ON THE DISSOLUTION VOLOCITY OF OXYGEN INTO WATER. PART II.

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Introduction. The oxidation velocity of sodium sulphite solution by means of air was found to be independent of the concentration of sodium sulphite under certain conditions.(1) This experimental fact can easily be explained if we consider that the observed reaction velocity is no other than the dissolution velocity of oxygen into water.

From this consideration, it was described in the previous paper,(2) that the dissolution velocity of oxygen D and the velocity constant k, calculated as a zero-order reaction, can be expressed by the following equations.

$$D=\frac{1}{4}k\times 10^{-4} \quad \text{moles per minute.} \qquad (1)$$

$$D=\frac{60\alpha p}{\sqrt{2\pi MRT}}\left(\frac{Vl}{20ru}+s_0\right) \quad \text{moles per minute.} \qquad (2)$$

$$k=\frac{24\alpha p\times 10^5}{\sqrt{2\pi MRT}}\left(\frac{Vl}{20ru}+s_0\right) \qquad (3)$$

where α = the ratio of the total number of the molecules of oxygen which enter into water and the total number of the molecules of oxygen which collide with the unit boundary surface per unit of time, the concentration of oxygen in the surface being kept to be zero.

p = the partial pressure of oxygen.

M = the molecular weight of oxygen.

R = gas constant.

T = absolute temperature.

V = the volume of the gas passed per minute.

l = the depth of the center of a bubble when it just leaves the exit.

r = the radius of a bubble.

u = the ascending velocity of the bubble.

s_0 = the surface area of the liquid which is in contact with the gas outside of the boundary surface of the bubbles.

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

(2) S. Miyamoto and T. Kaya, this Bulletin, **5** (1930), 123.

If all the values in the equations 2 and 3 be kept constant except the value of p, the values of D and k can then be expressed by

$$D = A\alpha p \qquad \text{(4)}$$

$$k = B\alpha p \qquad \text{(5)}$$

If the value of α be independent of the partial pressure of oxygen,

$$D = A'p \qquad \text{(6)}$$

$$k = B'p \qquad \text{(7)}$$

where A' and B' are constants.

The present research was undertaken to ascertain if the present theoretical consideration be acceptable.

Experimental. The mixture of oxygen and air was passed through a narrow glass tube into the solution of sodium sulphite at uniform velocity and the oxidation velocity was observed.

The reacting vessel employed is shown in Fig. 1. The gas mixture, washed by acidified potassium bichromate solution and alkali, was passed at uniform velocity into the solution of sodium sulphite contained in A, the total volume of the reacting solution being made to 40 c.c. in each measurement. After t-minutes, the gas current was stopped and the stopcocks B and D were opened and the total quantity of the solution was poured into C, which contains a known quantity of iodine solution acidified with hydrochloric acid. After A was repeatedly washed by water, the vessel C was taken out, and the excess of iodine was titrated back by means of sodium thiosulphate solution, v in the following tables being the volume of sodium thiosulphate solution of 0.1000 normal, equivalent to the amount of sodium sulphite remained after the t-minutes passage of the gas mixture.

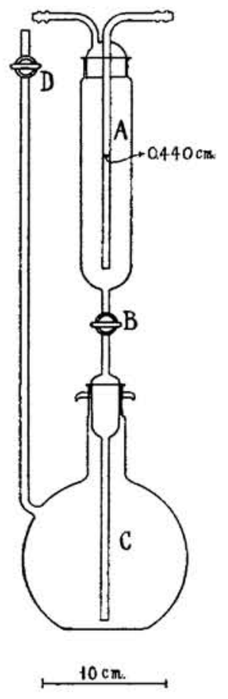

Fig. 1.

The experimental result shows that the oxidation velocity is independent of the concentration of sodium sulphite under the present conditions and the velocity constant k was calculated by

$$k = \frac{1}{t - t_0}(v_0 - v),$$

v_0 being the value of v at $t = t_0$. The values of $v_{calc.}$ were obtained by

$$v_{calc.} = v_0 - k(t - t_0)$$

using the mean value of k obtained experimentally.

The observed results are given in Tables 1 and 2, and graphically in Fig. 2. The partial pressure of oxygen, given in the first column of the Tables was calculated from the volumes of oxygen and air mixed.

Table 1.

