ON THE RATE OF SOLUTION OF OXYGEN INTO WATER. PART VI. THE RATE OF ABSORPTION OF OXYGEN BY SODIUM SULPHITE SOLUTION.

By Susumu MIYAMOTO and Tetsuo KAYA.

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Introduction.

It was confirmed in the previous research⁽¹⁾ that the velocity of oxidation of sodium sulphite solution by oxygen, when the main body of the solution is well agitated with a stirrer of special construction, increases with the increase of the concentration of sodium sulphite as far as it attains a certain maximum value, which remains constant with the further increase of the concentration of sodium sulphite and that this maximum value is proportional to the area of the boundary surface.

The fact that the maximum rate of oxidation of sodium sulphite solution is proportional to the partial pressure of oxygen was also confirmed⁽²⁾. The interpretation on these experimental facts, given by the present writers, is based upon the assumption that the maximum rate of oxidation of sodium sulphite solution is equivalent to the rate of solution of oxygen into water, in the surface of which no free oxygen is present.

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(1) S. Miyamoto and A. Nakata, this Bulletin, **6** (1931), 9.

(2) S. Miyamoto, T. Kaya and A. Nakata, ibid., **5** (1930), 229.

The comparison(1) of the rate of solution of oxygen, calculated from the maximum rate of oxidation of sodium sulphite solution, with the initial rate of solution of oxygen into pure water, obtained directly by several writers(2), confirmed that this assumption has great probability.

It is intended in the present paper to describe the results of the measurements of the rate of absorption of oxygen by sodium sulphite solution by the observation of the rate of the decrease of the volume of oxygen at constant temperature and pressure, which is in contact with sodium sulphite solution, the main body of which being well agitated with a stirrer of special constructions as in the previous research, and to discuss the phenomenon more precisely.

Experimental.

The apparatus employed is graphically shown in Fig. 1.

D is a gas burette (25 c.c.), E a glass tube of about the same magnitude as that of D, A and B stop-cocks, S a stirrer, whose wing is made to be at right angles to the boundary surface. The lower end of the outer tube of the stirrer is dipped in the solution to avoid the disturbance of the surface area, when it is put in motion, and the upper end of the tube is so constructed that the gas present in the vessel is separated with mercury from air, as will be seen in the figure.

The measurements were carried out in the following manner.

All parts of the apparatus were placed in a water thermostat regulated at a constant temperature. The tubes D and E were filled with water saturated with oxygen by the elevation of the tube F, the stop-cock B being opened. A definite quantity of newly distilled water was poured into

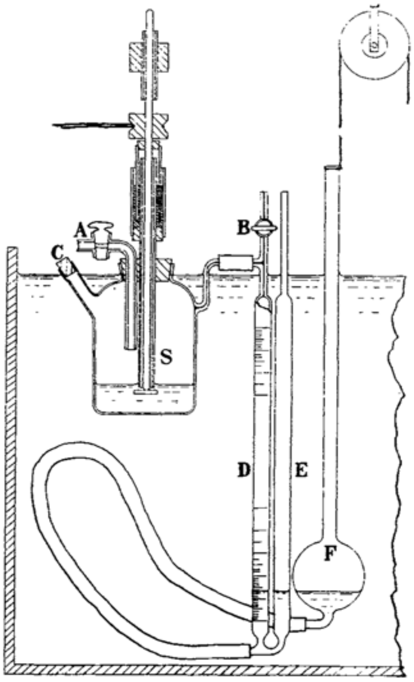

Fig. 1.

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(1) loc. cit.

(2) Adeney and Becker, *Phil. Mag.*, **38** (1919), 317; **39** (1920), 385; **42** (1921), 87, Davis and Crandall, *J. Am. Chem. Soc.*, **52** (1930), 3757, 3769.

the vessel through D, and oxygen gas, washed with acidified potassium bichromate solution and alkali, was passed through A into the vessel at a high velocity for about 30 minutes.

Oxygen gas employed is that manufactured from liquid air and its oxygen content was determined by analysis to be 97 per cent by volume. When the air in the vessel has been completely replaced with oxygen, the tube D was also filled with oxygen by lowering the tube F, and a definite quantity of sodium sulphite solution of known concentration was added into the vessel through C, the total volume of the solution being made up to 40 c.c.

The stop-cocks A and B were closed, the stirrer S was put in motion at about 400 revolutions per minute, and when the levels of water in D and E have been made to be at equal heights, the stop-watch was started. The levels of water in D and E were regulated to be always at equal heights by the elevation of the tube F and the height of water in the tube D was recorded from time to time. The rate of the decrease of the volume of oxygen at constant temperature and pressure was observed in this way.

Representative results are given in Table 1. The area of the interface is 27.75 cm^2. in each case.

Table 1.

