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

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Introduction. The oxidation velocity of sodium sulphite, when the mixture of oxygen and air is passed into the solution through a narrow glass-tube under various conditions, and the dissolution velocity of oxygen into water calculated from the observed value of the oxidation velocity, were reported in the previous papers.(1) In these measurements, the gas bubbles, which ascend in the solution, agitate the solution so violently that in the boundary surface layer a sufficient quantity of sodium sulphite is always present to react with the oxygen molecules which enter into the liquid phase, and the observed oxidation velocity of sodium sulphite gives the dissolution velocity of oxygen into water, when the concentration of sodium sulphite is not below a certain value.

It will be expected that the reaction velocity of the oxidation of sodium sulphite which takes place on the free surface layer of the solution in the atmosphere of oxygen will be independent of the contentration of sodium sulphite and give the dissolution velocity of oxygen into water, when the condition is satisfied under which a sufficient quantity of sodium sulphite is always present in the boundary surface layer.

As will be seen in the subsequent discussion, the dissolution velocity of oxygen, here described, is the value when the concentration of oxygen in the surface layer is maintained at zero.

It is intended in the present paper to report the observed oxidation velocity of sodium sulphite in the atmosphere of oxygen, studied under the following conditions and to give a theoretical consideration on the result.

The direct measurements of the rates of solution of oxygen into water were carried out by several writers.

Adeney and Becker(2) measured the dissolution velocity of oxygen into water from bubbles of known magnitudes. Davis and Crandall(3) carried out the direct measurement of the rates of solution of oxygen into water from the water surface of known area, the main body of water being agitated with a stirrer of special construction.

The initial rate of solution of oxygen into water, observed by these writers, should be equal to the dissolution velocity, calculated from the oxidation velocity of sodium sulphite, if the interpretation above described be acceptable. In Table 4 the values are compared.

Davis and Crandall explained the process of the dissolution velocity of a gas into a liquid by the two film theory,(4) and they assumed the surface of the liquid film is instantaneously saturated with the gas.

The existence of a thin film at the boundary surface may generally be accepted, but it will be difficult to explain the result of the present research

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(1) Miyamoto and Kaya, this Bulletin, **5** (1930), 123; Miyamoto, Kaya and Nakata, ibid., **5** (1930), 229; Miyamoto and Kaya, ibid., **5** (1930), 321.

(2) *Phil. Mag.*, **38** (1919), 317; **39** (920), 385; **42** (1921), 87.

(3) *J. Am. Chem. Soc.*, **52** (193), 3757, 3769.

(4) Lewis and Whitman, *Ind. Eng. Chem.*, **16** (1924), 1215.

by the assumption that the surface of the liquid film is instantaneously saturated with the gas, for the oxidation velocity of sodium sulphite is independent of its concentrations. One of the present writers (Miyamoto) has a different opinion on the mechanism of the rate of solution of a gas into a liquid, a part of which is described in the later. The precise discussion on the dissolution theory of a gas will be given in another occasion.

The direct measurement of the rate of solution of oxygen into water was also carried out by Morgan and Pyne,(1) but in their paper the numerical value of the boundary surface area is not given.

Experimental. The apparatus graphically shown in Fig. 1, was employed for the reacting vessel. Oxygen gas, washed by acidified potassium bichromate and sodium hydroxide solutions, is passed at a high velocity through A into the apparatus, which contains 30–50 c.c. of water, for about 30 minutes. When the air in the apparatus has been completely replaced by oxygen, the stirrer S is put in motion at the rate of about 400 revolutions per minute, and a definite quantity of sodium sulphite solution is added in the water from B. The stop-watch is started when about the half volume of the sodium sulphite solution has been poured in the vessel. Oxygen gas is passed at the rate of about 10 liters per hour. The quantity of sodium sulphite added is separately determined by the usual method of iodmetry. The stirrer is made of glass and it is so situated that its wing is vertical to the boundary surface to avoid the disturbance of the surface area.

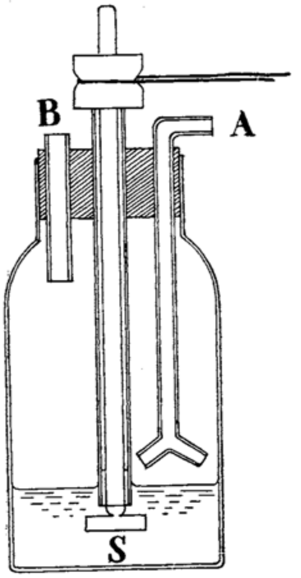

Fig. 1

After the elapse of t- minutes, the oxygen current is stopped and nitrogen gas is passed from B at a high velocity to replace the oxygen in the apparatus quickly. The total quantity of the solution is poured into a known quantity of iodine solution, acidified with hydrochloric acid, and the excess of iodine is titrated back by means of sodium thiosulphate solution.

