ON THE OXIDATION OF STANNOUS CHLORIDE IN SULPHURIC ACID SOLUTION BY AIR AND THE DISSOLUTION VELOCITY OF OXYGEN INTO SULPHURIC ACID SOLUTION.

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Introduction. The dissolution velocity of oxygen into sodium hydroxide, sodium carbonate and hydrochloric acid solutions of various concentrations when air is passed into the solution under certain conditions was obtained indirectly from the oxidation velocity of sodium sulphite, stannous chloride or ferrous hydroxide in the mentioned solutions.(1)

The present research was undertaken with an expectation that the oxidation velocity of stannous chloride in sulphuric acid solution will also give the dissolution velocity of oxygen into the solution under the same conditions.

Experimental. The experimental procedure was quite the same with that employed in the study of the oxidation of the same substance in hydrochloric acid solution by means of air.(2)

Air, washed by passing through acidic solution of potassium bichromate and sodium hydroxide solution, was passed into the reacting solution, contained in a large test tube (diameter $\fallingdotseq$ 3 cm.) through a glass tube (inside diameter $\fallingdotseq$ 4 mm., outside diameter $\fallingdotseq$ 6 mm.), at the rate of 7.78 litres per hour, the total volume of the reacting solution in the vessel being made to 40 c.c. in each measurement. After t-minutes the air current was stopped, and the total quantity of the substances contained in the vessel was poured into a known quantity of iodine solution, and the excess of iodine was titrated back by means of sodium thiosulphate solution. The value of v, given in the following tables, is the volume of sodium thiosulphate solution of 0.09962 normal, which is equivalent to the total quantity of stannous sulphate, remained after the t-minutes passage of air.

As will be shown later, the oxidation velocity was independent of the concentration of stannous sulphate, when the concentration of sulphuric acid is greater than about 0.8 normal under the conditions of the present experiment.

The observed results at 20°C. are given in Table 1, and illustrated in

(1) S. Miyamoto, this Bulletin, **3** (1928), 100 & 139; *Scientific Papers of the Institute of Physical and Chemical Research*, **8** (1928), 243; **9** (1928), 203.

(2) S. Miyamoto, this Bulletin, **2** (1927), 259; *Scientific Papers of the Institute of Physical and Chemical Research*, **8** (1928), 93.

the accompanying figure. The velocity constant k, given in the last column of the table, was calculated by an equation, $k=\frac{1}{t}(v_0-v)$, v_0 being the value of v at $t=0$. The calculated value of v by an equation, $v_{calc.}=v_0-kt$, using the mean value of k, is given in the fourth column of the table.

Table 1.

Temp.=20°C. Velocity of Air=7.78 litres per hour.

$C_{H_2SO_4}$ normal	t min.	v c. c.	$v_{calc.}$ c. c.	k
0.837	0	28.27	—	—
	20	25.96	25.97	0.116
	40	23.80	23.67	0.112
	60	21.36	21.37	0.115
	0	22.64	—	—
	20	20.06	20.34	0.129
	40	18.17	18.04	0.112
	60	16.32	15.74	0.105
	0	21.37	—	—
	20	18.99	19.07	0.119
	40	17.07	16.77	0.108
				Mean: 0.115
0.3900	0	20.11	—	—
	20	17.48	17.57	0.132
	40	14.98	15.03	0.128
	60	12.64	12.43	0.125
	0	13.94	—	—
	20	11.46	11.40	0.124
	40	8.81	8.86	0.128
				Mean: 0.127
0.9720	0	24.39	—	—
	20	21.85	21.97	0.127
	40	19.49	19.55	0.123
	60	17.37	17.13	0.117
	0	19.71	—	—
	20	17.33	17.29	0.119
	40	14.51	14.87	0.130
	60	12.98	12.45	0.112
				Mean: 0.121

Table 1. (*Continued.*)

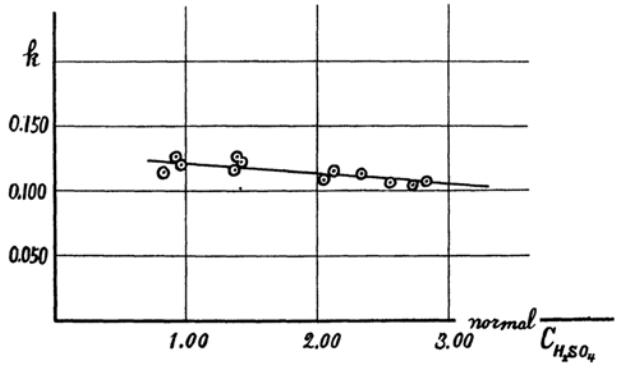
$C_{H_2SO_4}$ normal.	t min.	v c. c.	$v_{calc.}$ c.c.	k
1.377	0	18.53	—	—
	20	16.10	16.19	0.122
	40	13.91	13.85	0.116
	60	11.48	11.51	0.118
	0	16.94	—	—
	20	14.61	14.60	0.117
	40	12.18	12.26	0.119
	60	10.36	9.92	0.110
				Mean: 0.117
1.396	0	17.70	—	—
	20	15.08	15.16	0.131
	40	12.68	12.62	0.126
	60	10.06	10.08	0.127
	0	14.86	—	—
	20	12.29	12.32	0.129
	40	10.08	9.78	0.120
	60	7.12	7.24	0.129
				Mean: 0.127
1.423	0	16.56	—	—
	20	14.30	14.10	0.113
	40	11.57	11.64	0.125
	60	9.17	9.18	0.123
	0	24.32	—	—
	20	21.89	21.86	0.122
	40	19.44	19.40	0.122
	60	16.54	16.94	0.130
				Mean: 0.123
2.052	0	21.41	—	—
	20	19.18	19.23	0.112
	40	17.20	17.05	0.105
	60	14.80	14.87	0.110
	0	14.34	—	—
	20	12.13	12.16	0.111
	40	9.96	9.98	0.110
	60	8.09	7.80	0.104
				Mean: 0.109

