCl}_4$ (or some similar one) becomes more and more noticeable. In other words, we may have two equilibria, one very sensitive to dilution, the other very considerably less sensitive. Plotting these conditions graphically for the two equilibria independently of one another, in such a way that the ordinates represent the concentration of the dissociated part (left-hand members of the above equations) and abscissas either the total concentrations or undissociated concentrations, we should get curves similar to those in Fig. 4, *a* being for the more sensi-

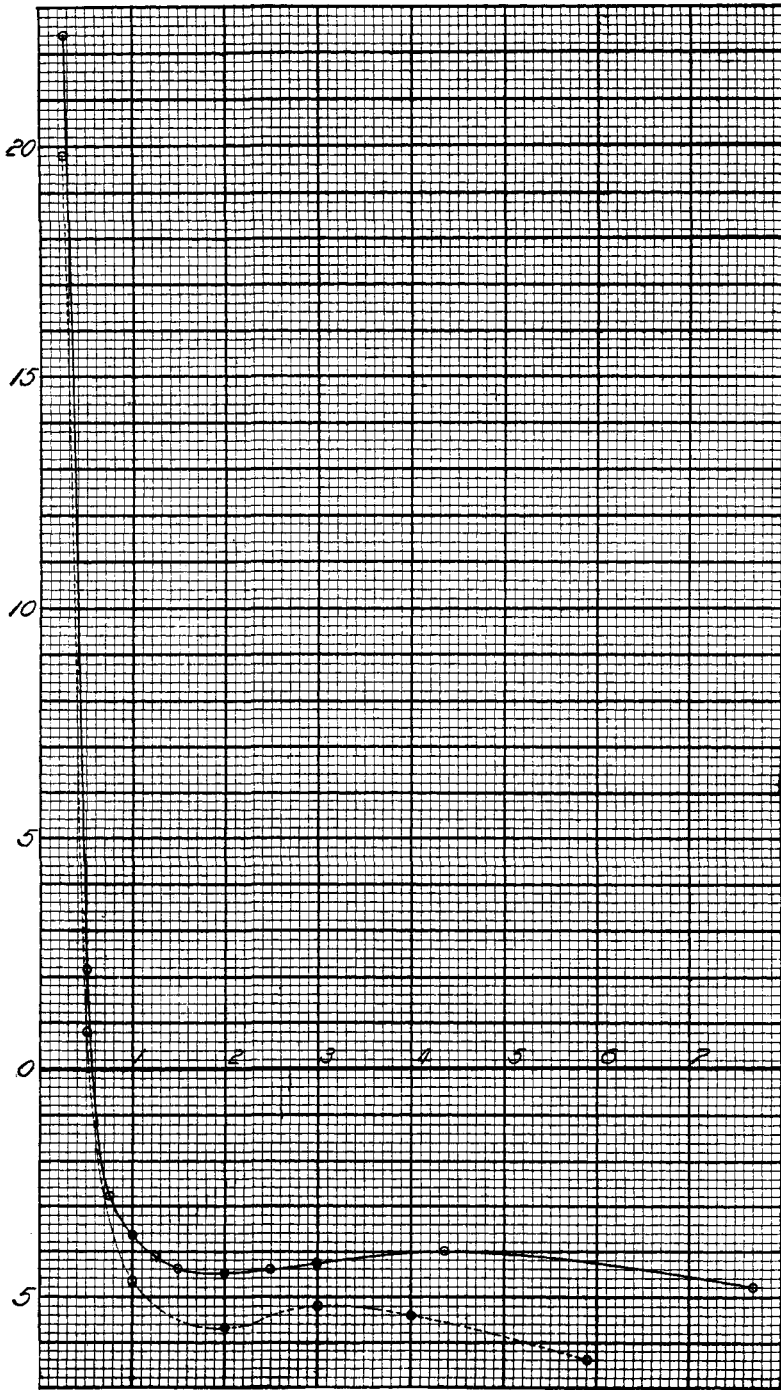


Fig. 3.

tive, and b for the less sensitive equilibrium. Then let cd represent the zero concentration for the dissociated part of the first equilibrium and ef that of the second. Then for the first curve there will be a point K' where the influence of the second equilibrium will become measurably large and a similar point K'' where the measurable influence of the first reaction will become

