THE RATE OF OXIDATION OF STANNOUS SALT BY OXYGEN AND THE ELECTRICAL CONDUCTIVITY OF MIXTURES OF SULPHURIC ACID AND STANNOUS SULPHATE.

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Introduction.

The effect of the positive and negative catalytic actions of a number of substances on the rate of oxidation of stannous chloride solution had been studied by S. W. Young.(1) The rate of oxidation of the same substances by passing air-bubbles was also studied by the present writer a few

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(1) *J. Am. Chem. Soc.*, **23** (1901), 119 and 450.

years ago, and the effect of substances such as sodium hydroxide, sodium carbonate, hydrochloric acid and sulphuric acid on the rate of oxidation of stannous salt was observed.

The experimental procedure was as follows.

Air, washed by acidified potassium bichromate solution and sodium hydroxide solution, was passed into the reacting solution, contained in a large test-tube (diameter = 3 cm.), through a glass tube of definite diameter at a constant velocity. After t-minutes the air current was stopped and the total amount of the solution was poured into a known quantity of iodine solution, acidified with hydrochloric acid, and the excess of iodine was titrated back with sodium thiosulphate solution of known concentration. The measurements were carried out in an ordinary water-thermostat. The amount of reacting solution was made up to 40 c.c. in each case, and the exit tube was kept at a fixed depth below the surface of the reacting solution.

(1) **The Effect of Sodium Hydroxide.**(1) As will be seen in Fig. 1, the relation between the rate of oxidation of stannous hydroxide and the concentration of sodium hydroxide solution can be shown graphically by a two-stage curve.

The rate of oxidation of stannous hydroxide increases rapidly with the increase of concentration of sodium hydroxide as far as it attains a maximum value, when the concentration of sodium hydroxide is about 0.18 normal. Further increases of the concentration of sodium hydroxide cause a gradual decrease on the rate of oxidation of stannous hydroxide.

(2) **The Effect of Sodium Carbonate.**(2) Contrary to expectation, stannous hydroxide oxidizes at an extremely slow rate in sodium carbonate solution, and the increase of concentration of sodium carbonate has nearly no effect upon the rate of oxidation of stannous hydroxide, as will be seen in Fig. 1.

(3) **The Effect of Hydrochloric Acid.**(3) The effect of hydrochloric acid on the rate of oxidation of stannous chloride was found to be analogous to that of sodium hydroxide on the rate of oxidation of stannous hydroxide. The effect again can be illustrated by a two-stage curve. The rate of oxidation of stannous chloride increases rapidly with the increase of the concentration of hydrochloric acid, as far as the concentration of the latter reaches about 0.25 normal. In the more concentrated solution of hydrochloric acid

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(1) Miyamoto, this Bulletin, **2** (1927), 155.

(2) Ibid., **3** (1928), 43.

(3) Ibid., **2** (1927), 259.

the rate of oxidation of stannous chloride is independent of its concentration, and the increase of concentration of hydrochloric acid has but little effect upon the rate of oxidation.

(4) **The Effect of Sulphuric Acid.**⑴ The influence of sulphuric acid is quite anologous to that of hydrochlorid acid, as will be seen in Fig. 1. The rate of oxidation increases with the increase of the concentration of sulphuric acid as far as the concentration of the latter attains the value of about 0.8 normal. Further increases of the concentration of sulphuric acid have only a slight effect upon the rate of oxidation of stannous salt.

The observed values of the rate of oxidation of stannous salt solution by air in the presence of the above mentioned acid or alkali were already published in the previous papers.⑵ The representative values are summarized in Table 1, in which $\frac{\Delta v}{\Delta t}$ means the volume of sodium thiosulphate solution of 0.0996 normal, equivalent to the quantity of stannous salt oxidized per minute under the conditions described in the previous paper.⑵

Table 1.

Temp. = 20°C. Velocity of air passed = 7.78 liters per hour.

