ON THE DISSOLUTION VELOCITY OF OXYGEN INTO WATER. PART I.

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Introduction. One of the authors⁽¹⁾ had studied the oxidation velocities of sodium sulphite, stannous hydroxide and ferrous hydroxide in alkaline or in acidic solutions by means of air and found that the observed velocities

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(1) S. Miyamoto, this Bulletin, **2** (1927), 74; **2** (1927), 155; **2** (1927) 259; **3** (1928), 76; **3** (1928), 137; **4** (1929), 48. *Scientific Papers of the Institute of Physical and Chemical Research*, **7** (1927), 40; **7** (1927), 189; **8** (1928), 93; **8** (1928), 230; **9** (1928), 203; **10** (1929), 7.

were independent of the concentrations of these oxidizable substances under the conditions of the author's experiments. The results were interpreted by the consideration that the dissolution velocity of oxygen is much slower than the true reaction velocity and the observed value will mean the dissolution velocity of oxygen into the liquid.

The phenomenon is a special case of the heterogeneous reaction between gaseous and liquid phases and the mechanism can be explained by the following considerations.

The difference between the number of molecules of a gas which enter into the liquid phase and the number of molecules of the gas which leave the liquid phase through definite boundary surface area per unit of time can be called the dissolution velocity of the gas into the liquid at the given temperature and pressure. It is evident that the dissolution velocity of a gas into a liquid depends upon the partial pressure of the gas and the nature of the boundary surface. We can then expect that the dissolution velocity of a gas into a given liquid at the given temperature and pressure will have a maximum value when the concentration of the gas in the boundary surface is kept zero.

This state can be maintained if the sufficient quantity of a substance be present in the surface layer to react with all of the molecules of the gas which enter into the liquid phase per unit of time. Under this condition, the dissolution velocity of the gas will be independent of the concentration of the reacting substances, if the presence of the necessary quantity of the latter in the surface have not much effect upon the nature of the boundary surface. The reaction velocity of the substance with the gas will also be maximum under this condition, and it can not increase however its concentration is increased, as the reaction velocity with the gas can not be greater than the maximum dissolution velocity of the gas into the liquid.

The phenomenon is in some degree analogous to that of the saturation current conducted by electrons emitted by a heated body in an electric field. The current can not be greater than a definite value however the strength of the field is increased, if the temperature of the heated body be kept constant.

Under the conditions of the present research, the oxidation velocity of sodium sulphite solution by means of air is independent of its concentrations. According to the viewpoint, above described, the result should mean the maximum reaction velocity of the solution with air at the given temperature, and the dissolution velocity of oxygen into water, obtained from the result, should mean the maximum dissolution velocity of oxygen into water at the given temperature and pressure.

Mitsukuri(1) has explained the dissolution velocity of carbon dioxide into sodium hydroxide solution by the consideration that the reaction takes place in the thin liquid surface layer. The result of this investigation will also be able to interprete by Mitsukuri's theory, if we only consider the thickness of the diffusion layer of oxygen is extremely small and the concentration of the reacting substance is sufficiently great. It will be impossible to decide whether it is necessary to assume the existence of the liquid film at the surface in order to interprete the present results.

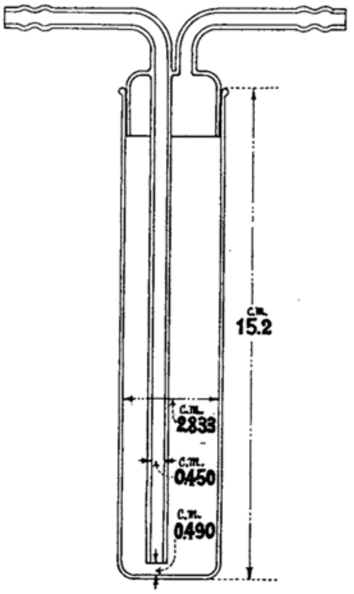

Fig. 1

Experimental. The oxidation velocities of sodium sulphite solution were observed when air is passed at various velocities. The experimental procedure is quite the same as that described in the previous papers.(2) The reacting vessel employed is shown in Fig. 1. Air, washed by acidified potassium bichromate solution and alkali, was passed at uniform velocity into the solution of sodium sulphite of known concentration, the total volume of the solution being made to 40 c.c. in each case. After t-minutes, the air current was stopped and the total quantity of the solution was poured into a known quantity of iodine solution, acidified with hydrochloric acid, 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.