Temp.=20°C. Velocity of Gas Passed=60.3 c.c./min.

p_{O_2} atm.	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.21	3	18.18	—	—
	43	11.87	12.06	0.158
	3	18.48	—	—
	33	13.78	13.89	0.157
	3	27.70	—	—
	33	23.06	23.11	0.155
	3	32.10	—	—
	33	27.46	27.51	0.155
	3	39.23	—	—
	43	33.12	33.11	0.153
	3	39.33	—	—
	39	33.80	33.82	0.154
	3	46.27	—	—
	43	40.10	40.15	0.154
	3	50.97	—	—
	43	44.97	44.85	0.150
	3	57.95	—	—
	33	53.46	53.36	0.150
	3	59.49	—	—
	43	53.69	54.37	0.146
	3	62.18	—	—
	33	57.59	57.57	0.153
			Mean	0.153

Table 1.—(*Continued*)

Temp. = 20°C. Velocity of Gas Passed = 60.3 c.c./min.

p_{O_2} atm.	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.33	3	25.30	—	—
	33	17.95	18.04	0.245
	3	38.82	—	—
	33	31.26	31.56	0.252
	3	53.66	—	—
	33	46.20	46.40	0.249
	3	60.39	—	—
	33	53.70	53.13	0.223
			Mean	0.242
0.48	3	24.37	—	—
	33	13.79	14.41	0.353
	3	35.46	—	—
	33	25.55	25.50	0.330
	3	49.51	—	—
	33	39.68	39.55	0.328
	3	63.40	—	—
	33	53.87	53.44	0.317
			Mean	0.332
0.60	3	26.18	—	—
	33	13.88	14.09	0.410
	3	37.70	—	—
	33	25.26	25.61	0.415
	3	50.68	—	—
	35	37.74	37.78	0.404
	3	64.34	—	—
	33	52.86	52.25	0.383
			Mean	0.403

Table 1.—(*Continued*)

Temp.=20°C. Velocity of Gas Passed=60.3 c.c./min.

p_{O_2} atm.	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.74	3	25.82	—	—
	33	10.74	11.06	0.503
	3	27.23	—	—
	33	12.37	12.47	0.495
	3	37.50	—	—
	33	22.46	22.74	0.501
	3	40.00	—	—
	33	25.60	25.24	0.480
	3	49.33	—	—
	34	33.74	34.08	0.503
	3	53.93	—	—
	33	39.17	39.17	0.492
	3	61.10	—	—
	33	46.85	46.34	0.475
	3	62.37	—	—
	33	47.85	47.61	0.484
			Mean	0.492
0.88	3	20.10	—	—
	23	8.60	8.74	0.575
	3	32.73	—	—
	33	16.43	15.69	0.543
	3	52.51	—	—
	33	35.25	35.47	0.575
	3	64.09	—	—
	33	46.77	46.05	0.577
			Mean	0.568

Table 1.—(*Concluded*)

Temp. = 20°C. Velocity of Gas Passed = 60.3 c.c./min.

p_{O_2} atm.	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.97	3	22.88	—	—
	18	13.06	13.07	0.655
	3	23.58	—	—
	23	10.03	10.50	0.678
	3	29.75	—	—
	33	10.66	10.13	0.636
	3	32.32	—	—
	33	12.47	12.70	0.662
	3	33.22	—	—
	33	13.76	13.60	0.649
	3	37.79	—	—
	34	17.52	17.52	0.654
	3	39.28	—	—
	28	22.29	22.93	0.680
	3	43.73	—	—
	33	24.21	24.11	0.651
	3	44.01	—	—
	33	25.10	24.39	0.630
	3	49.09	—	—
	33	29.21	29.47	0.663
	3	52.36	—	—
	33	32.48	32.74	0.663
	3	55.51	—	—
	33	35.82	35.89	0.656
	3	60.90	—	—
	38	38.49	38.01	0.643
	3	63.46	—	—
	33	44.25	43.84	0.640
	3	65.72	—	—
	33	46.00	46.10	0.657
				Mean 0.654

Table 2.