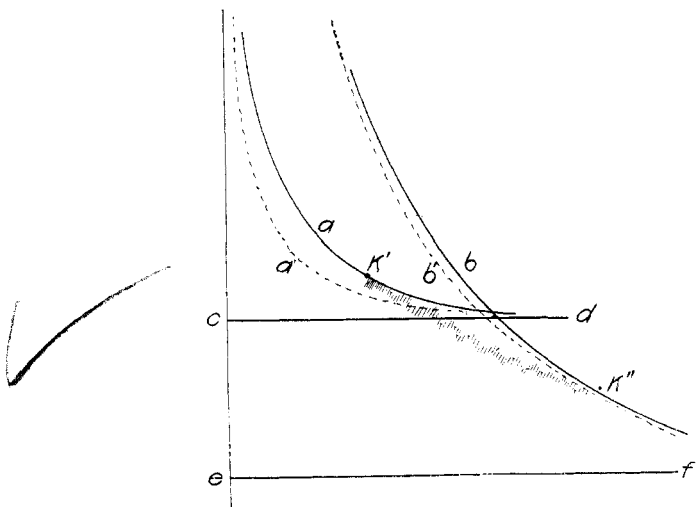


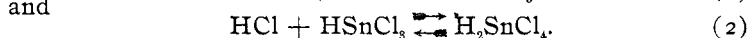
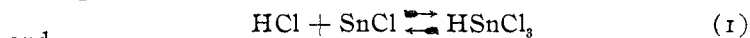
Fig. 4.

constant because one component (in the conditions of the above experiments the free stannous chloride) will have ceased to exist in the solution. Between K' and K'' will be a field where both condensation products (in this case assumed to be HSnCl_3 and H_2SnCl_4) will be measurably removed from complete dissociation and from complete association. In this field the condition will be a resultant of the two equilibria, dependent upon the values of the two equilibrium constants. The path of the curve between K' and K'' could be determined if these two constants were known. If we consider that the reduction of the conductivity of such solutions is even qualitatively a measure of the degree of association we get a very simple explanation of the above-mentioned peculiarities. Further, also, we get an explanation of the fact that the abnormal course of the curve is more marked at 0°C. than at 25°C. if we assume that the equilibrium which is

more sensitive to dilution is also more sensitive to temperature changes (*i. e.*, has a greater heat of reaction). In this case the association consequent upon reduction of temperature will be greater in the case of the first equilibrium than in the second and the curves (Fig. 4) will take on more of the form shown in the dotted lines and the buckle in the curve will be sharper.

It may be mentioned that the above considerations are in no way in disaccord with the general principles of equilibrium. No assumption is made that the two equilibria are independent of one another, but merely that at great dilutions, the influence of the one, and at small dilutions the influence of the other, becomes insignificant. It is by the same assumption that we neglect the influence of hydrolysis in moderately acid solutions of most salts.

In the above, the *assumption* is made, for sake of illustration, that the two equilibria in the solutions are represented by the two equations :



It may be stated that, so far as the work has gone at present, there is no particular evidence that this assumption is well founded. All the evidence that we really have as to the probable composition of these molecular complexes, comes from our knowledge of the molecular complexes that are known to exist in the solid state, such as Engel's (l. c.) $\text{SnCl}_2 \cdot \text{HCl} \cdot 3\text{H}_2\text{O}$, iodostannous acid, HSnI_3 , and the various double salts of tin, and we have really no ground for assuming that the complexes that exist in solution, stand in any fixed or simple relation to those that exist in the solid state. Only further investigation will be able to clear up these points.

THE INFLUENCE OF POTASSIUM CHLORIDE.

The following measurements were made with the view of gaining some idea as to the relative tendencies of potassium chloride and hydrochloric acid to form molecular complexes with stannous chloride. The difficulties of calculation of this influence from conductivity data are, as will be seen, very considerable.

In Table IVa are given measurements of the conductivities of solutions of stannous chloride in solvents which were always 0.5

normal in hydrochloric acid and of varying concentrations as to potassium chloride. In Table IV*b* are similar measurements for solvents of normal concentration in hydrochloric acid and variable potassium chloride. Table V contains a summary of values from these two tables for normality in stannous chloride.

TABLE IV*a*. INFLUENCE OF KCl.RESULTS WITH $\frac{1}{2}$ NORMAL HCl.

$\frac{1}{2}$ normal KCl.			$\frac{1}{2}$ normal KCl.		
$C \frac{\text{SnCl}_2}{2}$	$K \times 10^4$	$\frac{\Delta K \times 10^4}{C}$	$C \frac{\text{SnCl}_2}{2}$	$K \times 10^4$	$\frac{\Delta K \times 10^4}{C}$
0.000	1871	0.000	2152
0.0255	1868	-117	0.066	2146	-91
0.058	1866	-86	0.200	2144	-40
0.147	1874	+20	0.328	2142	-35
0.312	1878	+21	0.430	2141	-26
0.488	1879	+16	0.565	2138	-25
1.045	1898	+26	1.015	2132	-20

Normal KCl.			2 normal HCl.		
$C \frac{\text{SnCl}_2}{2}$	$K \times 10^4$	$\frac{\Delta K \times 10^4}{C}$	$C \frac{\text{SnCl}_2}{2}$	$K \times 10^4$	$\frac{\Delta K \times 10^4}{C}$
0.000	2498	0.000	3285
0.037	2493	-135	0.032	3275	-312
0.0535	2490	-149	0.057	3266	-333
0.1140	2478	-175	0.165	3251	-210
0.1265	2477	-167	0.296	3228	-190
0.2520	2473	-99	0.465	3200	-180
0.5050	2455	-79	0.770	3147	-178

TABLE IV*b*. INFLUENCE OF KCl.