The values of k are 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 $v_{calc.}$ given in the tables were obtained by the equation $v_{calc.}=v_0-k\ (t-t_0)$, using the mean value of k.

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(1) S. Mitsukuri, *The Science Reports of the Tohoku Imperial University*, Series 1, Vol. 18, No. 2. (June 1929).

(2) Loc. cit.

Table 1.

Temp. = 25°C.

Velocity of air c.c. / min.	t min.	v c.c.	$v_{calc.}$ c.c.	k.
30.5	3	19.83	—	—
	23	17.54	17.63	0.115
	43	15.21	15.43	0.116
	3	27.71	—	—
	23	25.39	25.51	0.116
	43	23.31	23.31	0.110
	3	33.68	—	—
	24	31.21	31.37	0.118
	43	29.17	29.28	0.113
	3	38.32	—	—
	23	36.10	36.12	0.111
	43	34.01	33.92	0.108
	3	47.50	—	—
	21	45.65	45.52	0.103
	41	43.39	43.32	0.108
	3	52.37	—	—
	23	50.49	50.17	0.094
	43	48.19	47.97	0.105
			Mean	0.110
60.3	3	19.45	—	—
	23	16.23	16.11	0.161
	43	12.99	12.77	0.162
	3	27.58	—	—
	23	24.24	24.24	0.167
	43	20.97	20.90	0.165
	3	34.49	—	—
	23	31.01	31.15	0.174
	43	27.67	27.81	0.171
	3	40.66	—	—
	23	37.14	37.32	0.176
	43	33.83	33.98	0.171
	3	47.60	—	—
	23	44.24	44.26	0.168
	43	41.11	40.92	0.162
	3	54.03	—	—
	23	50.80	50.69	0.162
	43	47.42	47.35	0.165
			Mean	0.167

Table 1.—(*Continued*).

Velocity of air c.c. / min.	t min.	v. c c.	$v_{calc.}$ c.c.	k.
86.7	3	16.32	—	—
	23	12.24	12.14	0.204
	43	7.49	7.96	0.221
	3	17.66	—	—
	43	9.16	9.30	0.213
	3	18.89	—	—
	23	14.95	14.71	0.197
	43	9.91	10.53	0.225
	3	20.01	—	—
	23	15.76	15.83	0.213
	43	11.70	11.65	0.208
	3	23.82	—	—
	23	19.82	19.64	0.200
	43	15.40	15.46	0.210
	3	26.53	—	—
	23	22.27	22.35	0.213
	43	18.62	18.17	0.198
	3	27.52	—	—
	23	23.59	23.34	0.197
	43	19.25	19.16	0.202
	3	30.21	—	—
	23	26.06	26.03	0.208
	43	22.18	21.85	0.202
	3	33.21	—	—
	23	28.95	29.03	0.213
	43	24.58	24.85	0.216
	3	33.68	—	—
	7	32.84	32.84	0.210
	28	28.21	28.45	0.219
	3	41.46	—	—
	23	37.68	37.28	0.189
	43	33.18	33.10	0.207
	3	46.60	—	—
	23	42.27	42.42	0.217
	43	38.01	38.24	0.215
	3	51.26	—	—
	23	46.99	47.08	0.214
	44	42.20	42.69	0.221
			Mean	0.209

Table 1.—(*Continued*).

Velocity of air c.c. / min.	t min.	v c.c.	$v_{calc.}$ c.c.	k.
111.7	3	16.60	—	—
	23	11.77	11.58	0.242
	43	7.07	6.58	0.238
	3	18.91	—	—
	23	14.11	13.89	0.240
	43	8.49	8.87	0.261
	3	22.20	—	—
	43	12.57	12.16	0.241
	3	22.58	—	—
	23	17.43	17.56	0.258
	43	12.20	12.54	0.260
	3	24.82	—	—
	23	19.80	19.80	0.251
	43	14.27	14.78	0.264
	3	28.64	—	—
	23	23.78	23.62	0.243
	43	18.47	18.60	0.254
	3	28.87	—	—
	23	24.04	23.85	0.242
	43	18.40	18.83	0.262
	3	32.70	—	—
	23	27.77	27.68	0.247
	43	21.98	22.66	0.268
	3	40.01	—	—
	23	35.06	34.99	0.248
	43	30.00	29.97	0.250
			Mean	0.251
137.0	3	20.90	—	—
	43	8.54	9.06	0.309
	3	23.00	—	—
	23	17.16	17.08	0.292
	43	11.87	11.16	0.278
	3	31.01	—	—
	23	24.95	25.09	0.303
	43	18.48	19.17	0.313
	3	35.16	—	—
	23	29.40	29.24	0.288
	43	23.70	23.32	0.287
	3	39.77	—	—
	43	28.16	27.93	0.290
	3	44.93	—	—
	43	33.29	33.09	0.291
	3	45.13	—	—
	23	39.25	39.21	0.294
	43	33.07	33.29	0.302
	3	52.15	—	—
	23	46.22	46.23	0.297
	43	40.37	40.31	0.295
	3	58.72	—	—
	23.5	52.58	52.65	0.300
	43.5	46.52	46.73	0.301
			Mean	0.296