Temp. = 20°C. Velocity of Gas Passed = 30.5 c.c./min.

p_{O_2} atm.	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.21	3	18.62	—	—
	53	13.79	13.77	0.097
	3	26.59	—	—
	54	21.67	21.64	0.096
	3	32.95	—	—
	53	28.09	28.10	0.097
	3	38.04	—	—
	53	33.11	33.19	0.099
	3	46.04	—	—
	53	41.21	41.19	0.097
	3	52.36	—	—
	63	46.58	46.54	0.096
	3	59.12	—	—
	53	54.29	54.27	0.097
	3	64.60	—	—
	63	58.80	58.78	0.097
			Mean	0.097
0.34	3	18.21	—	—
	33	13.51	13.59	0.157
	3	25.70	—	—
	43	19.72	19.54	0.150
	3	32.09	—	—
	43	25.81	25.93	0.157
	3	39.05	—	—
	33	34.56	34.43	0.150
	3	46.37	—	—
	53	38.65	38.67	0.154
	3	52.97	—	—
	33	48.30	48.35	0.156
	3	59.71	—	—
	43	53.51	53.55	0.155
			Mean	0.154.

Table 2.—(*Continued*)

Temp. $=20°$C. Velocity of Gas Passed $=30.5$ c.c./min.

p_{O_2} atm.	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.46	3	18.72	—	—
	43	10.54	10.52	0.205
	3	23.68	—	—
	43	15.36	15.48	0.208
	3	39.43	—	—
	43	31.15	31.23	0.207
	3	45.42	—	—
	43	37.21	37.22	0.205
	3	52.88	—	—
	43	44.86	44.68	0.201
	3	65.96	—	—
	43	57.76	57.76	0.205
			Mean	0.205
0.59	3	18.56	—	—
	33	10.63	10.64	0.264
	3	23.64	—	—
	43	12.89	13.08	0.269
	3	32.29	—	—
	43	21.90	21.73	0.260
	3	45.69	—	—
	43	35.16	35.13	0.263
	3	51.81	—	—
	43	41.36	41.25	0.261
	3	58.74	—	—
	43	48.15	48.18	0.265
			Mean	0.264

Table 2.—(*Continued*)

Temp.=20°C. Velocity of Gas Passed=30.5 c.c./min.

p_{O_2} atm.	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.72	3	18.57	—	—
	26	11.25	11.30	0.318
	3	26.90	—	—
	33	17.33	17.42	0.319
	3	32.81	—	—
	33	23.21	23.33	0.320
	3	41.49	—	—
	43	28.83	28.85	0.317
	3	45.70	—	—
	43	33.10	33.06	0.315
	3	57.61	—	—
	43	45.07	44.97	0.314
	3	61.25	—	—
	43	48.79	48.61	0.312
	3	66.40	—	—
	43	53.95	53.76	0.311
			Mean	0.316
0.84	3	19.67	—	—
	34	8.44	8.42	0.362
	3	26.43	—	—
	33	15.46	15.54	0.366
	3	31.47	—	—
	43	16.79	16.95	0.367
	3	37.86	—	—
	43	23.47	23.34	0.360
	3	52.73	—	—
	53	34.38	34.48	0.367
	3	61.07	—	—
	33	50.30	50.18	0.359
	3	64.02	—	—
	53	46.09	45.77	0.359
			Mean	0.363

Table 2.—(*Concluded*)

Temp. = 20°C. Velocity of Gas Passed = 30.5 c.c./min.

p_{O_2} atm.	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.97	3	18.62	—	—
	23.5	9.98	10.05	0.424
	3	22.17	—	—
	35	8.92	8.79	0.414
	3	31.72	—	—
	43	14.98	15.00	0.419
	3	37.29	—	—
	44	19.99	20.15	0.422
	3	45.71	—	—
	43	28.98	28.99	0.418
	3	51.74	—	—
	53	31.11	30.84	0.413
	3	58.71	—	—
	43	41.92	41.99	0.420
	3	63.89	—	—
	53	43.07	42.99	0.416
				Mean 0.413

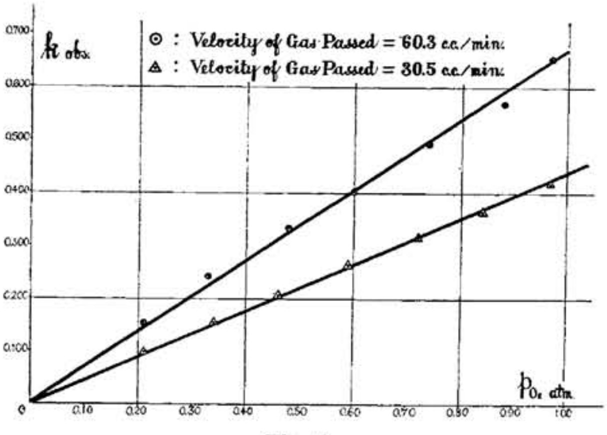

Fig. 2.