RESULTS WITH NORMAL HCl.

$\frac{1}{2}$ normal KCl.			$\frac{1}{2}$ normal KCl.		
$C \frac{\text{SnCl}_2}{2}$	$K \times 10^4$	$\frac{\Delta K \times 10^4}{C}$	$C \frac{\text{SnCl}_2}{2}$	$K \times 10^4$	$\frac{\Delta K \times 10^4}{2}$
0.000	3324	0.000	3485
0.062	3311	-210	0.061	3473	-197
0.174	3295	-166	0.158	3459	-165
0.293	3283	-140	0.276	3442	-155
0.438	3265	-135	0.405	3420	-160
0.565	3247	-136	0.560	3398	-154
0.978	3199	-126	0.980	3339	-149

Normal KCl.			2 normal KCl.		
$C \frac{\text{SnCl}_2}{2}$	$K \times 10^4$	$\frac{\Delta K \times 10^4}{C}$	$C \frac{\text{SnCl}_2}{2}$	$K \times 10^4$	$\frac{\Delta K \times 10^4}{C}$
0.000	3758	0.000	4437
0.062	3741	-274	0.061	4419	-295
0.116	3731	-233	0.148	4398	-264
0.235	3714	-187	0.270	4368	-255
0.398	3684	-186	0.387	4336	-260
0.590	3649	-184	0.585	4292	-247
1.000	3571	-187	1.005	4193	-244

TABLE V. SUMMARY OF RESULTS WITH KCl FOR NORMAL SnCl_2 .

$\frac{1}{2}$ normal HCl.				
CkCl.	$K \times 10^4$, $\text{SnCl}_2 = 0.$	$K \times 10^4$, $\text{SnCl}_2 = N.$	$\frac{\Delta K \times 10^4}{C_N}$	Per cent.
0.25 N	1871	1898	+ 26	+1.39
0.50	2152	2132	- 20	-0.93
1.00	2498	2455	- 79	-3.16
2.00	3285	3147	-178	-5.42

Normal HCl.				
CkCl.	$K \times 10^4$, $\text{SnCl}_2 = 0.$	$K \times 10^4$, $\text{SnCl}_2 = N.$	$\frac{\Delta K \times 10^4}{C_N}$	Per cent.
0.25 N	3324	3199	-126	-3.82
0.50	3485	3339	-149	-4.33
1.00	3758	3571	-187	-4.98
2.00	4437	4193	-244	-5.50

An inspection of these results discloses a distinct tendency for the values of $\frac{\Delta K \times 10^4}{C}$ to decrease with C (the concentration of stannous chloride). This is also noticeable in the results for hydrochloric acid alone, although in a much less degree. So small is the variation in those results, that it might be considered within the experimental error. In the results with potassium chloride, the variations are more marked, and although the values of $\frac{\Delta K \times 10^4}{C}$ at small concentrations of stannous chloride are subject to great error, nevertheless, the perpetual recurrence of these variations in all sets of measurements, and in the same direction, would seem to indicate that they are not wholly experimental. Particularly noticeable is this variation in the case of 0.5 normal hydrochloric acid, and 0.25 normal potassium chloride, where at small concentrations of stannous chloride, a reduction of the con-

ductivity, at larger concentrations an increase in conductivity, occurs. Since the variable factors in such solutions are so numerous, one might formulate a half dozen explanations of these peculiarities, which would be a process of very little value. However, it is to be expected from the general ideas of equilibrium that the reduction of conductivity *per unit of concentration* of stannous chloride would be a quantity which would decrease with increasing concentration.

When we come to compare the values of $\frac{\Delta K \times 10^4}{C (=N)}$ for these

solutions (Table 5) in $\frac{1}{\Omega}$'s and in percentages, with those for hydrochloric acid alone (Table IIIa), we find difficulty in deciding upon a basis for this comparison.