Table 1.—(*Continued*).

Velocity of air c.c. / min.	t min.	v c.c.	$v_{calc.}$ c.c.	k.
160.8	3	21.80	—	—
	43	8.34	8.48	0.337
	3	22.50	—	—
	23	16.19	15.84	0.316
	43	9.90	9.18	0.315
	3	31.17	—	—
	23	24.61	24.51	0.328
	43	17.69	17.85	0.337
	3	33.43	—	—
	43	20.41	20.11	0.326
	3	38.75	—	—
	23	32.29	32.09	0.323
	43	24.89	25.43	0.347
	3	43.33	—	—
	43	29.97	30.01	0.334
	3	45.51	—	—
	23	38.75	38.85	0.338
	43	32.13	32.19	0.335
	3	55.96	—	—
	23	49.17	49.30	0.340
	43	42.46	42.64	0.338
	3	57.22	—	—
	42	43.44	44.23	0.353
			Mean	0.333
182.8	3	31.29	—	—
	43	17.07	17.01	0.356
	3	31.67	—	—
	43	17.30	17.39	0.359
	3	52.78	—	—
	43	38.80	38.50	0.350
	3	58.22	—	—
	43	43.51	43.94	0.368
	3	68.88	—	—
	43	54.72	54.60	0.354
			Mean	0.357

Table 1.—(*Continued*).

Velocity of air c.c. / min.	t min.	v c.c.	$v_{calc.}$ c.c.	k.
201.8	3	34.20	—	—
	23	26.40	26.22	0.390
	43	17.77	18.24	0.411
	3	42.41	—	—
	43	26.09	26.45	0.408
	3	45.65	—	—
	23	37.85	37.67	0.390
	43	29.82	29.69	0.396
	3	45.76	—	—
	43	29.72	29.80	0.401
	3	50.26	—	—
	23	42.12	42.28	0.407
	43	34.51	34.30	0.394
	3	50.94	—	—
	43	34.36	34.98	0.415
	3	58.41	—	—
	23	50.64	50.44	0.389
	43	42.17	42.46	0.406
	3	66.93	—	—
	43	51.66	50.97	0.382
			Mean	0.399

Table 2.

Temp. = 25°C.

V (Velocity of air) c.c./min.	$k_{obs.}$	$k_{calc.}$	$D_{obs.}$ (Dissolution velocity of oxygen) moles/min.	$D_{calc.}$ (Dissolution velocity of oxygen) moles/min.
30.5	0.110	0.115	2.75×10^{-6}	2.89×10^{-6}
60.3	0.167	0.165	4.18 ,,	4.12 ,,
86.7	0.209	0.208	5.23 ,,	5.20 ,,
111.7	0.251	0.249	6.28 ,,	6.23 ,,
137.0	0.296	0.291	7.40 ,,	7.28 ,,
160.8	0.333	0.330	8.33 ,,	8.26 ,,
182.8	0.357	0.366	8.93 ,,	9.16 ,,
201.8	0.399	0.398	9.98 ,,	9.95 ,,

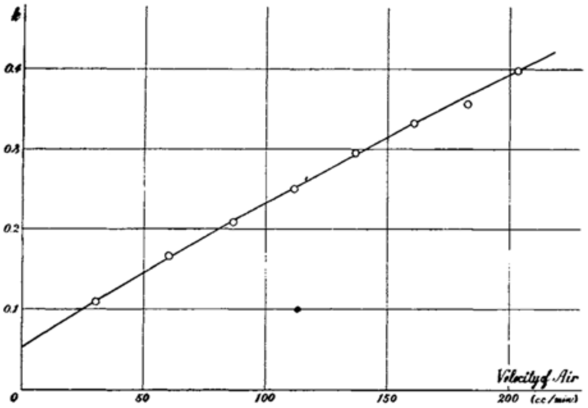

Fig. 2.