Table 3.

Temp. = 20°C. Velocity of Gas Passed = 60.3 c.c. / min.

p_{O_2} atm.	$k_{obs.}$	$k_{calc.}$	$D_{obs.}$ (Dissolution velocity of oxygen) moles / min.	$D_{calc.}$ (Dissolution velocity of oxygen) moles / min.
0.21	0.153	0.141	3.83×10^{-6}	3.51×10^{-6}
0.33	0.242	0.221	6.05 ,,	5.52 ,,
0.48	0.332	0.321	8.30 ,,	8.03 ,,
0.60	0.403	0.401	10.08 ,,	10.04 ,,
0.74	0.492	0.495	12.30 ,,	12.38 ,,
0.88	0.568	0.589	14.20 ,,	14.72 ,,
0.98	0.654	0.649	16.35 ,,	16.23 ,,

Table 4.

Temp. = 20°C. Velocity of Gas Passed = 30.5 c.c, / min.

p_{O_2} atm.	$k_{obs.}$	$k_{calc.}$	$D_{obs.}$ (Dissolution velocity of oxygen) moles / min.	$D_{calc.}$ (Dissolution velocity of oxygen) moles / min.
0.21	0.097	0.092	2.43×10^{-6}	2.29×10^{-6}
0.34	0.154	0.149	3.85 ,,	3.72 ,,
0.46	0.205	0.201	5.13 ,,	5.03 ,,
0.59	0.264	0.258	6.60 ,,	6.45 ,,
0.72	0.316	0.315	7.90 ,,	7.87 ,,
0.84	0.363	0.367	9.08 ,,	9.18 ,,
0.97	0.418	0.424	10.45 ,,	10.60 ,,

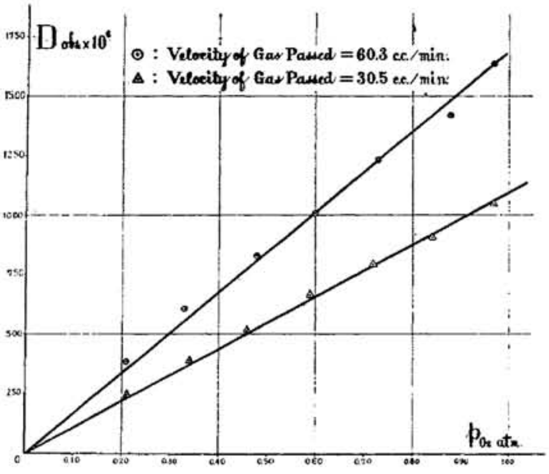

Fig. 3.

The values of $D_{obs.}$ in Tables 3 and 4 were calculated by the equation 1 using the observed values of k.

As will be seen in Tables 3 and 4 and in Figs. 2 and 3, the values of $k_{obs.}$ and $D_{obs.}$ can be expressed as a linear function of the partial pressure of oxygen of the gas passed. The values of $k_{calc.}$ and $D_{calc.}$ in the tables were calculated by the equations,

$$k_{calc.} = 0.669\,p$$
$$D_{calc.} = 16.73 \times 10^{-6}\,p$$

when the gas mixture was passed at the rate of 60.3 c.c. per minute, and

$$k_{calc.} = 0.437\,p$$
$$D_{calc.} = 10.93 \times 10^{-6}\,p$$

when the gas mixture was passed at the rate of 30.5 c.c. per minute.

The expectation was fullfiled; it was proved that the equations 6 and 7 can express the effect of the change of the partial pressure of oxygen on the velocity constant k or on the dissolution velocity D. The result confirms the author's consideration on the mechanism of this heterogeneous chemical reaction, described in the previous paper.

It was also verified that the value of α in the equations 2 and 3 can be regarded to be independent of the values of the partial pressure of oxygen of the gas mixture passed.

Summary.

(1) The oxidation velocity of sodium sulphite was observed when the mixture of oxygen and air was passed at uniform velocity under certain conditions.

(2) The observed oxidation velocities were independent of the concentration of sodium sulphite under the present conditions, and the velocity constant was found to be expressed as a linear function of the partial pressure of oxygen passed, as was expected.

(3) The theoretical interpretation on the observed result was given.

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