C_{NaOH} normal.	$\frac{\Delta v}{\Delta t}$ c.c./min.	$C_{Na_2CO_3}$ normal.	$\frac{\Delta v}{\Delta t}$ c.c./min.	C_{HCl} normal.	$\frac{\Delta v}{\Delta t}$ c.c./min.	$C_{H_2SO_4}$ normal.	$\frac{\Delta v}{\Delta t}$ c.c./min.
0.00595	0.0224	0.0155	0.00600	0.00647	0.0170	0.01410	0.0304
0.02170	0.0531	0.1655	0.00766	0.09672	0.0227	0.2959	0.0389
0.04057	0.0893	0.4655	0.00689	0.1682	0.0657	0.7185	0.0710
0.1081	0.230	0.8405	0.00660	0.3235	0.106	0.8370	0.115
0.1706	0.257	1.216	0.00585	0.4587	0.118	0.9720	0.121
0.2204	0.259			0.8151	0.118	1.377	0.117
0.3252	0.246			1.360	0.115	1.396	0.127
0.5500	0.215			1.811	0.132	1.423	0.123
1.130	0.168			2.262	0.139	2.052	0.109
1.704	0.126					2.558	0.107
2.312	0.0998					2.727	0.105
						2.832	0.108

The above mentioned substances, with the exception of sodium carbonate, have thus similar influence upon the rate of oxidation of stannous

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⑴ Miyamoto, this Bulletin, **4** (1929), 48.

⑵ Loc. cit.

salt. The effect of each of them is illustrated by a two-stage curve in Fig. 1. At low concentrations of the alkali or the acid, the rate of oxidation of stannous salt increases rapidly as the concentration of the alkali or the acid increases.

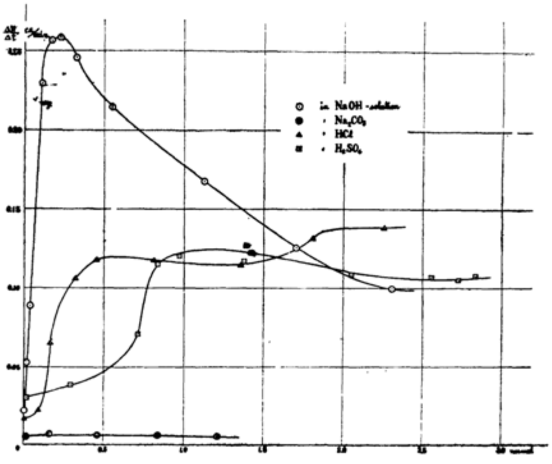

Fig. 1.

At high concentrations of the alkali or the acid, the rate of oxidation of stannous salt is not much influenced by the increase of concentration of these substances, and it was also confirmed, that in this region the rate of oxidation is independent of the concentration of stannous salt. The present writer explained the phenomenon by the assumption⁽¹⁾ that the rate of oxidation, observed in this region, is not the characteristic value of stannous salt, but is equivalent to the rate of solution of oxygen into alkaline or acidic solution, free from oxygen. This assumption is very probable as was discussed in the previous papers,⁽²⁾ and it will be of no use to repeat the discussion of the assumption, proposed to interpret the mechanism of this part.

This paper is intended to interpret why the rate of oxidation of stannous salt solution by oxygen increases with the increase of concentration of sodium hydroxide, hydrochloric acid or sulphuric acid in the initial stage. The following assumptions are proposed by the present writer to interpret the phenomenon.

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(1) Miyamoto, this Bulletin, **3** (1928), 98.

(2) Loc. cit.

Stannous ion is oxidized by oxygen at an extremely slow rate, and the formation of some complex ion, containing the tin atom, causes the rapid increase in the rate of oxidation of stannous salt. This assumption will be very probable as will be discussed in the following. It is a well known fact that stannous hydroxide, precipitated from stannous salt solution by the addition of sodium hydroxide, dissolves in the excess of sodium hydroxide, forming a complex compound, sodium stannite. If we apply the assumption, above described, in this case, stannous hydroxide is oxidized at an extremely slow rate, while sodium stannite, the concentration of which increases with the increase of concentration of sodium hydroxide, is oxidized rapidly.

Then the experimental fact is clearly interpreted as follows. The rate of oxidation of stannous hydroxide increases with the increase of concentration of sodium hydroxide, as a result of the formation of stannite, as far as it attains the maximum rate of solution of oxygen into sodium hydroxide solution. The decrease of the rate of oxidation of stannous hydroxide with the further increase of concentration of sodium hydroxide at the second stage takes place from quite a different cause. It is due to the decrease of the maximum rate of solution of oxygen into sodium hydroxide solution with the increase of concentration of sodium hydroxide, according to the opinion of the present writer.

The experimental fact, that stannous hydroxide is oxidized at a very slow rate in sodium carbonate solution, in which a minute quantity of stannite is formed, is another fact favourable for the present theory. It was experimentally confirmed,(1) that oxygen dissolves into sodium carbonate solution at nearly the same rate as into sodium hydroxide solution, and it can be described that the slow rate of oxidation of stannous hydroxide in sodium carbonate solution has no relation to the rate of solution of oxygen into the solution.