In Table 1, v is the volume of sodium thiosulphate solution of 0.1000 normal, equivalent to the amount of sodium sulphite remained in the vessel. The velocity constant k is calculated by

$$k=\frac{v_0-v}{t},$$

where v_0 is the value of v at $t=0$.

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(1) *J. Phys. Chem.*, **34** (1930), 1818.

Table 1.

Temp.	p_{O_2} atm.	S cm.^{2}	t min.	v c.c.	$v_{calc.}$ c c.	k
15°C.	0.954	17.11	0	148.01	——	——
			50	137.17	137.11	0.217
			0	174.07	——	——
			50	163.05	163.17	0.220
			0	203.71	——	——
			50	193.10	192.81	0.212
			0	230.51	——	——
			50	219.58	219.61	0.219
			0	263.34	——	——
			50	252.30	252.44	0.221
					Mean	0.218
		26.31	0	145.26	——	——
			30	134.54	134.34	0.357
			0	145.41	——	——
			30	134.40	134.49	0.367
			0	179.96	——	——
			30	169.15	169.04	0.360
			0	227.06	——	——
			30	216.13	216.14	0.364
			0	263.06	——	——
			30	251.94	252.14	0.371
					Mean	0.364

Table 1.—(*Continued*)

Temp.	p_{O_2} atm.	S cm.^{2}	t min.	v c.c.	$v_{calc.}$ c.c.	k
25°C.	0.941	9.22	0	75.24	——	——
			90	54.06	54.45	0.235
			0	93·58	——	——
			90	75.58	72.79	0.225
			0	99.18	——	——
			90	78.58	78.39	0.229
			0	198.11	——	——
			90	177.49	177.32	0.229
			0	220.93	——	——
			96	198.00	198.75	0.239
					Mean	0.231
		17.11	0	134.65	——	——
			50	113.03	112.60	0.432
			0	139.29	——	——
			50	116.00	117.24	0.466
			0	159.77	——	——
			50	137.94	137.72	0.437
			0	185.22	——	——
			50	163.64	163.17	0.432
			0	189.57	——	——
			50	167.76	167.52	0.436
			0	240.14	——	——
			50	218.02	218.09	0.442
					Mean	0.441

Table 1.—(*Continued*)

Temp.	p_{O_2} atm.	S cm.^{2}	t min.	v c.c.	$v_{calc.}$ c.c.	k
25°C.	0.941	26.31	0	119.67	—	—
			30	98.86	99.21	0.694
			0	121.87	—	—
			30	101.64	101.41	0.674
			0	133.33	—	—
			31	112.05	112.19	0.686
			0	134.67	—	—
			30	114.68	114.21	0.666
			0	140.08	—	—
			30	120.14	119.62	0.665
			0	164.57	—	—
			30	143.88	144.11	0.690
			0	189.52	—	—
			30	168.59	169.06	0.698
			0	209.11	—	—
			30	188.64	188.65	0.682
					Mean	0.682
		42.75	0	122.37	—	—
			20.33	99.83	100.01	1.109
			0	136.47	—	—
			20	113.96	114.47	1.126
			0	163.30	—	—
			50	108.83	108.30	1.089
			0	187.65	—	—
			51.5	130.92	131.00	1.102
			0	209.68	—	—
			50	154.97	154.68	1.094
			0	234.03	—	—
			50	179.86	179.03	1.083
					Mean	1.101

Table 1.—(*Concluded*)

Temp.	p_{O_2} atm.	S cm.^{2}	t min.	v c.c.	$v_{calc.}$ c.c.	k
35°C.	0.916	17.11	0	146.99	—	—
			50	114.88	113.69	0.642
			0	178.43	—	—
			50	146.22	145.13	0.644
			0	205.95	—	—
			50.33	171.15	172.43	0.691
			0	231.99	—	—
			50	198.62	198.69	0.667
			0	261.14	—	—
			50	226.82	227.84	0.686
					Mean	0.666
		26.31	0	147.92	—	—
			30	118.63	117.08	0.976
			0	204.35	—	—
			30.25	173.06	173.25	1.034
			0	235.54	—	—
			30	203.27	204.70	1.076
			0	262.06	—	—
			30	231.50	1.22	1.019
			0	288.99	—	—
			30	257.93	258.15	1.035
					Mean	1.028

The values of $v_{calc.}$ given in the Table, are obtained by

$$v_{calc.}=v_0-kt\ ,$$

using the mean value of k.

