THE EFFECT OF HYDROCHLORIC ACID ON THE OXIDATION OF STANNOUS CHLORIDE WITH AIR.

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The catalytic effects of many substances on the oxidation of stannous chloride in hydrochloric acid solution by means of free oxygen were studied by S. W. Young.(1) The present research was undertaken to know the effect of hydrochloric acid on the oxidation of stannous chloride with air more precisely by a new method in connection with the study on the effect of sodium hydroxide.(2) The experimental procedure is quite the same with that described in the previous paper.(3)

In the following tables, v is the volume of sodium thiosulphate solution of 0.0996 normal, which is equivalent to the quantity of stannous chloride; k_1 was calculated by $k_1=\frac{1}{t}(v_0-v)$, v_0 being the value of v at $t=o$; $\frac{k_2}{2.303}$ was calculated by $\frac{k_2}{2.303}=\frac{1}{t}\log\frac{v_0}{v}$ and $v_{calc.}$ was obtained by $v_{calc.}=v_0-k_1 t$ or $v_{calc.}=v_0 e^{-k_2 t}$ using the mean value of k_1 or k_2.

TABLE 1.

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

C HCl normal	t min.	v c.c.	v calc. c.c.	k_1	$\frac{k_2}{2.303}$
0.00647	0	12.75	—	—	—
	60	11.68	11.74	—	0.000635
	120	10.71	10.81	—	0.000631
	150	10.32	10.37	—	0.000612
	0	13.59	—	—	—
	60	12.54	12.51	—	0.000582
	90	11.99	12.00	—	0.000604
	0	17.85	—	—	—
	60	16.40	16.43	—	0.000613
	90	15.82	15.77	—	0.000583
	150	14.86	14.41	—	0.000530
				—	mean: 0.000599

(1) Young, *J. Am. Chem. Soc.*, 23 (1901), 119 & 450.
(2) S. Miyamoto, this journal, 2 (1927), 155.
(3) S. Miyamoto, ibid.

Table 1. (*Continued.*)

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

C HCl normal	t min.	v c.c.	v calc. c.c.	k_1	$\frac{k_2}{2.303}$
0.07117	0	12.17	—	—	—
	60	10.65	10.54	—	0.000963
	90	9.78	9.81	—	0.00106
	120	9.40	9.13	—	0.000935
	150	8.62	8.50	—	0.000999
	0	16.99	—	—	—
	60	14.68	14.72	—	0.00106
	90	13.49	13.70	—	0.00111
	150	11.55	11.86	—	0.00112
					mean: 0.00104
0.09672	0	11.56	—	—	—
	60	9.98	9.98	—	0.00106
	120	8.84	8.63	—	0.000971
	150	7.88	8.02	—	0.00111
	0	17.66	—	—	—
	60	15.50	15.25	—	0.000945
	100	13.69	13.84	—	0.00111
	160	11.61	11.95	—	0.00114
					mean: 0.00106
0.1359	0	12.01	—	—	—
	40	10.51	10.42	—	0.00145
	80	8.88	9.04	—	0.00164
	120	7.51	7.85	—	0.00170
	0	18.43	—	—	—
	60	15.19	14.90	—	0.00140
	80	13.96	13.88	—	0.00151
	120	12.10	12.04	—	0.00152
					mean: 0.00154
0.1682	0	7.52	—	—	—
	90	4.20	—	0.0369	0.00281
	0	12.73	—	—	—
	60	8.78	—	0.0658	0.00269
	120	6.01	—	0.0560	0.00272
	0	12.33	—	—	—
	70	7.73	—	0.0657	0.00290
	0	18.07	—	—	—
	30	15.83	—	0.0747	0.00192
	60	13.82	—	0.0708	0.00194
	90	11.14	—	0.0770	0.00233

TABLE 1. (*Continued.*)

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

C HCl normal	t min.	v c.c.	v *calc.* c.c.	k_1	$\frac{k_2}{2.303}$
0.3235	0	10.47	—	—	—
	20	8.39	8.35	0.104	—
	30	7.24	7.29	0.108	—
	50	5.04	5.17	0.109	—
	0	17.13	—	—	—
	40	12.65	12.89	0.112	—
	0	18.41	—	—	—
	15	16.87	16.82	0.103	—
	35	14.55	14.70	0.110	—
	50	13.66	13.11	0.0950	—
				mean: 0.106	
0.4587	0	11.13	—	—	—
	30	7.90	7.59	0.108	—
	40	6.74	6.41	0.110	—
	60	4.30	4.05	0.114	—
	0	17.21	—	—	—
	10	15.96	16.03	0.125	—
	20	14.85	14.85	0.118	—
	40	12.01	12.49	0.130	—
				mean: 0.118	
0.8151	0	11.84	—	—	—
	20	9.32	9.48	0.126	—
	30	8.10	8.30	0.125	—
	60	4.64	4.76	0.120	—
	0	18.02	—	—	—
	15	16.36	16.25	0.111	—
	25	15.14	15.07	0,115	—
	50	12.51	12.12	0.110	—
				mean: 0.118	