Table 1. (*Continued.*)

$C_{H_2SO_4}$ normal	t min.	v c.c.	$v_{calc.}$ c.c.	k
2.127	0	20.23	—	—
	20	18.11	17.91	0.106
	40	15.76	15.59	0.112
	60	13.29	13.27	0.116
	0	24.36	—	—
	20	21.88	22.04	0.124
	40	19.54	19.72	0.121
	60	17.34	17.40	0.117
				Mean: 0.116
2.335	0	21.40	—	—
	20	19.25	19.12	0.108
	40	16.84	16.84	0.114
	60	14.82	14.56	0.110
	0	12.99	—	—
	20	10.67	10.71	0.116
	40	8.22	8.43	0.119
	60	5.96	6.15	0.117
				Mean: 0.114
2.558	0	20.50	—	—
	20	18.45	18.36	0.103
	40	16.20	16.22	0.108
	60	13.99	14.08	0.109
	0	19.77	—	—
	20	17.67	17.63	0.105
	40	15.38	15.49	0.110
	60	13.53	13.35	0.104
				Mean: 0.107
2.727	0	19.66	—	—
	20	17.52	17.56	0.107
	40	15.36	15.46	0.108
	60	13.45	13.36	0.104
	0	18.04	—	—
	20	15.98	15.94	0.103
	40	13.93	13.84	0.103
				Mean: 0.105

Table 1. (*Continued.*)

$C_{H_2SO_4}$ normal	t min.	v c.c.	$v_{calc.}$ c.c.	k
2.832	0	18.15	—	—
	20	15.93	15.99	0.111
	40	13.91	13.83	0.106
	60	11.38	11.67	0.113
	0	24.66	—	—
	20	22.58	22.50	0.104
	40	20.50	20.34	0.104
	60	18.17	18.18	0.108
				Mean: 0.108



When the concentration of sulphuric acid is less than about 0.8 normal, the oxidation velocity of stannous sulphate depends upon its initial concentration and decreases as the concentration of sulphuric acid decreases.

The experimental error was great, and no sufficient experimental results, a part of which being given in Table 2, for the quantitative discussion was obtained, but it can only qualitatively be described that the oxidation velocity increases slowly with the increase of the concentration of sulphuric acid until it reaches the dissolution velocity of oxygen when the concentration of the latter is about 0.8 normal. In the case of the oxidation of stannous chloride in hydrochloric acid solution, the oxidation velocity increases more rapidly with the increase of the concentration of hydrochloric acid and attains the dissolution velocity of oxygen into the solution when the concentration of hydrochloric acid is about 0.2 normal.[1]

(1) Loc. cit.

Table 2.

Temp.=20°C. Velocity of Air=7.78 litres per hour.

$C_{H_2SO_4}$ normal	t min.	v c.c.	v_0-v c.c.
0.01410	0	14.12	—
	10	13.79	0.33
	50	12.54	1.58
	120	10.47	3.65
0.2959	0	13.69	—
	10	13.47	0.22
	50	11.94	1.75
	120	9.02	4.67
0.7185	0	13.85	—
	10	12.91	0.94
	50	10.46	3.39
	0	15.66	—
	10	14.41	1.25
	50	12.11	3.55

The effect of the concentration of sulphuric acid. The relation between the velocity constant k and the concentration of sulphuric acid can be expressed approximately as a linear function, when the concentration of sulphuric acid is greater than about 0.8 normal. The calculated values of k by an equation,

$$k=0.128-0.00718C_{H_2SO_4}$$

are given as $k_{calc.}$ in the third column of Table 3.

The effect of temperature. The values of the oxidation velocity, observed at 30°C. and 40°C., are given in Table 4. By comparing Table 1 with Table 4 it will be seen that the change of temperature has negligible effect on the oxidation velocity when the concentration of sulphuric acid is greater than about 0.8 normal. The result means only that the effect of temperature on the dissolution velocity of oxygen, not on the true reaction velocity, is negligible. The effect of temperature on the oxidation velocity, when the concentration of sulphuric acid is less than about 0.8 normal, can be expected to be more complex, but it was not the purpose of the present study.