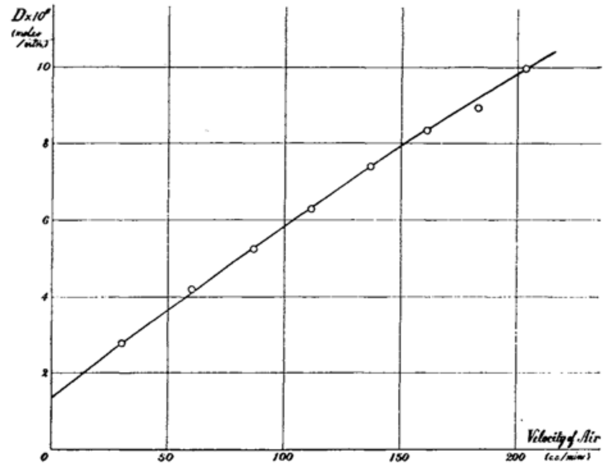

Fig. 3.

The oxidation velocity observed is thus independent of the concentration of sodium sulphite. According to the viewpoint above described, the observed value is the maximum oxidation velocity of sodium sulphite by means of air.

From the results it can be seen that the velocity constant is a linear function of the velocity of air passed, as is shown graphically in Fig. 2. The values of $k_{calc.}$, given in the third column of Table 2, were calculated by

$$k_{calc.}=0.001648V+0.0652 \quad \ldots\ldots \quad (1)$$

where V is the velocity of air passed.

The observed velocity constant k means the volume of sodium thiosulphate solution of 0.1000 normal equivalent to the amount of sodium sulphite oxidized per minute. Then the dissolution velocity of oxygen into water under this special condition can be expressed by

$$D_{obs.}=\frac{1}{4}k_{obs.}\times 10^{-4} \text{ moles per minute.} \quad \ldots\ldots \quad (2)$$

The calculated values of D by this equation are given as $D_{obs.}$ in the fourth column of Table 2. It is evident that $D_{obs.}$ is a linear function of the velocity of air passed in this case. It is shown graphically in Fig. 3. The values of $D_{calc.}$ given in the last column of Table 2 are those calculated by

$$D_{calc.}=4.121\times 10^{-8}V+1.630\times 10^{-6} \quad \ldots\ldots \quad (3)$$

Theoretical. According to the kinetic theory of gases, total number of molecules which collide with unit boundary surface area per unit of time can be expressed by

$$\frac{NP}{\sqrt{2\pi MRT}} \quad \ldots\ldots \quad (4)$$

where N=Avogadro's constant,
P =partial pressure of the gas,
M=molecular weight of the gas,
R =the gas constant,
T =absolute temperature.

Total number of molecules which enter into the liquid phase per unit of time through unit boundary surface area can be expressed by

$$\frac{\alpha NP}{\sqrt{2\pi MRT}} \quad \ldots\ldots \quad (5)$$

where α is a quantity which depends upon the nature of the gas and the liquid and the partial pressure of the gas. With regard to one liquid, in the surface of which the concentration of the gas is kept zero, α may be represented by

$$\alpha=f(P) \quad \ldots\ldots \quad (6)$$

Under this condition α may be taken to be constant if the partial pressure of the gas be constant.

The total boundary surface area which is in contact with the gas can be represented in the present experiment by

$$4\pi r^2 n \frac{l}{u} + s_0 \quad \cdots\cdots \quad (7)$$

where r=radius of a bubble,

n=number of bubbles passed per second,

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

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.

From (5) and (7) we can represent the total number of molecules which enter into the liquid phase per second by

$$\frac{aNP}{\sqrt{2\pi MRT}}\left(4\pi r^2 n \frac{l}{u} + s_0\right) \quad \cdots\cdots \quad (8)$$

The dissolution velocity of the gas can then be represented by

$$D = \frac{60aP}{\sqrt{2\pi MRT}}\left(4\pi r^2 n \frac{l}{u} + s_0\right) \text{ moles per minute.} \quad \cdots\cdots \quad (9)$$

when the concentration of the gas in the surface layer is kept zero. Now,

$$n = \frac{1}{60}\frac{V}{\frac{4}{3}\pi n^3} \quad \cdots\cdots \quad (10)$$

where V denotes the volume of the gas passed per minute.