The above described assumption can quite similarly be applied for the interpretation of the effect of hydrochloric acid. By the measurement of electrical conductivity of the mixture of stannous chloride and hydrochloric acid solution, S. W. Young(2) confirmed that at least two complex compounds, such as hydrotrichlorostannous acid $HSnCl_3$ and hydrotetrachlorostannous acid H_2SnCl_4 are formed in the hydrochloric acid solution of stannous chloride.

Then the influence of the increase of concentration of hydrochloric acid on the rate of oxidation of stannous chloride can be interpreted in the same

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(1) Miyamoto, this Bulletin, **3** (1928), 76.

(2) *J. Am. Chem. Soc.*, **23** (1901), 21.

manner as in the previous case by the assumptions that stannous chloride itself oxidized at an extremely slow rate, and that the formation of complex acids, whose concentrations increase with the increase of concentration of hydrochloric acid, is the cause of the increase of the rate of oxidation of stannous chloride.

From the result of the study of the effect of sulphuric acid on the rate of oxidation of stannous salt solution, it can be expected that some complex compound will be formed in the mixture of stannous sulphate and sulphuric acid solution, if the assumption, above described, be acceptable. In other words, the effect of sulphuric acid on the rate of oxidation of stannous salt can be interpreted in the same way as in the previous cases, if the formation of some complex compound in sulphuric acid solution of stannous salt be experimentally confirmed.

The measurement of electrical conductivity of the solution will be one of the suitable methods to ascertain whether the combination of stannous sulphate and sulphuric acid takes place in the solution, and the following experiment was carried out for this purpose.

Experimental.

Sulphuric acid, Kahlbaum for analysis, was employed. Stannous sulphate was prepared by the method of C. M. Carson⁽¹⁾ from copper sulphate, Kahlbaum for analysis, tin, Kahlbahm for analysis, and sulphuric acid. The white crystals of pure stannous sulphate were easily obtained by this method in the laboratory.

The conductivity cell of a suitable type for the present purpose, shown graphically in Fig. 2, was manufactured in the laboratory with hard glass. Its cell constant is about 30. The experimental procedure was the ordinary Wheatstone bridge method, slide wire bridge of 2000 division and precision decade resistance box, manufactured and examined by Ando Co., being employed. The cell constant of the conductivity vessel was determined by measuring the conductance of potassium chloride solution as usual. It is not necessary to use conductivity water of a high degree of purity for the present purpose. Distilled water from tin vessel, freed from carbon dioxide by drawing a current of air, free from carbon dioxide, through the water, was employed. The measurements were carried out in an electrically heated and controlled water thermostat, whose temperature was kept constant within fluctuations of less than 0.03°C.

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(1) *J. Am. Chem. Soc.*, **48** (1926), 906.

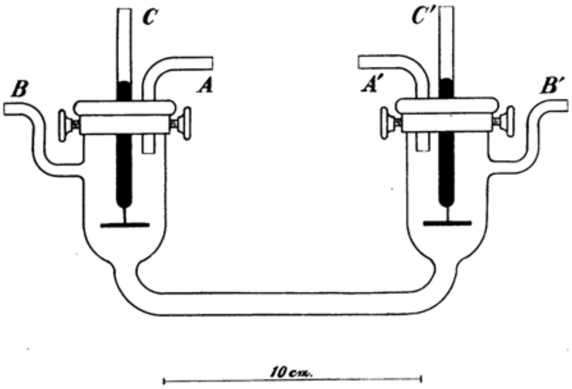

Fig. 2.

As stannous sulphate in sulphuric acid solution is oxidized by air, the preparation of the solution and the measurement of conductivity were carried out in the atmosphere of nitrogen as follows. The measured quantity of stannous sulphate crystals was placed in an Erlenmeyer flask, and when the air in the flask had been replaced by nitrogen, a definite quantity of sulphuric acid solution of known concentration was poured into the flask. The air in the conductivity cell was also entirely replaced by nitrogen, before the solution was poured into the cell, and during the observation, nitrogen gas was passed continuously in the cell through A and A′ (Fig. 2) to prevent the oxidation of stannous sulphate. The specific conductance of pure sulphuric acid solution was also observed, although it is given in Landolt-Börnstein Tabellen.

