

ON THE OXIDATION OF SODIUM SULPHITE IN SODIUM CARBONATE SOLUTION WITH AIR.

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In connection with the former study on the effect of sodium hydroxide on the oxidation of sodium sulphite⁽¹⁾ with air, the present research was carried out under the same condition, expecting that it will be able to calculate the dissolution velocity of oxygen into sodium carbonate solution from the result.

The experimental procedure was quite the same as that described in the previous paper⁽²⁾. In the following tables, v is the volume of sodium thio-sulphate solution of 0.0996 normal, which is equivalent to the quantity of sodium sulphite; k was calculated by $k = \frac{1}{t}(v_0 - v)$, v_0 being the value of v at $t=0$; $v_{calc.}$ was obtained by $v_{calc.} = v_0 - kt$, using the mean value of k . The value of k , when $C_{Na_2CO_3} = 0$, given in the following tables, is that obtained in the previous study⁽³⁾.

(1) S. Miyamoto, this journal, 2 (1927), 74; *Scientific Papers of the Institute of Physical and Chemical Research*, 7 (1927), 40.

(2) Ibid.

(3) Ibid.

TABLE 1.
Temp. = 20°C. Velocity of air = 7.78 litres per hour.

$C_{\text{Na}_2\text{CO}_3}$ normal	t min.	v c.c.	$v_{\text{calc.}}$ c.c.	k	$C_{\text{Na}_2\text{CO}_3}$ normal	t min.	v c.c.	$v_{\text{calc.}}$ c.c.	k	
0	—	—	—	0.330	0.0750	0	18.08	—	—	
0.01875	0	23.57	—	—		10	15.61	15.59	0.247	
	10	20.81	20.72	0.276		25	12.01	11.85	0.243	
	25	16.43	16.44	0.286		50	6.05	5.63	0.241	
	50	9.14	9.32	0.289		0	11.58	—	—	
	0	19.24	—	—		9	9.39	9.34	0.243	
	10	16.48	16.39	0.276		20	6.58	6.60	0.250	
	20	13.22	13.54	0.301		Mean: 0.249				
	40	6.99	7.84	0.306		0.1875	0	22.77	—	—
	0	14.62	—	—			10	20.32	20.39	0.245
	10	11.84	11.77	0.278	25		16.61	16.82	0.246	
	20	9.13	8.92	0.275	55		9.47	9.68	0.242	
	35	4.50	4.64	0.289	0		15.14	—	—	
	0	11.31	—	—	10		12.74	12.76	0.240	
	9	8.78	8.74	0.281	25		9.14	9.19	0.240	
	15	7.04	7.03	0.285	50		4.33	3.24	0.216	
	25	4.45	4.18	0.274	0		12.44	—	—	
Mean: 0.285				9	10.26		10.30	0.242		
0.0375	0	22.53	—	—	20		7.49	7.68	0.248	
	10	19.82	19.89	0.271	35		4.50	4.11	0.227	
	20	17.13	17.25	0.270	Mean: 0.238					
	50	9.12	9.33	0.268	0		20.21	—	—	
	0	20.81	—	—	10		17.82	17.94	0.239	
	10	18.16	18.17	0.265	25		14.40	14.53	0.232	
	20	15.81	15.53	0.250	55	7.50	7.72	0.231		
	50	7.20	7.61	0.272	0	14.32	—	—		
	0	16.15	—	—	10	11.97	12.05	0.235		
	10	13.48	13.51	0.267	25	8.64	8.64	0.227		
	20	10.94	10.87	0.261	0	13.49	—	—		
	45	4.80	4.27	0.252	10	11.21	11.22	0.228		
Mean: 0.264				25	7.96	7.81	0.221			
0.0750	0	18.91	—	—	45	4.29	3.27	0.204		
	10	16.34	16.42	0.257	Mean: 0.227					
	25	12.42	12.68	0.260	0	19.18	—	—		
	50	6.36	6.46	0.251	10	16.95	16.97	0.223		
0.0750	0	18.91	—	—	25	13.75	13.65	0.217		
	10	16.34	16.42	0.257	55	7.20	7.58	0.218		
	25	12.42	12.68	0.260						
	50	6.36	6.46	0.251						

TABLE 1. (Continued.)