Under the present conditions, the oxidation velocity is independent of the concentration of sodium sulphite and is proportional to the boundary surface area, as will be seen in Table 1.

The result is easily interpreted by the assumption that the oxidation velocity of sodium sulphite, when it is independent of its concentrations, is not the real reaction velocity but the dissolution velocity of oxygen into water. Then the relation between the observed velocity constant and the dissolution velocity of oxygen is given by

$$D_0=\frac{1}{4}k\times 10^{-4} \text{ moles per minute, } \ldots\ldots\ldots\ldots\ (1)$$

where D_0 means the dissolution velocity of oxygen into water when its concetration in the surface layer is kept at zero.

The values of $k_{obs.}$ and the dissolution velocity D_0, calculated by the equation (1), are given in the 4th and the 6th column of Table 2.

In the 5th and the 7th column, the values of $k_{calc.}$ and $D_{calc.}$, calculated by the following linear equations with respect to the surface area S, are given.

$$k_{calc.}=0.0133\,S,\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (2)$$

$$D_{0calc.}=0.332\times 10^{-6}\,S,\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (3)$$

at 15°C.,

$$k_{calc.}=0.0258\,S,\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (2')$$

$$D_{0calc.}=0.645\times 10^{-6}\,S,\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (3')$$

at 25°C. and

$$k_{calc.}=0.0390\,S,\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (2'')$$

$$D_{0calc.}=0.975\times 10^{-6}\,S,\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (3'')$$

at 35°C. .

The surface area S is obtained by the measurement of the rise of the level for the addition of a definite volume of water into the vessel.

The partial pressure of oxygen, given in the 2nd column of Table 1 or 2, were calculated from the composition of the gas passed and for the vapour pressure of the solution the vapour pressure of pure water was employed as a first approximation.

Table 2.

Temp.	p_{O_2} atm.	S cm.^{2}	$k_{obs.}$	$k_{calc.}$	D_0 *obs.* moles/min.	D_0 *calc.* moles/min.
15°C.	0.954	17.11	0.218	0.228	5.45×10^{-6}	$5.70\times10^{-}$
		26.31	0.364	0.350	9.10 ,,	8.75 ,,
25°C.	0.941	9.22	0.231	0.233	5.78×10^{-6}	5.95×10^{-6}
		17.11	0.441	0.441	11.03 ,,	11.03 ,,
		26.31	0.682	0.679	17.05 ,,	16.98 ,,
		42.75	1.101	1.103	27.53 ,,	27.58 ,,
35°C.	0.916	17.11	0.666	0.667	16.65×10^{-6}	16.68×10^{-6}
		26.31	1.028	1.026	25.70 ,,	25.65 ,,

The observed result is graphically shown in Fig. 2 and Fig. 3.

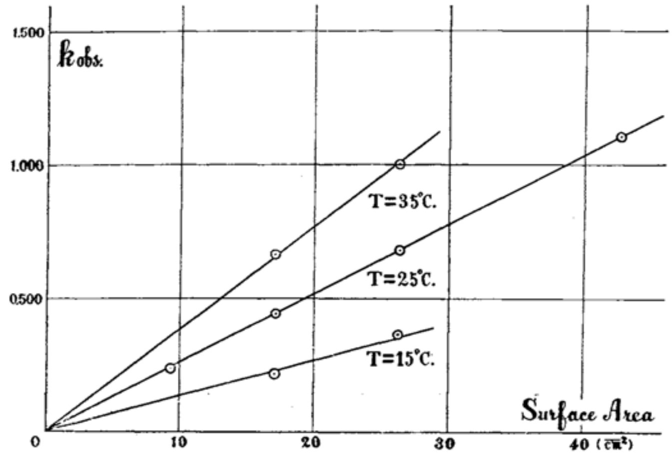

Fig. 2.

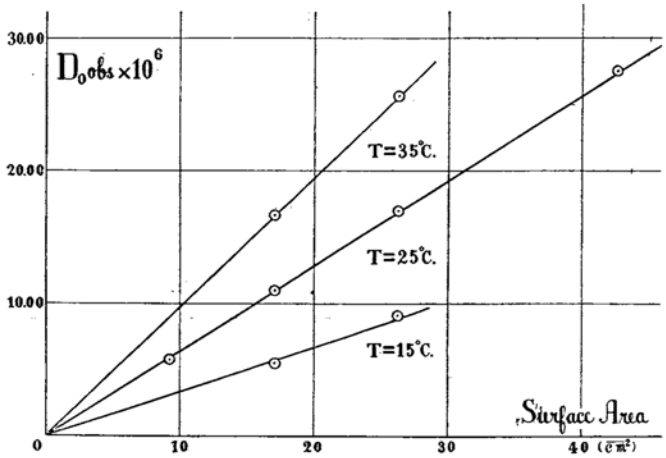

Fig. 3.