The results, observed at 18°C. and at 25°C., are given in Tables 2 and 3 respectively. They are shown graphically in Fig. 3. In the Tables, K means the specific conductance of the mixture, ΔK the difference of specific conductance of the mixture and that of pure sulphuric acid solution.

Discussion.

As was expected, the influence of stannous sulphate on the specific conductance of sulphuric acid solution was confirmed to be similar to that of stannous chloride on the specific conductance of hydrochloric acid solution, which had been studied by S. W. Young.(1) When the concentration of sulphuric acid is less than about 0.6 normal, the specific conductance

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(1) Loc. cit.

Table 2.

Temp. = 18°C.

$C_{H_2SO_4}$ normal.	C_{SnSO_4} normal.	K	ΔK	$\frac{\Delta K}{C_{SnSO_4}}$
0.2596	0	0.05564	0	0
	0.2000	0.05690	+0.00126	+0.00630
	0.4000	0.05874	+0.00310	+0.00775
	0.6000	0.06099	+0.00535	+0.00892
	1.000	0.06631	+0.01067	+0.01067
0.5330	0	0.1091	0	0
	0.4012	0.1098	+0.0007	+0.0017
	0.6007	0.1107	+0.0016	+0.0027
	1.001	0.1130	+0.0039	+0.0039
1.066	0	0.2093	0	0
	0.1998	0.2073	−0.0020	−0.0100
	0.4001	0.2055	−0.0038	−0.0095
	0.6000	0.2039	−0.0054	−0.0090
	0.9998	0.2000	−0.0093	−0.0093
1.853	0	0.3423	0	0
	0.4012	0.3304	−0.0119	−0.0297
	0.6000	0.3266	−0.0157	−0.0262
	1.004	0.3166	−0.0257	−0.0256
3.044	0	0.5056	0	0
	0.4000	0.4860	−0.0196	−0.0490
	0.6002	0.4737	−0.0319	−0.0532
	1.000	0.4573	−0.0483	−0.0483
3.706	0	0.5762	0	0
	0.1998	0.5636	−0.0126	−0.0630
	0.4000	0.5507	−0.0255	−0.0638
	0.5999	0.5388	−0.0374	−0.0623
	1.000	0.5155	−0.0607	−0.0607
6.088	0	0.7198	0	0
	0.1999	0.7009	−0.0189	−0.0945
	0.3004	0.6913	−0.0285	−0.0950
	0.4000	0.6823	−0.0375	−0.0938

Table 3.

Temp. = 25°C.

$C_{H_2SO_4}$ normal.	C_{SnSO_4} normal.	K	ΔK	$\frac{\Delta K}{C_{SnSO_4}}$
0.2591	0	0.05977	0	0
	0.1999	0.06141	+0.00164	+0.0082
	0.4001	0.06329	+0.00352	+0.0088
	0.6000	0.06605	+0.00628	+0.0105
	0.8000	0.06898	+0.00921	+0.0115
	1.000	0.07208	+0.01231	+0.0123
	1.200	0.07533	+0.01556	+0.0130
0.5320	0	0.1180	0	0
	0.3999	0.1187	+0.0007	+0.0018
	0.6000	0.1196	+0.0016	+0.0027
1.064	0	0.2266	0	0
	0.2000	0.2242	−0.0024	−0.0120
	0.3999	0.2224	−0.0042	−0.0105
	0.6001	0.2207	−0.0059	−0.0098
	1.000	0.2180	−0.0086	−0.0086
	1.400	0.2156	−0.0110	−0.0079
1.850	0	0.3718	0	0
	0.4000	0.3604	−0.0114	−0.0285
	0.6000	0.3552	−0.0166	−0.0277
2.431	0	0.4656	0	0
	0.2000	0.4581	−0.0075	−0.0375
	0.4000	0.4501	−0.0155	−0.0388
	0.6002	0.4420	−0.0236	−0.0393
	1.000	0.4271	−0.0385	−0.0385
3.034	0	0.5535	0	0
	0.4000	0.5323	−0.0212	−0.0530
	0.6001	0.5216	−0.0319	−0.0532
3.701	0	0.6319	0	0
	0.2000	0.6185	−0.0134	−0.0670
	0.4000	0.6055	−0.0264	−0.0660
	0.6000	0.5928	−0.0391	−0.0652
	1.000	0.5683	−0.0636	−0.0636
6.068	0	0.7983	0	0
	0.2000	0.7783	−0.0200	−0.1000
	0.2999	0.7685	−0.0298	−0.0993
	0.4000	0.7587	−0.0396	−0.0990