TABLE 1. (*Continued.*)

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

C HCl normal	t min.	v c.c.	v calc. c.c.	k_1	$\frac{k_2}{2.303}$
1.360	0	11.64	—	—	—
	15	9.88	9.91	0.117	—
	30	8.31	8.19	0.111	—
	45	6.96	6.46	0.104	—
	0	12.28	—	—	—
	15	10.53	10.55	0.117	—
	20	9.97	9.98	0.116	—
	45	7.38	7.10	0.109	—
	0	18.18	—	—	—
	40	13.23	13.58	0.124	—
	50	12.18	12.43	0.120	—
				mean: 0.115	
1.811	0	11.84	—	—	—
	20	9.12	9.20	0.136	—
	30	7.87	7.88	0.132	—
	40	6.60	6.56	0.131	—
	50	5.19	5.24	0.133	—
	0	18.18	—	—	—
	30	14.34	14.22	0.128	—
	50	11.68	11.58	0.130	—
				mean: 0.132	
2.262	0	12.66	—	—	—
	15	10.53	10.57	0.142	—
	30	8.58	8.49	0.136	—
	45	6.31	6.40	0.141	—
	50	5.70	5.71	0.139	—
	0	18.28	—	—	—
	30	14.08	14.11	0.140	—
	70	8.85	8.55	0.135	—
				mean: 0.139	

TABLE 2.

Temp. = 30°C. Air = 7.78 litres per hour.

C HCl normal	t min.	v c.c.	v calc. c.c.	k_1	$\frac{k_2}{2.303}$
0.00670	0	13.94	—	—	—
	60	12.37	—	0.0262	0.000865
	80	11.99	—	0.0244	0.000818
	150	10.60	—	0.0223	0.000793
	0	17.81	—	—	—
	50	16.43	—	0.0276	0.000700
	90	15.70	—	0.0234	0.000608
	140	14.68	—	0.0224	0.000600
0.1407	0	11.92	—	—	—
	26	9.80	—	0.0815	0.00327
	45	8.63	—	0.0731	0.00312
	80	7.05	—	0.0609	0.00285
	0	19.17	—	—	—
	20	17.20	—	0.0985	0.00235
	40	15.40	—	0.0943	0.00238
	70	14.28	—	0.0699	0.00183
0.2077	0	11.43	—	—	—
	20	9.30	—	0.107	0.00448
	40	7.48	—	0.0988	0.00460
	60	6.20	—	0.0872	0.00443
	0	18.26	—	—	—
	20	15.87	—	0.120	0.00305
	30	13.51	—	0.119	0.00327
	60	11.91	—	0.106	0.00309
0.2605	0	10.89	—	—	—
	15	8.91	8.97	0.132	—
	30	6.99	7.05	0.131	—
	45	5.45	5.13	0.121	—
	0	17.42	—	—	—
	15	15.60	15.50	0.121	—
	30	13.40	13.58	0.134	—
	45	11.50	11.66	0.131	—
				mean: 0.128	
0.3417	0	10.85	—	—	—
	15	9.00	9.03	0.123	—
	30	7.47	7.22	0.113	—
	45	5.92	5.40	0.110	—
	0	16.36	—	—	—
	15	14.32	14.54	0.136	—
	30	12.71	12.73	0.122	—
	45	11.00	10.91	0.119	—
				mean: 0.121	

TABLE 2. (*Continued.*)

Temp. = 30°C. Air = 7.78 litres per hour.