Probably as satisfactory a method as any will be to compare the percentage effects of addition of stannous chloride to solvent containing the same concentration of chlorine. Thus the percentage change on adding stannous chloride to normality to a solution of 0.75 normal hydrochloric acid is - 2.81 per cent., and to a 0.25 normal KCl. 0.5 normal HCl the change is +1.39; for a normal hydrochloric acid, - 3.64 per cent.; for a 0.5 normal KCl. 0.5 normal HCl, - 0.93 per cent.; for a 1.5 normal hydrochloric acid, - 4.41 per cent.; for a normal KCl. 0.5 HCl, - 3.16 per cent.; for 2.5 HCl, - 4.40 per cent.; 2 normal KCl. 0.5 normal HCl, - 5.42 per cent. With the results for normal hydrochloric acid and potassium chloride we find: for 1.25 normal HCl, - 4.20 per cent.; for normal HCl.0.25 KCl, - 3.82 per cent.; for 1.5 normal HCl, - 4.41 per cent.; for normal HCl. 0.5 KCl, - 4.33 per cent.; for 2 normal HCl, - 4.50 per cent.; for normal HCl. normal KCl, - 4.98 per cent.; for 3 normal HCl, - 4.35 per cent.; for normal HCl.2 normal KCl, - 5.5 per cent.

By this method of comparison, it would seem that, at small concentrations, the influence of potassium chloride was less than that of hydrochloric acid, but that it increases more rapidly with the concentration and exceeds that of hydrochloric acid at greater concentrations. In this connection, it is to be said, however, that this method of calculation is sure to give results favoring the greater influence of hydrochloric acid, particularly at small concentrations of potassium chloride, since under these

circumstances the larger part of the conductivity is due to hydrochloric acid, and although the influence of the small quantity of potassium chloride might be relatively large, it would still show as but a small percentage of the whole conductivity. I have also calculated the influence of potassium chloride by one or two other methods which may be considered as rough approximations, and have invariably found that at least at high concentrations potassium chloride seems to act more strongly in producing molecular complexes than does hydrochloric acid. The whole point might be easily settled, if we could prepare isohydric solutions of stannous chloride, hydrochloric acid, and potassium chloride. The trouble is however that, apart from the interference of hydrolysis in stannous chloride solutions, we have at present no means of telling what solution of stannous chloride would contain chlorine ions at the same concentration as a given solution of hydrochloric acid. This might be determined by measurements of electromotive force, but I have not as yet been able to devise a method for this purpose that works satisfactorily with stannous chloride. Silver and silver chloride electrodes will not work, because, although silver chloride is not noticeably reduced by stannous chloride, nevertheless the reduction potential between them is easily measurable and prevents the use of such an electrode for the determination of the concentration of chlorine ions.

The above data on the influence of potassium may now be applied without very serious objection to the determination of the relative influence of other salts of about the same equivalent conductivity and degree of dissociation, as for example sodium chloride, bromide, or iodide, and potassium bromide or iodide. A few measurements were made to determine the influence of potassium iodide. The results are as follows:

Normal potassium iodide + 0.5 normal hydrochloric acid gave without stannous chloride a conductivity of 2633.

On addition of stannous chloride to 0.09 normal the conductivity fell to 2594, which gives $\frac{\Delta K \times 10^4}{C} = -433$. Potassium chloride under the same circumstances gave $\frac{\Delta K \times 10^4}{C} = -175$.

A further addition of stannous chloride to the above solution caused separation of red stannous iodide in solid form.

A second set of measurements carried out with 0.5 normal KI + 4 normal HCl gave :

$C \frac{\text{SnCl}_2}{2}$	$K \times 10^4$	$\frac{\Delta K \times 10^4}{C}$
0.000	7918
0.119	7866	-433
0.304	7785	-435
0.950	7515	-424

These values are considerably greater than for hydrochloric acid alone of 4.28 normal concentration; *viz.*, - 330 to - 350, and they are noticeably greater than the values for even hydrochloric acid of 7.7 normal; *viz.*, - 402. It is hoped soon to investigate this field more thoroughly.

From the results of the foregoing measurements we may consider the following conclusions as probable :

(1) Stannous chloride and hydrochloric acid form molecular complexes in solution, the formation of such complexes increasing with the concentration.

(2) In so far as reduction of electrical conductivity may be taken as a measure of such association, evidence is shown of the existence of two distinct forms of association, one being considerably more sensitive to dilution than the other; *i. e.*, having a larger dissociation constant.

(3) Potassium chloride shows a greater power of association at large concentrations than does hydrochloric acid, and it is quite probable that the same will be found to be true at lower concentrations also.

(4) From what evidence is at hand, potassium iodide shows a still greater influence in the direction of forming complex substances in solutions of stannous chloride. This is in keeping with the well-known behavior of iodides in forming double salts.

It has been my pleasure to have carried out the above investigation in the laboratory of the Physical-Chemical Institute, at Leipzig. I wish to take this opportunity to thank the director of the institute, Prof. Ostwald, and the assistants in the institute, especially Drs. Bredig and Luther, for the kindly consideration and timely suggestions which they gave me during my all too brief stay at Leipzig.