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

$C_{Na_2CO_3}$ normal	t min.	v c.c.	$v_{calc.}$ c.c.	k	$C_{Na_2CO_3}$ normal	t min.	v c.c.	$v_{calc.}$ c.c.	k	
0.3750	0	19.00	—	—	0.938	0	19.61	—	—	
	10	16.72	16.79	0.228		15	17.39	17.36	0.148	
	25	13.31	13.47	0.228		30	15.11	15.11	0.150	
						60	10.36	10.61	0.154	
	0	14.53	—	—		0	14.39	—	—	
	10	12.33	12.32	0.220		15	12.22	12.14	0.145	
	25	8.94	9.00	0.224		30	10.09	9.89	0.143	
	45	5.22	4.58	0.207		60	5.05	5.39	0.156	
	Mean: 0.221					Mean: 0.150				
	0.563	0	22.20	—		—	1.125	0	23.95	—
15		19.41	19.38	0.186	10	22.58		22.62	0.137	
30		16.76	16.56	0.181	25	20.61		20.62	0.134	
					50	17.25		17.30	0.134	
0		21.82	—	—	0	22.88		—	—	
10		19.84	19.94	0.198	15	20.89		20.88	0.133	
25		16.92	17.12	0.196	30	18.92		18.89	0.132	
55		11.40	11.48	0.189	60	14.57		14.90	0.139	
0		14.47	—	—	0	14.17		—	—	
15		11.74	11.65	0.182	15	12.37		12.17	0.120	
30		8.82	8.83	0.188	30	10.24		10.18	0.131	
55		4.58	4.13	0.180	60	5.97		6.19	0.137	
Mean: 0.188				Mean: 0.133						
0.750		0	24.77	—	—	1.313		0	28.49	—
	10	23.06	23.12	0.171	25		25.29	25.41	0.128	
	30	19.60	19.82	0.172	50		22.49	22.34	0.120	
	60	14.37	14.87	0.173	0		25.08	—	—	
					25		21.80	22.00	0.131	
	0	23.93	—	—	50		18.97	18.93	0.122	
	10	22.30	22.28	0.163	0		14.99	—	—	
	25	19.79	19.80	0.166	15		13.27	13.14	0.115	
	60	14.33	14.03	0.160	30		11.45	11.30	0.118	
	0	14.75	—	—	55		8.47	8.22	0.119	
	15	12.29	12.27	0.164	0		12.34	—	—	
	30	9.79	9.80	0.165	15		10.31	10.49	0.135	
	60	5.57	4.85	0.153	30		7.74	8.65	0.120	
	Mean: 0.165				55		5.83	5.57	0.118	
	0.938	0	25.63	—	—		Mean: 0.123			
		15	23.30	23.38	0.155					
30		21.18	21.13	0.148						
60		16.63	16.63	0.150						

The Effect of Sodium Carbonate. Table 1 shows that the oxidation velocity of sodium sulphite in sodium carbonate solution decreases with the increase of the concentration of the latter, quite the same way as in the case of its oxidation in sodium hydroxide solution. The velocity constant seems to be expressed as a linear function of $C_{\text{Na}_2\text{CO}_3}$, when $C_{\text{Na}_2\text{CO}_3}$ is greater than about 0.02 normal; $k_{\text{calc.}}$ in Table 3 was calculated by $k_{\text{calc.}} = 0.258 - 0.114 C_{\text{Na}_2\text{CO}_3}$.

TABLE 2.
Velocity of air = 7.78 litres per hour.

Temp.	$C_{\text{Na}_2\text{CO}_3}$ normal	t min.	v c.c.	$v_{\text{calc.}}$ c.c.	k
30°C.	0.1875	0	22.28	—	—
		10	19.48	19.57	0.280
		25	15.25	15.50	0.281
		55	7.42	7.37	0.270
		0	15.52	—	—
		10	12.96	12.81	0.256
		20	10.18	10.10	0.267
		40	4.62	4.68	0.273
		Mean: 0.271			
		0	24.77	—	—
		10	22.26	22.28	0.251
		30	17.47	17.30	0.243
		60	9.85	9.83	0.249
		0	15.78	—	—
		10	13.28	13.29	0.250
30°C.	0.3750	20	10.76	10.80	0.251
		45	4.67	4.57	0.247
		Mean: 0.249			
		0	29.33	—	—
		10	27.53	27.62	0.180
		30	23.89	24.20	0.181
		60	18.95	19.07	0.173
		0	14.51	—	—
		15	12.10	11.94	0.161
		30	9.47	9.38	0.168
		60	4.13	4.25	0.173
		0	12.17	—	—
		15	9.73	9.60	0.163
		30	7.23	7.04	0.165
		55	2.77	2.76	0.171
		Mean: 0.171			

TABLE 2. (Continued.)
Velocity of air=7.78 litres per hour.