C HCl normal	t min.	v c.c.	v calc. c.c.	k_1	$\frac{k_2}{2.303}$
0.4297	0	12.34	—	—	—
	15	10.28	10.27	0.137	—
	30	8.32	8.20	0.134	—
	45	6.25	6.13	0.135	—
	0	18.78	—	—	—
	15	16.70	16.71	0.139	—
	30	14.45	14.64	0.144	—
	45	12.56	12.57	0.138	—
				mean: 0.138	
0.8527	0	12.47	—	—	—
	15	10.55	10.59	0.128	—
	20	10.03	9.97	0.122	—
	30	8.93	8.72	0.118	—
	45	6.62	6.84	0.130	—
				mean: 0.125	
1.276	0	11.89	—	—	—
	15	10.16	10.13	0.115	—
	20	9.49	9.55	0.120	—
	30	8.40	8.38	0.116	—
	45	6.73	6.62	0.115	—
				mean: 0.117	
1.699	0	12.47	—	—	—
	15	10.38	10.44	0.139	—
	20	9.77	9.77	0.135	—
	30	8.40	8.42	0.136	—
	45	6.64	6.39	0.130	—
				mean: 0.135	
2.122	0	12.19	—	—	—
	15	10.01	10.12	0.145	—
	20	9.45	9.43	0.137	—
	30	8.12	8.05	0.136	—
	45	6.16	5.99	0.134	—
				mean: 0.138	

TABLE 3.

Temp.=40°C. Air=7.78 litres per hour.

C HCl normal	t min.	c.c.	v *calc.* c.c.	k_1	$\frac{k_2}{2.303}$
0.00670	0	12.41	—	—	—
	40	11.37	—	0.0260	0.000950
	80	10.75	—	0.0208	0.000780
	120	9.86	—	0.0213	0.000832
	0	19.00	—	—	—
	40	17.62	—	0.0345	0.000819
	80	16.94	—	0.0258	0.000623
	120	15.99	—	0.0251	0.000624
0.04020	0	12.44	—	—	—
	40	10.87	—	0.0393	0.00146
	80	10.04	—	0.0300	0.00116
	120	9.37	—	0.0256	0.00103
	0	18.35	—	—	—
	50	16.37	—	0.0396	0.000992
	80	15.65	—	0.0338	0.000864
	130	14.90	—	0.0265	0.000696
0.0737	0	11.30	—	—	—
	40	9.56	—	0.0435	0.00182
	80	8.10	—	0.0400	0.00181
	120	7.57	—	0.0311	0.00145
	0	18.72	—	—	—
	40	16.43	—	0.0573	0.00142
	80	14.80	—	0.0490	0.00128
	120	13.74	—	0.0415	0.00112
0.0913	0	11.42	—	—	—
	40	9.44	—	0.0495	0.00207
	80	8.21	—	0.0401	0.00179
	120	7.41	—	0.0334	0.00157
	0	17.82	—	—	—
	40	15.28	—	0.0635	0.00167
	80	13.63	—	0.0524	0.00146
	120	12.63	—	0.0433	0.00125

TABLE 3. (*Continued.*)

Temp. = 40°C. Air = 7.78 litres per hour.

C HCl normal	t min.	v c.c.	v calc. c.c.	k_1	$\frac{k_2}{2.303}$
0.1407	0	12.54	—	—	—
	25	10.33	—	0.0884	0.00337
	50	8.92	—	0.0724	0.00296
	75	7.84	—	0.0627	0.00272
	0	18.14	—	—	—
	25	15.49	—	0.106	0.00274
	50	13.76	—	0.0876	0.00740
	75	12.50	—	0.0752	0.00216
0.2077	0	12.11	—	—	—
	20	9.63	—	0.124	0.00498
	40	7.79	—	0.108	0.00479
	60	6.35	—	0.0960	0.00467
	0	18.95	—	—	—
	20	16.22	—	0.137	0.00338
	40	13.96	—	0.125	0.00332
	60	12.04	—	0.115	0.00328
0.2605	0	12.39	—	—	—
	15	10.17	10.14	0.148	—
	30	8.00	7.89	0.146	—
	45	6.23	5.64	0.137	—
	0	18.52	—	—	—
	15	16.12	16.27	0.160	—
	30	13.84	14.02	0.156	—
	45	11.68	11.77	0.152	—
				mean: 0.150	
0.3417	0	11.62	—	—	—
	15	9.81	9.70	0.121	—
	30	7.88	7.78	0.125	—
	45	6.10	5.86	0.123	—
	0	18.89	—	—	—
	15	16.88	16.97	0.134	—
	30	15.01	15.05	0.129	—
	45	12.84	13.13	0.134	—
				mean: 0.128	

TABLE 3. (*Continued.*)

Temp.=40°C. Air=7.78 litres per hour.