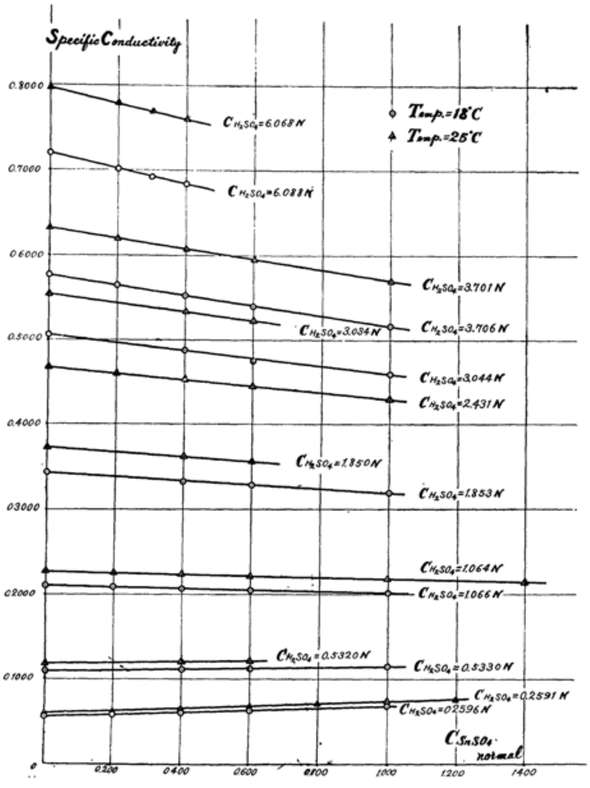

Fig. 3.

of the mixture increases gradually with the increase of concentration of stannous sulphate. The addition of stannous sulphate into sulphuric acid solution of proper concentration (approximately 0.7 normal) will have no effect on the specific conductance of the solution. When the concentration of sulphuric acid is greater than about 1 normal, the specific conductance of the mixture decreases with the increase of concentration of stannous sulphate. The decrease of the specific conductance of the solution, caused by the addition of stannous sulphate is considerably great, and it will be unable to be interpreted as the effect of commen ion. The formation of some complex compound will be evident.

The relation between the percentage influence, $\left(\frac{\Delta K}{C_{\mathrm{SnSO_4}}}\right) \div \left(K_{C_{\mathrm{SnSO_4}}=0}\right)$, and the concentration of sulphuric acid, can be calculated from the results, given in Tables 2 and 3. The calculated values, when the concentration of stannous sulphate is about 0.4 normal, are shown in Table 4, and graphically in Fig. 4. As will be seen in the figure, the curve does not show a

Table 4.

Temp.	$C_{\mathrm{H_2SO_4}}$	K $C_{\mathrm{SnSO_4}=0}$	K $C_{\mathrm{SnSO_4}} \doteqdot 0.4000$	$\dfrac{\Delta K}{C_{\mathrm{SnSO_4}}}$	$\left(\dfrac{\Delta K}{C_{\mathrm{SnSO_4}}}\right) \div \left(\dfrac{K}{C_{\mathrm{SnSO_4}=0}}\right)$
18°C.	0.2596	0.05564	0.05874	+0.00775	+0.139
	0.5330	0.1091	0.1098	+0.0017	+0.0156
	1.066	0.2093	0.2055	−0.0095	−0.0454
	1.853	0.3423	0.3304	−0.0297	−0.0868
	3.044	0.5056	0.4860	−0.0490	−0.0969
	3.706	0.5762	0.5507	−0.0638	−0.1107
	6.088	0.7198	0.6823	−0.0938	−0.130
25°C.	0.2591	0.05977	0.06329	+0.0088	+0.147
	0.5320	0.1180	0.1187	+0.0018	+0.0153
	1.064	0.2266	0.2224	−0.0105	−0.0463
	1.850	0.3718	0.3604	−0.0285	−0.0767
	2.431	0.4656	0.4501	−0.0388	−0.0833
	3.034	0.5535	0.5323	−0.0530	−0.0958
	3.701	0.6319	0.6055	−0.0660	−0.1044
	6.068	0.7983	0.7587	−0.0990	−0.1240