Temp.	$C_{\text{Na}_2\text{CO}_3}$ normal	t min.	v c.c.	$v_{\text{calc.}}$ c.c.	k
40°C.	0.1875	0	23.96	—	—
		10	21.06	21.08	0.290
		25	16.51	16.76	0.298
		55	8.29	8.12	0.285
		0	15.33	—	—
		10	12.44	12.45	0.289
		20	9.61	9.57	0.286
		40	4.05	3.81	0.282
		Mean: 0.288			
40°C.	0.3750	0	22.82	—	—
		15	18.68	18.93	0.276
		30	15.03	15.05	0.260
		60	7.53	7.28	0.255
		0	15.94	—	—
		10	13.33	12.35	0.261
		20	10.91	10.76	0.252
		45	4.69	4.28	0.250
		Mean: 0.259			
40°C.	0.938	0	23.67	—	—
		15	20.97	20.82	0.180
		30	17.68	17.97	0.200
		60	11.96	12.27	0.195
		0	14.15	—	—
		15	11.17	11.30	0.199
		30	8.75	8.45	0.180
		55	3.90	3.70	0.186
		Mean: 0.190			

The Effect of Temperature. The results of the measurements at 30°C. and 40°C. are given in Table 2. The effect of temperature was small, as can be expected.

$$\begin{aligned}
 \frac{k_{30^\circ}}{k_{20^\circ}} &= \frac{0.271}{0.238} = 1.14, & \frac{k_{40^\circ}}{k_{30^\circ}} &= \frac{0.288}{0.271} = 1.06 & \text{when } C_{\text{Na}_2\text{CO}_3} &= 0.1875 \text{ N.} \\
 \frac{k_{30^\circ}}{k_{20^\circ}} &= \frac{0.249}{0.221} = 1.13, & \frac{k_{40^\circ}}{k_{30^\circ}} &= \frac{0.259}{0.249} = 1.04 & \text{when } C_{\text{Na}_2\text{CO}_3} &= 0.3750 \text{ N.} \\
 \frac{k_{30^\circ}}{k_{20^\circ}} &= \frac{0.171}{0.150} = 1.14, & \frac{k_{40^\circ}}{k_{30^\circ}} &= \frac{0.190}{0.171} = 1.11 & \text{when } C_{\text{Na}_2\text{CO}_3} &= 0.938 \text{ N.}
 \end{aligned}$$

TABLE 3.

Temp.	$C_{\text{Na}_2\text{CO}_3}$ normal	k	$k_{\text{calc.}}$	Dissolution velocity of oxygen mols per minute.
20°C.	0	0.330	—	8.2×10^{-6}
	0.01875	0.285	0.256	7.1 "
	0.03750	0.264	0.254	6.6 "
	0.0750	0.249	0.249	6.2 "
	0.1875	0.238	0.237	5.9 "
	0.2625	0.227	0.228	5.7 "
	0.3750	0.221	0.215	5.5 "
	0.5630	0.188	0.194	4.7 "
	0.750	0.165	0.172	4.1 "
	0.938	0.150	0.151	3.7 "
	1.125	0.133	0.130	3.3 "
	1.313	0.123	0.108	3.1 "
30°C.	0	0.345	—	8.6 "
	0.1875	0.271	—	6.7 "
	0.3750	0.249	—	6.2 "
	0.938	0.171	—	4.3 "
40°C.	0	0.382	—	9.5 "
	0.1875	0.288	—	7.2 "
	0.3750	0.259	—	6.4 "
	0.938	0.190	—	4.7 "

The Dissolution Velocity of Air. As was expected, the oxidation velocity of sodium sulphite in sodium carbonate solution was independent of its concentration under the condition of this experiment. The result can be explained by the assumption that the oxidation velocity thus measured is no other than the dissolution velocity of oxygen into sodium carbonate solution. The dissolution velocity, given in Table 3, is that of oxygen, when air was passed into 40 c.c. of sodium carbonate solution in a test tube (diameter \div 3 cm.) through a glass tube (inside diameter \div 4 mm., outside diameter \div 6 mm.) at the rate of 7.78 litres per hour, and was calculated from the value of k . The dissolution velocity of oxygen into sodium carbonate solution seems to be a little smaller than that into sodium hydroxide solution, obtained in the previous study⁽¹⁾.

(1) S. Miyamoto, this journal, 2 (1927), 158; *Scientific Papers of the Institute of Physical and Chemical Research*, 7 (1927), 192.

Summary.

(1) The oxidation velocity of sodium sulphite in sodium carbonate solution of various concentrations was observed. The oxidation velocity was independent of the concentration of sodium sulphite under the condition of the present experiment, and the velocity constant was expressed as a linear function of the concentration of sodium carbonate approximately, when $C_{\text{Na}_2\text{CO}_3}$ is greater than about 0.02 normal.

(2) The effect of temperature was small.

(3) The dissolution velocity of oxygen into sodium carbonate solution of various concentrations was obtained indirectly.

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