C HCl norma	*t* min.	*v* c.c.	*v. calc.* c c.	k_1	$\frac{k_2}{2.303}$
0.4297	0	11.82	—	—	—
	15	9.64	9.66	0.145	—
	20	9.02	8.94	0.140	—
	30	7.33	7.50	0.150	—
	45	5.43	5.34	0.142	—
				mean: 0.144	
0.8527	0	12.07	—	—	—
	16	9.98	9.96	0.131	—
	20	9.41	9.43	0.133	—
	30	8.13	8.11	0.131	—
	46	6.01	6.00	0.132	—
				mean: 0.132	
1.276	0	11.63	—	—	—
	15	9.50	9.50	0.142	—
	20	8.79	8.79	0.142	—
	30	7.34	7.37	0.143	—
	45	5.33	5.24	0.140	—
				mean: 0.142	
1.699	0	11.97	—	—	—
	15	9.66	9.67	0.154	—
	20	8.97	8.91	0.150	—
	30	7.29	7.38	0.156	—
	45	5.13	5.08	0.152	—
				mean: 0.153	
2.122	0	11.94	—	—	—
	15	9.65	9.58	0.153	—
	20	8.90	8.80	0.152	—
	30	7.12	7.23	0.161	—
	45	4.68	4.87	0.161	—
				mean: 0.157	

As is seen in Table 1, 2 and 3, the oxidation velocity is independent of the concentration of stannous chloride when the concentration of hydrochloric acid is greater than about 0.25 normal under the condition of this experiment. This can be explained by the assumption that the oxidation velocity thus measured is no other than the dissolution velocity of oxygen into the solution.

When the concentration of hydrochloric acid is smaller than about 0.25 normal, the reaction seems to be between first and zero order. The concentration of hydrochloric acid, the initial values of which are given in the tables, can not be considered to be constant during the reaction; it decreases by the formation of stannic chloride. The decrease is not negligible when the concentration is smaller than about 0.25 normal, for in this region the oxidation velocity of stannous chloride increases rapidly with the increase of the concentration of hydrochloric acid. This will be one of the causes of the decrease of the values of k_1 or k_2 in Table 2 and 3 with time when the concentration of hydrochloric acid is small.

Anyhow from the above results it can be said that the oxidation velocity of stannous chloride increases rapidly with the increase of the concentration of hydrochloric acid, until it reaches the dissolution velocity of oxygen into the solution, which is almost constant when the concentration of hydrochloric acid is greater than about 0.25 normal under the condition of this experiment.

By comparing Table 1, 2 and 3, it can be said that the effect of temperature on the reaction is small.

The Dissolution Velocity of Oxygen into Hydrochloric Acid Solution. The approximate values of the dissolution velocity of oxygen into hydrochloric acid of various concentrations, when air was passed into 40 cc. of the solution in a test tube (diameter = 3 cm.) through a glass tube (inside diameter = 4 mm., outside diameter = 6 mm.) at the rate of 7.78 litres per hour, were calculated from the above results.

The dissolution velocity, given in Table 4, when the concentration of hybrochloric acid is zero, was calculated from the oxidation velocity of sodium sulphite with air.[1] As is seen in Table 4 the dissolution velocity of oxygen into water decreases rapidly by adding hydrochloric acid until the concentration of hydrochloric acid reaches about 0.25 normal, and further addition of hydrochloric acid has almost no effect on the dissolution velocity, which is smaller than that into sodium hydroxide solution, calculated quite the same way in the previous paper.[2]

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(1) S. Miyamoto, this journal, 2 (1927), 74.
(2) S. Miyamoto, ibid., 2 (1927), 158.

Table 4.

Temp.	C HCl normal	k_1	Dissolution velocity of oxygen $\times 10^6$ mols per minute
20°C.	0	0.330	8.2
	0.3235	0.106	2.6
	0.4587	0.118	2.9
	0.8151	0.118	2.9
	1.360	0.115	2.9
	1.811	0.132	2.3
	2.262	0.139	3.5
30°C.	0	0.345	8.6
	0.2605	0.128	3.2
	0.3417	0.121	3.0
	0.4297	0.138	3.4
	0.8527	0.125	3.1
	1.276	0.117	2.9
	1.699	0.135	3.4
	2.122	0.138	3.4
40°C.	0	0.382	9.6
	0.2605	0.150	3.7
	0.3417	0.128	3.2
	0.4297	0.144	3.6
	0.8527	0.132	3.3
	1.276	0.142	3.5
	1.699	0.153	3.8
	2.122	0.157	3.9

Summary.

1. The oxidation velocity of stannous chloride in hydrochloric acid with air was studied. When the concentration of hydrochloric acid is smaller than about 0.25 normal, the reaction seems to be between first and zero order. When the concentration of hydrochloric acid is greater than about 0.25 normal, the velocity is independent of the concentration of stannous chloride.

2. The effect of temperature is small.

3. The dissolution velocity of oxygen into hydrochloric acid of various concentrations was obtained indirectly.

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