ON THE OXIDATION OF THE MIXTURE OF STANNOUS CHLORIDE AND SODIUM SULPHITE IN ALKALINE SOLUTION WITH AIR.

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Introduction. It was described in the previous papers that the oxidation velocity of sodium sulphite[1] or stannous chloride[2] in alkaline solution with air is independent of their concentrations, unless their concentrations are extremely small, and that their velocity constants decrease with the increase of the concentration of alkali and coincide with each other, when the concentration of sodium hydroxide is greater than about 0.2 normal under the condition of the previous study. To explain these results an assumption was proposed that the velocity of the dissolution of oxygen into the solution is smaller than that of the oxidation of these compounds.

If this assumption be correct, the oxidation velocity of the mixture of sodium sulphite and stannous chloride in alkaline solution with air can not be greater than that of each. The present research was undertaken to ascertain this assumption, but the results were not simple; the oxidation of the mixture seems to be a kind of induced reaction.

Method of Observation. Air, washed by an acidic solution of potassium dichromate and sodium hydroxide solution, was passed through a mixture of stannous chloride and sodium sulphite in sodium hydroxide solution of known concentration at the rate of 7.78 litres per hour.

The total volume was made to 40 c.c. in each case. After t minutes, air current was stopped and the total amount of the mixture 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. In

(1) S. Miyamoto, this Journal, **2** (1927), 74.
(2) S. Miyamoto, this Journal, **2** (1927), 155.

the following tables, v is the volume of sodium thiosulphate solution of 0.0996 normal which is equivalent to the total amount of sodium sulphite and stannous chloride; k was calculated by $k = \frac{1}{t}(v_0 - v)$, v_0 being the value of v at $t = 0$, and $v_{calc.}$ was obtained by $v_{calc.} = v_0 - kt$, using the mean value of k. Initial amounts of sodium sulphite and stannous chloride are given by $v_{0\,(Na_2SO_3)}$ and $v_{0\,(Sn\,Cl_2)}$.

TABLE 1.

Temp.=20° C. C_{NaOH}=0.525 normal. Air=7.78 litres per hour.

$v_0(SnCl_2)$ c.c.	$v_0(Na_2SO_3)$ c.c.	t min.	v c.c.	$v_{calc.}$ c.c.	k
—	0	From Fig. 1 in the previous paper,			0.220.
13.89	0.53	0	14.42	—	—
		10	12.50	12.49	0.192
		15	11.51	11.52	0.194
		20	10.52	10.56	0.195
		30	8.69	8.63	0.191
				mean:	0.193
10.89	0.74	0	11.63	—	—
		10	9.71	9.73	0.192
		20	7.87	7.83	0.188
		30	5.93	5.93	0.190
				mean:	0.190
10.89	2.76	0	13.65	—	—
		10	11.63	11.66	0.202
		20	9.67	9.67	0.199
		30	7.81	7.68	0.195
				mean:	0.199
11.61	4.76	0	16.37	—	—
		10	14.26	14.31	0.211
		20	12.13	12.25	0.212
		30	10.48	10.19	0.196
				mean:	0.206
9.13	5.40	0	14.53	—	—
		10	12.38	12.52	0.215
		25	9.61	9.50	0.197
		35	7.88	7.49	0.190
				mean:	0.201
7.24	5.84	0	13.08	—	—
		10	11.14	11.18	0.194
		20	9.34	9.28	0.187
		30	7.43	7.38	0.188
				mean:	0.190

TABLE 1. (*Continued.*)

Temp.=20° C. C_{NaOH} = 0.525 normal. Air = 7.78 litres per hour.

$v_0(SnCl_2)$ c.c.	$v_0(Na_2SO_3)$ c.c.	t min.	v c.c.	$v$calc. c.c.	k
7.95	11.46	0	19.41	—	—
		10	17.28	17.38	0.213
		20	15.41	15.35	0.200
		30	13.55	13.32	0.195
				mean:	0.203
10.31	16.12	0	26.43	—	—
		10	24.32	24.38	0.211
		20	22.26	22.33	0.209
		30	20.58	20.28	0.195
				mean:	0.205
4.44	8.74	0	13.18	—	—
		10	11.30	11.41	0.188
		20	9.59	9.64	0.180
		30	8.27	7.87	0.164
				mean:	0.177
3.77	10.80	0	14.57	—	—
		10	12.82	12.87	0.175
		20	11.35	11.17	0.161
		40	7.63	7.77	0.174
				mean:	0.170
1.26	19.94	0	22.20	—	—
		10	20.96	—	0.124
		20	18.80	—	0.170
		30	16.63	—	0.186
1.23	13.64	0	14.87	—	—
		10	13.61	—	0.126
		20	11.52	—	0.168
		40	7.49	—	0.185
0.48	13.52	0	14.00	—	—
		10	12.42	—	0.158
		20	10.73	—	0.164
		40	6.75	—	0.181
0	—	From Fig. 1 in the previous paper,			0.220.