Table 3.

Temp.=20°C. Air=7.78 litres per hour.

$C_{H_2SO_4}$ normal	$k_{obs.}$	$k_{calc.}$ ($=0.128-0.00718C_{H_2SO_4}$)	Dissolution velocity of oxygen. moles per minute.
(0)	—	—	(8.2×10^{-6})
0.837	0.115	0.122	2.9×10^{-6}
0.930	0.127	0.121	3.2 ,,
0.972	0.121	0.121	3.0 ,,
1.377	0.117	0.118	2.9 ,,
1.396	0.127	0.118	3.2 ,,
1.423	0.123	0.118	3.1 ,,
2.052	0.109	0.113	2.7 ,,
2.127	0.116	0.113	2.9 ,,
2.335	0.114	0.111	2.8 ,,
2.558	0.107	0.110	2.7 ,,
2.727	0.105	0.108	2.6 ,,
2.832	0.108	0.108	2.7 ,,

Table 4.

Velocity of Air=7.78 litres per hour.

Temp.	$C_{H_2SO_4}$ normal	t min.	v c.c.	$v_{calc.}$ c.c.	k
30°C.	1.423	0	23.37	—	—
		20	20.81	20.85	0.128
		40	18.48	18.33	0.122
		60	15.99	15.81	0.123
		0	24.58	—	—
		20	21.98	22.06	0.130
		40	19.47	19.54	0.128
		60	17.10	17.02	0.125
					Mean: 0.126
30°C.	2.127	0	17.14	—	—
		20	14.52	14.68	0.131
		40	12.31	12.22	0.121
		60	9.95	9.76	0.120
		0	26.73	—	—
		20	24.19	24.27	0.127
		40	22.01	21.81	0.118
		60	19.50	19.35	0.121
					Mean: 0.123

Table 4. (*Continued.*)

Temp.	$C_{H_2SO_4}$ normal	t min.	v c.c.	$v_{calc.}$ c.c.	k
40°C.	1.423	0	18.10	—	—
		20	15.73	15.46	0.119
		40	12.76	12.82	0.134
		0	24.31	—	—
		20	21.58	21.67	0.137
		40	18.83	19.03	0.137
					Mean: 0.132
40°C.	2.127	0	16.91	—	—
		20	14.31	14.35	0.130
		40	12.11	11.79	0.120
		60	9.71	9.23	0.120
		0	24.31	—	—
		20	21.59	21.75	0.136
		40	19.00	19.19	0.133
		60	16.72	16.63	0.127
					Mean: 0.128

The dissolution velocity of oxygen into sulphuric acid solution. It is quite probable to consider that the observed oxidation velocity, given in Table 1, is not the true reaction velocity, but the dissolution velocity of oxygen into the solution. According to this consideration it is able to calculate the approximate values of the dissolution velocity of oxygen into sulphuric acid solution of various concentrations under the conditions of this experiment from the observed values of the velocity constant k.

The calculated values are given in the last column of Table 3. The dissolution velocity of oxygen into pure water, given in the Table, is the value obtained from the oxidation velocity of sodium sulphite in water.[1]

From Table 3 it can be described that the dissolution velocity of oxygen into sulphuric acid solution decrease rapidly with the increase of the concentration of sulphuric acid as far as it attains a certain value which is nearly unaltered by the further increase of the concentration of sulphuric acid, quite the same way as in the case of the dissolution velocity into hydrochloric acid solution, which was given in the previous paper.[2]

We see also that the dissolution velocity has almost the same value for both of sulphuric acid and hydrochloric acid solutions, when their concentrations are not small. It can be explained by the consideration that the ratio

(1) S. Miyamoto, this Bulletin, **3** (1928), 100; *Scientific Papers of the Institute of Physical and Chemical Research*, **8** (1928), 243.
(2) Loc. cit.

of the number of molecules of oxygen which enters into the surface film, and the total number of molecules which hit the liquid surface, has almost the same value for both of the liquids, neglecting the small difference of the total surface area of the air bubbles for both of the solutions.

Summary.

(1) The oxidation velocity of stannous chloride in sulphuric acid solution was observed under quite the same conditions as in the case of the oxidation of the same substance in hydrochloric acid solution, which was reported in the previous paper. The velocity increases slowly as the concentration of sulphuric acid increases as far as it reaches the dissolution velocity of oxygen into the solution, when the concentration of sulphuric acid attains about 0.8 normal, and the further increase of the concentration of sulphuric acid has almost no effect on the oxidation velocity, which was found to be almost independent of the initial concentration of stannous sulphate. The velocity constants, calculated as a zero-order reaction, were approximately expressed as a linear function of the concentration of sulphuric acid.

(2) The dissolution velocity of oxygen into sulphuric acid of various concentrations was calculated from the oxidation velocity observed. The dissolution velocity has nearly the same value as that into hydrochloric acid solution under the same conditions.

(3) The effect of temperature on the oxidation velocity, when the concentration of sulphuric acid is greater than about 0.8 normal, was ascertained to be negligible under the present conditions.

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