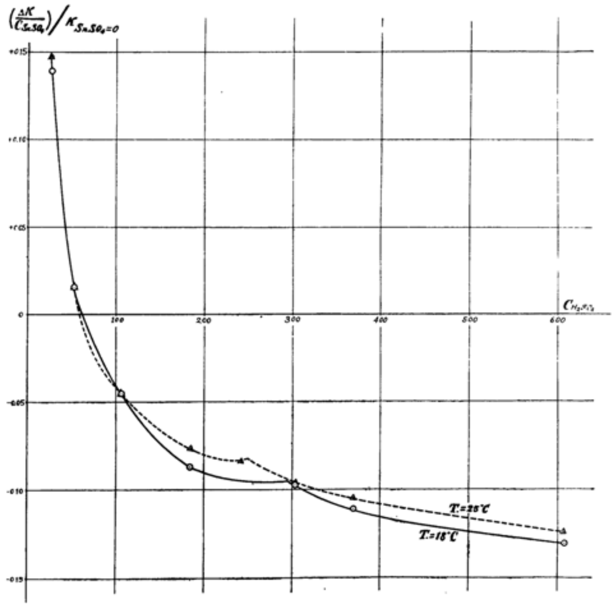

Fig. 4.

maximum or a minimum, but it has a turning point at about 3 normal when the temperature is 18°C., and at about 2.5 normal when the temperature is 25°C. In other words, the graph which represents the relation between the percentage influence and the concentration of sulphuric acid solution is composed of two curves.

For the interpretation of the result, it will be necessary to assume the formation of two kinds of molecular complexes, quite the same way as in the case of stannous chloride solution containing excess of hydrochloric acid.(1) It is highly probable that compounds are formed in the solution, with molecular complexes of the type shown in the following reactions.

$$2\,SnSO_4+H_2SO_4 = H_2Sn_2(SO_4)_3, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$H_2Sn_2(SO_4)_3+H_2SO_4 = 2H_2Sn(SO_4)_2 \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

The potassium salts of these complex acids, $K_2\,Sn_2(SO_4)_3$ and $K_2\,Sn(SO_4)_2$, had heen found by Marignac.(2) The assumption, that at low concentrations of sulphuric acid solution the equilibrium of the first reaction (1) predominates, and at high concentrations the equilibrium of the second reaction (2) becomes noticeable, will be sufficient to interpret the observed phenomenon clearly.

Thus the assumption that the rate of oxidation of stannous salt itself by oxygen is extremely small, and the formation of some molecular complexes causes the increase of the rate of oxidation of stannous salt solution will be applied for the interpretation of the rate of oxidation of stannous salt containing sulphuric acid also. This assumption will generally be applied for the interpretation of the rate of oxidation of stannous salt in the presence of a large quantity of other substances.

When the solvent is not water, the mechanism of the oxidation will be different, and the assumption, above described, will not be satisfied. For example, it was confirmed in the laboratory of the present writer by a preliminary experiment, that the alcoholic solution of anhydrous stannous chloride is oxidized by oxygen at a considerably rapid rate.

The assumption, which attributes the increase of the rate of oxidation of stannous salt solution with the increase of concentrations of acid or alkali to the catalytic action of the acid or the alkali, will not be justifiable. Stannous salt is oxidized rapidly in sodium hydroxide solution, while it is oxidized at an extremely slow rate in sodium carbonate solution, in which Na- and OH- ions are also present.

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(1) Loc. cit.

(2) Mellor: Treatise on Inorganic and Theoretical Chemistry, Vol. VII, p. 478.

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Summary.

(1) The effects of sodium hydroxide, sodium carbonate, hydrochloric acid and sulphuric acid on the rate of oxidation of stannous salt solution by air were described.

(2) The specific conductance of sulphuric acid solution containing stannous sulphate was observed. When the concentration of sulphuric acid is less than about 0.6 normal, specific conductance of the mixture increases with the increase of concentration of stannous sulphate and when the concentration of sulphuric acid is greater than about 1 normal, the specific conductance of the mixture decreases with the increase of concentration of stannous sulphate. The assumption, that two kinds of molecular complexes are formed in the solution, was proposed for the interpretation of the result, and as the most probable molecular complexes, $H_2Sn_2(SO_4)_3$ and $H_2Sn(SO_4)_2$ were mentioned.

(3) The assumptions, that the rate of oxidation of stannous salt itself by oxygen is extremely small, and that the rate of oxidation increases as a result of the formation of some complex compounds in the solution, were proposed. The assumptions were applied for the interpretation of the effect of sodium hydroxide, sodium carbonate, hydrochloric acid and sulphuric acid on the rate of oxidation of stannous salt solution by air.

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