Temp.	C_0 Na_2SO_3 normal	t min.	Δv cor. c.c.	$\Delta n \times 10^5$ moles	$\frac{\Delta n}{\Delta t} \times 10^5$ moles/min.
15°C.	0.3714	0	—	—	—
		20	4.17	18.59	0.929
		30	6.47	28.86	0.962
		40	8.70	38.81	0.970
		50	10.91	48.67	0.973
		60	13.13	58.61	0.976
					Mean 0.962
	0.5811	0	—	—	—
		30	6.21	27.71	0.924
		40	8.31	37.07	0.927
		50	10.45	46.65	0.933
					Mean 0.928
	0.6299	0	—	—	—
		10	2.05	9.13	0.913
		30	6.16	27.47	0.916
		40	8.26	36.84	0.921
		50	10.52	46.94	0.939
					Mean 0.922
					Mean Value = 0.937

Table 1—(*Continued*).

Temp.	C_0 Na_2SO_3 normal	t min.	Δv cor. c.c.	$\Delta n \times 10^5$ moles	$\frac{\Delta n}{\Delta t} \times 10^5$ moles/min.
20°C.	0.4356	0	—	—	—
		15	4.22	18.85	1.26
		25	7.24	32.28	1.29
		30	8.88	39.62	1.32
					Mean 1.290
	0.5050	0	—	—	—
		20	5.70	25.44	1.27
		40	11.75	52.44	1.31
		50	15.32	68.38	1.37
					Mean 1.317
	0.5800	0	—	—	—
		30	8.78	39.19	1.31
		40	11.89	53.07	1.32
					Mean 1.315
	0.7440	0	—	—	—
		10	3.02	13.48	1.35
		20	6.09	27.16	1.35
		30	9.34	41.66	1.39
					Mean 1.363
	Mean Value = 1.321				
25°C.	0.4202	0	—	—	—
		20	7.95	35.47	1.77
		30	12.39	55.29	1.84
		40	16.89	75.38	1.88
					Mean 1.830
	0.4805	0	—	—	—
		10	4.06	18.12	1.81
		20	8.05	35.91	1.80
		30	12.39	55.31	1.84
					Mean 1.817
	0.4964	0	—	—	—
		10	3.82	17.05	1.70
		20	7.77	34.69	1.73
		30	12.21	54.48	1.82
		40	17.01	75.90	1.90
					Mean 1.788
	0.573	0	—	—	—
		10	4.27	19.05	1.91
		20	8.58	38.30	1.92
		30	13.02	58.11	1.94
					Mean 1.923

Table 1—(*Concluded*).

Temp.	C_0 Na_2SO_3 normal	t min.	Δv cor. c.c.	$\Delta n \times 10^5$ moles	$\frac{\Delta n}{\Delta t} \times 10^5$ moles/min.
25°C.	0.6110	0	—	—	—
		20	8.18	36.51	1.83
		30	12.30	54.91	1.83
		40	16.34	72.90	1.82
					Mean 1.827
	0.6281	0	—	—	—
		10	3.98	17.78	1.78
		20	8.10	36.16	1.81
		30	12.54	55.96	1.86
					Mean 1.817
	0.702	0	—	—	—
		10	4.43	19.76	1.98
		20	8.88	39.64	1.98
		30	13.44	59.96	2.00
					Mean 1.987
					Mean Value = 1.856
35°C.	0.499	0	—	—	—
		10	6.04	26.94	2.69
		15	9.21	41.11	2.74
		20	12.64	56.41	2.82
		25	16.15	72.08	2.88
					Mean 2.78
	0.633	0	—	—	—
		10	6.19	27.61	2.76
		15	9.37	41.80	2.79
		20	12.58	56.15	2.81
		25	15.86	70.76	2.83
					Mean 2.80
	0.715	0	—	—	—
		5	3.12	13.92	2.78
		10	6.30	28.11	2.81
		15	9.41	41.99	2.80
		20	12.65	56.44	2.82
		25	15.94	71.12	2.84
					Mean 2.81
					Mean Value = 2.797

Initial concentrations of sodium sulphite solutions employed are given in the second column of the table. The values Δv_{cor}, given in the fourth column of the table, are the quantity of oxygen absorbed during t- minutes expressed by the volume of oxygen at 0°C. and 1 atmosphere, the vapour pressure of the solution and the barometric height being taken into calculation. The absorbed quantities of oxygen expressed in the unit of gram molecules are given in the fifth column of the table, the rate of absorption being given in the last column.

As was expected, the rate of absorption of oxygen by the solution is independent of the concentration of sodium sulphite. The rate of absorption does not increase with the increase of the concentration of sodium sulphite in the range of its concentrations, given in the table.

It was reported by Milbauer and Pazourek(1) that the rate of oxidation of sodium sulphite solution of high concentration is smaller than that of lower concentration. As was above described, the rate of absorption of

Table 2.