TABLE 2.

Temp. = 20°C. C_{NaOH} = 0.752 normal. Air = 7.78 litres per hour.

$v_0(SnCl_2)$ c.c.	$v_0(Na_2SO_3)$ c.c.	t min.	v c.c.	$v$calc. c.c.	k
—	0	From Fig. 1 in the previous paper,			0.199
11.72	0.39	0	12.11	—	—
		10	10.31	10.35	0.180
		15	9.50	9.47	0.174
		20	8.59	8.59	0.176
		30	6.91	6.83	0.173
				mean:	0.176
11.88	1.39	0	13.27	—	—
		10	11.45	11.52	0.182
		20	9.78	9.77	0.175
		30	8.20	8.02	0.169
				mean:	0.175
9.11	4.45	0	13.56	—	—
		10	11.72	11.82	0.184
		15	10.94	10.95	0.175
		20	10.00	10.08	0.175
		30	8.70	8.34	0.162
				mean:	0.174
1.27	11.99	0	13.26	—	—
		10	12.23	—	0.103
		20	10.30	—	0.148
		30	8.60	—	0.155
1.14	19.22	0	20.36	—	—
		10	19.35	—	0.101
		20	17.85	—	0.126
		30	15.54	—	0.161
0.50	14.47	0	14.97	—	—
		10	13.50	—	0.147
		20	11.59	—	0.169
		30	10.11	—	0.162
0	—	From Fig. 1 in the previous paper,			0.199.

TABLE 3.

Temp. = 20°C. C_{NaON} = 1.092 normal. Air = 7.78 litres per hour.

$v_0(SnCl_2)$ c.c.	$v_0(Na_2SO_3)$ c.c.	t min.	v c.c.	vcalc. c.c.	k
—	0	From Fig. 1 in the previous paper,			0.164
12.37	1.13	0	13.50	—	—
		10	12.10	12.08	0.140
		20	10.54	10.66	0.148
		30	9.24	9.24	0.142
		40	7.96	7.82	0.139
				mean:	0.142
8.34	4.46	0	12.80	—	—
		10	11.42	11.42	0.138
		20	9.93	10.02	0.144
		30	8.78	8.63	0.134
				mean:	0.139
3.48	8.04	0	11.52	—	—
		15	9.45	9.54	0.138
		25	8.27	8.32	0.130
		40	6.36	6.24	0.129
				mean:	0.132
1.46	13.33	0	14.79	—	—
		10	13.64	—	0.115
		20	12.15	—	0.132
		30	10.84	—	0.132
1.39	19.49	0	20.88	—	—
		10	19.68	—	0.120
		20	18.04	—	0.142
		30	16.75	—	0.138
1.09	12.93	0	14.02	—	—
		10	12.85	—	0.117
		20	11.52	—	0.125
		30	10.21	—	0.124
0	—	From Fig. 1 in the previous paper,			0.164

As is seen in tables 1, 2 and 3, the results are complex. When the initial concentration of stannous chloride is not small, the oxidation velocity

of the mixture is independent of their concentrations, and is rather smaller than that of sodium sulphite or stannous chloride in alkaline solution. When the initial concentration of stannous chloride is small, the oxidation of the mixture takes place slowly first and increases with time.

The author has an opinion to explain these results by the transference of active states quite the same way as induced reaction,[1] but the theoretical discussion is left for the later study.

Summary.

1. The oxidation velocity of the mixture of sodium sulphite and stannous chloride in alkaline solution with air was studied.

2. When the initial concentration of stannous chloride is not small, the oxidation velocity is independent of their concentrations and is smaller than that of each.

3. When the initial concentration of stannous chloride is small, the oxidation of the mixture takes place at a slow rate first, and increases with time.

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(1) S. Miyamoto, *Scientific Papers of the Institute of Physical and Chemical Reserch*, 4 (1926), 257.