Theoretical. The dissolution velocity of a gas into a liquid can generally be given by

$$D=N''S-f(c)\,S\,, \quad\dots\dots\dots\dots\dots\dots\dots\dots \quad (4)$$

where N'' = the number of the molecules which enter into the liquid phase through the unit boundary surface area per unit of time,

$f(c)$ = the number of the molecules which leave the liquid phase through the unit boundary surface area per unit of time, and this value can be considered to be a function of the concentration of the gas in the surface layer,

S = the area of the boundary surface.

When the concentration of the gas in the surface layer is kept at zero, the dissolution velocity is represented by

$$D_0=N''S\,. \quad\dots\dots\dots\dots\dots\dots\dots\dots \quad (5)$$

This state is maintained so long as the sufficient quantity of a substance which reacts readily with the gas, be always present in the surface layer as in the case of the present experiment.

$$N''=\beta N'\,, \quad\dots\dots\dots\dots\dots\dots\dots\dots \quad (6)$$

where N' = the number of the molecules which collide with the unit area of the boundary surface per unit of time,

β = the ratio of the number of the molecules which penetrate into the liquid phase and the number of the molecules which collide with the liquid surface.

By Maxwell's distribution law of velocities,

$$dN=\frac{N}{\sqrt{\pi}\,\alpha}e^{-\frac{u^2}{\alpha^2}}du\,, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

where dN= the number of the molecules whose component of velocity parallel to one axis lies between u and $u+du$ among N molecules.

$$\alpha^2=\frac{2RT}{M}\,, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

where R= the gas constant,
M= the molecular weight of the gas.

Then,

$$N'=\int_0^\infty \frac{N}{V\sqrt{\pi}\,\alpha}u\,e^{-\frac{u^2}{\alpha^2}}du=\frac{N\alpha}{2V\sqrt{\pi}}\,, \quad \ldots\ldots\ldots\ldots (9)$$

where N= Avogadro's constant,
V= the molar volume.

From (8) and (9),

$$N'=\frac{Np}{\sqrt{2\pi MRT}}\,. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

Now the following assumption, which has great probability, is adopted. Among the molecules, which collide with the liquid surface, only those molecules, whose components of velocity vertical to the surface are greater than a threshold value u_0, are able to enter into the liquid phase. Then,

$$N''=\int_{u_0}^\infty \frac{N}{V\sqrt{\pi}\,\alpha}u\,e^{-\frac{u^2}{\alpha^2}}du=\frac{N\alpha}{2V\sqrt{\pi}}e^{-\frac{u_0^2}{\alpha^2}}\,, \quad \ldots\ldots\ldots (11)$$

or,

$$N''=\frac{Np}{\sqrt{2\pi MRT}}e^{-\frac{Mu_0^2}{2RT}}\,. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (12)$$

From (6), (10) and (12) we have,

$$\beta=e^{-\frac{Mu_0^2}{2RT}}\,. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (13)$$

From (5) and (12),

$$D_0=\frac{Np}{\sqrt{2\pi MRT}}e^{-\frac{Mu_0^2}{2RT}}S \text{ molecules / sec.}$$

$$=\frac{60p}{\sqrt{2\pi MRT}}e^{-\frac{Mu_0^2}{2RT}}S \text{ moles / min.} \qquad \ldots\ldots\ldots\ldots (14)$$

From (1) and (14),

$$k=\frac{24p\times 10^{-5}}{\sqrt{2\pi MRT}}e^{-\frac{Mu_0^2}{2RT}}S\,. \qquad \ldots\ldots\ldots\ldots (15)$$

When all the values except the surface area are kept at constant,

$$D_0=AS\,, \qquad \ldots\ldots\ldots\ldots (16)$$

$$k=BS\,, \qquad \ldots\ldots\ldots\ldots (17)$$

where A and B are constants.

Thus the experimental equations, above obtained, are theoretically endorsed.

The calculation of the threshold value u_0. From the equations (13) and (15),

$$\beta=\frac{\sqrt{2\pi MRT}}{24p_{o_2}\times 10^5}\frac{k}{S}\,, \qquad \ldots\ldots\ldots\ldots (18)$$

$$u_0=\sqrt{\frac{-2RT\ln\beta}{M}}\,. \qquad \ldots\ldots\ldots\ldots (19)$$

The value of β, which stands for the ratio of the number of the molecules of oxygen which enter into water and the number of the molecules of oxygen which collide with the liquid surface, can be calculated by the equation (18), using the experimentally obtained values of $\frac{k}{S}$, given in the equations (2), (2′) and (2″).