Then,

$$D = \frac{60aP}{\sqrt{2\pi MRT}}\left(\frac{Vl}{20ru} + s_0\right) \text{ moles per minute.} \quad \cdots\cdots \quad (11)$$

Under the conditions of this research, the dissolution velocity of oxygen should be regarded as the maximum value, and the value of a can be considered to have a definite maximum value. As the values of P, T, r, and u are constant, from the equation (11) we have,

$$D = AV + B \quad \cdots\cdots \quad (12)$$

where A and B are constants.

From (2) and (11) we have,

$$k = \frac{24aP \times 10^5}{\sqrt{2\pi MRT}}\left(\frac{Vl}{20ru} + s_0\right) \quad \cdots\cdots \quad (13)$$

Under the present conditions,

$$k = A'V + B' \qquad (14)$$

where A' and B' are constants.

The equations (12) and (14) are in good agreement with the experimental facts, above described.

The calculation of the values of α and s_0. The value of α in the above equations depends upon the condition of the boundary surface and the partial pressure of the gas. If the concentration of the gas in the surface layer be kept zero, α will have a definite specific value with regard to the liquid and gas. From the present experimental results we can calculate the maximum value of α concerning water and oxygen, whose partial pressure is 15.96 cm. Hg.

From the equations (3) and (11) we obtain,

$$\frac{3\alpha Pl}{r\, u \sqrt{2\pi MRT}} = 4.121 \times 10^{-8} \qquad (15)$$

If we know the values of l, r, and u we can calculate the value of α from the equation (15).

The value of r was obtained by the following process. Air was passed into the reacting vessel from a gas burette at uniform velocity. From the volume of air passed, we can calculate the radius of one bubble by counting the number of bubbles. A slight difference of the radius of the bubble was observed, when we change the velocity of air passed. The mean value of the radius of a bubble was found to be 0.334 cm. when the mean value of the velocity of air passed is about 19.64 c.c. per minute. This value was employed for the calculation as an approximate value of the radius of a bubble.

According to the study on the motion of an air bubble rising in water by O. Miyagi,(1) the ascending velocity of an air bubble attains an uniform value almost immediately when it leaves the exit, and the ascending velocity is 23.1 cm. per second when the radius of the bubble is 0.334 cm. As the viscosity of sodium sulphite solution of such concentration as that employed in the present research is not much different from that of pure water, it can be expected that the ascending velocity of the air bubble in the solution will nearly be the same as that in pure water. The value 23.1 cm. per second was employed as an approximate value of u in the following calculations.

The value of l was observed directly to be 6.20 cm.

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(1) *Phil. Mag.*, **50** (1925), 112.

By introducing these values in the equation (15) we have,

$$\alpha=\frac{4.121\times10^{-8}r\,u\sqrt{2\pi MRT}}{3Pl}=1.794\times10^{-7}$$

This value means 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 when the partial pressure of oxygen is about 0.21 atmosphere, the concentration of oxygen in the surface being maintained to be zero. The obtained value of α is the definite specific value with regard to water and oxygen at the given temperature and pressure.

The present chemical method will be able to employ in order to calculate the value of α with regard to various liquids and gases.

From the equations (3) and (11) we have,

$$\frac{60\alpha P}{\sqrt{2\pi MRT}}s_0=1.630\times10^{-6}$$

By introducing the value of α above obtained,

$$s_0=1.59\ \text{cm.}^2$$

The calculated value of s_0 from Fig. 1 is about 5 cm.^{2} It is not curious that the calculated value of s_0 is much smaller than this value, for the most part of the upper surface of the liquid is occupied by the surface of the bubbles passed incessantly.

Summary.

(1) The oxidation velocity of sodium sulphite solution was observed when air is passed at various velocities.

(2) It was found that the oxidation velocities are independent of the concentration of sodium sulphite and the velocity constant was expressed as a linear function of the velocity of air passed.

(3) The dissolution velocity of oxygen into water when the concentration of oxygen in the surface layer is kept zero, was calculated from the obserbed reaction velocity, and it was found to be expressed as a linear function of the velocity of air passed.

(4) An interpretation of the mechanism of this reaction under the observed conditions was given.

(5) The maximum value of the ratio of the total number of molecules of oxygen which enter into water to the total number of molecules of oxygen which collide with the unit boundary surface per unit of time at 25° C. was calculated from the observed results.

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