Then the threshold value u_0 can be calculated by the equation (19).

The values of β and u_0, thus obtained, are given in the 4th and the 5th column of Table 3.

The present calculation is based upon the assumption, that among the molecules of oxygen which collide with the water surface, only the molecule, whose component of velocity is greater than the threshold value u_0, can enter into the liquid phase.

Table 3.

Temp.	p_{O_2} atm.	$\frac{k}{S}$	β	u_0 cm./sec.	$\sqrt{\bar{c}^2}$ cm./sec.
15°C.	0.954	0.0133	1.258×10^{-8}	1.650×10^{5}	4.74×10^{4}
25°C.	0.941	0.0258	2.517×10^{-8}	1.646×10^{5}	4.82×10^{4}
35°C.	0.916	0.0390	3.974×10^{-8}	1.651×10^{5}	4.90×10^{4}

It was first expected that the value u_0 would depend upon the temperature, but the calculated values of u_0 at 15°C., 25°C. and 35°C. are almost identical. It was thus confirmed that the value u_0 is independent of the temperature within the observed region.

The root-mean-square velocity of oxygen molecules, calculated by

$$\sqrt{\bar{c}^2}=\sqrt{\frac{3RT}{M}}\,,$$

is given in the last column of Table 3.

It follows from the present research that only the molecule of oxygen, whose vertical component of velocity is greater than approximately 3.4 times the root-mean-square velocity, can enter into water.

The initial rates of solution of oxygen into water. The initial rates of solution of oxygen into water should be equal to the value D_0, calculated from the maximum oxidation velocity of sodium sulphite, when the water employed is perfectly free from oxygen.

From the equations (3), (3′) and (3″), the dissolution velocity of oxygen from unit surface area per second can be calculated.

Becker⁽¹⁾ measured the absorption velocity of oxygen from air into alkaline water containing suspensions of ferrous hydroxide. It was confirmed that the absorption rate tend to a maximum, independent of further increases in the stirring speed, but the effect of the amount of ferrous hydroxide was not studied. The maximum value should be equal to the initial rates of solution into the alkaline solution. The dissolution velocity of oxygen into alkaline solution is not the same as that into water.⁽²⁾

In Table 4 the initial rates of solution of oxygen into water, directly observed, are given in comparison with the values, chemically obtained.

Adeney and Becker observed the initial rates of solution is independent of temperature, while the value, calculated from the oxidation velocity of sodium sulphite by the present writer, depends upon temperature.

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(1) *Phil. Mag.*, **45** (1923), 581.
(2) Miyamoto, this Bulletin, **2** (1927), 74; **3** (1928), 98.

Table 4.

Observer	Method	Temp.	Initial rates of solution moles per cm.^{2} per sec.
Davis and Crandall	directly	25°C.	4.5×10^{-9}
,,	,,	25°C.	2.6×10^{-9}
Adeney and Becker	,,	35.1°C.	10.6×10^{-9}
,,	,,	25.2°C.	11×10^{-9}
,,	,,	15.5°C.	11×10^{-9}
,,	,,	2.5°C.	11.3×10^{-9}
Conant and Scherp	,,	25°C.	28×10^{-9}
,,	,,	25°C.	24×10^{-9}
Davis and Crandall	100 c.c. 1N·K_2SO_4 $+Fe(OH)_2$	25°C.	1.0×10^{-9}
Becker	100 c.c. water containing $Fe(OH)_2 + KOH$		5.2×10^{-9}
Miyamoto and Nakata	40 c.c. water containing	15°C.	5.53×10^{-9}
,,	Na_2SO_3 of various	25°C.	11.75×10^{-9}
,,	concentrations	35°C.	16.25×10^{-9}

Summary.

(1) The oxidation velocity of sodium sulphite was studied, when the condition is satisfied, under which the concentration of oxygen in the boundary surface layer is always zero. The oxidation velocity is independent of the concentration of sodium sulphite and is proportional to the boundary surface area.

(2) The theoretical considerations on the observed oxidation velocity was given.

(3) The assumption that only the molecule of oxygen, whose component of velocity vertical to the boundary surface is greater than a threshold value u_0 is able to enter into the liquid phase, was given, and the values of u_0 were calculated at 15°C., 25°C. and 35°C. from the experimentally obtained result.

The calculated value of u_0 is 1.65×10^5 cm. per sec. and is independent of the temperature within the observed region.

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