Temp.	C_0 Na_2SO_3 normal	t min.	Δv cor. c.c.	$\Delta n \times 10^5$ moles	$\frac{\Delta n}{\Delta t} \times 10^5$ moles / min.
15°C.	1.421	0	—	—	—
		10	1.19	5.29	0.529
		30	3.54	15.79	0.526
		40	4.65	20.74	0.519
		60	6.93	30.91	0.515
					Mean 0.522
	2.138	0	—	—	—
		10	0.46	2.06	0.206
		20	0.94	4.20	0.210
		30	1.42	6.34	0.211
		40	1.84	8.23	0.206
		50	2.29	10.20	0.204
		60	2.72	12.14	0.202
					Mean 0.2065
25°C.	1.425	0	—	—	—
		10	2.44	10.89	1.09
		20	4.87	21.75	1.09
		40	9.83	43.86	1.10
		60	14.67	65.45	1.09
					Mean 1.093
	2.140	0	—	—	—
		10	0.75	3.37	0.337
		20	1.46	6.51	0.326
		40	2.82	12.58	0.315
		60	4.32	19.30	0.322
					Mean 0.3250

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(1) *Bull. Soc. Chim.*, **31** (1922), 676.

oxygen by sodium sulphite solution is independent of its concentration, when the concentration lies in the range of about 0.35—0.75 normal. The measurements were carried out when the concentration of sodium sulphite is comparatively high, and the representative results are given in Table 2. The phenomenon observed by Milbauer and Pazourek was confirmed. The rate of absorption of oxygen by sodium sulphite solution of high concentration decreases with the increase of the concentration of sodium sulphite.

It was ascertained by the preliminary experiments, that when the concentration of sodium sulphite solution is lower than about 0.35 normal, the rate of oxidation of sodium sulphite solution increases with the increase of the concentration of sodium sulphite as far as it attains the maximum value, given in Table 1.

Discussion.

From the results of the experiments above described, it will easily be seen that there are three different stages when the effect of the increase of the concentration of sodium sulphite solution on the rate of oxidation of sodium sulphite solution is observed. The behaviour is graphically shown in Fig. 2.

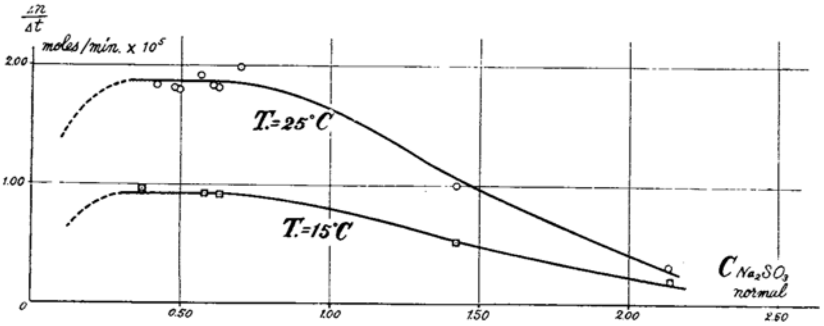

Fig. 2.

At low concentrations of sodium sulphite solutions, the rate of oxidation of sodium sulphite solution increases with the increase of the concentration of sodium sulphite as far as it attains a certain maximum value.

At middle concentrations of sodium sulphite solutions, the rate of oxidation of sodium sulphite solution is maximum and independent of the concentration of sodium sulphite.

At high concentrations of sodium sulphite solution the rate of absorption decreases with the increase of the concentration of sodium sulphite.

Under the conditions of the present experiments it was confirmed⁽¹⁾ that there exists no stationary liquid film at the interface, and according to the theory of one of the present writers (Miyamoto) the phenomenon can be interpreted in the following manner.

At low concentrations of sodium sulphite solution the number of the molecules of sodium sulphite at the upper surface layer is not sufficient to react with all of the molecules of oxygen, which enter into the liquid phase per unit time. Then in this case a part of the molecules of oxygen, which could not react with sodium sulphite, will go back into the gas phase, and a part of them diffuses into the main body of the solution. Under special condition, the upper surface of the liquid will be saturated with the molecules of oxygen in a short time, and a part of the molecules which diffuse towards the deeper layer of the liquid, will react with the molecules of sodium sulphite, which diffuse towards the reacting zone from the main body of the solution. Under this condition, the rate of solution may be expressed by the following equation, proposed by Davis and Crandall.⁽²⁾

$$\frac{1}{S}\left(\frac{dn}{dt}\right) = k\,(C_m + C_\infty),$$

where C_m is the concentration of sodium sulphite solution, C_∞ the saturation concentration of oxygen in water, S the area of the boundary surface, k a constant, n the number of moles of oxygen in the liquid phase.

When the quantity C_∞ is negligible compared with C_m, the equation becomes

$$\frac{1}{S}\left(\frac{dn}{dt}\right) = k\,C_m.$$

In the second stage, the number of molecules of sodium sulphite at the boundary surface is quite sufficient to react with all the molecules of oxygen, which enter into the liquid phase per unit of time, and therefore the concentration of oxygen at the interface is always kept at zero. Under these conditions, it will easily be accepted that the rate of oxidation of sodium sulphite solution, which is, in this case, equal to the rate of solution of oxygen into the solution, is equivalent to the rate of solution of oxygen into water, in the surface of which no free oxygen exists, and that the rate of absorption of oxygen by the solution is maximum, which is independent of the concentration of sodium sulphite.

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(1) S. Miyamoto, T. Kaya and A. Nakata, this Bulletin, **6** (1931), 133.

(2) *J. Am. Chem. Soc.*, **52** (1930), 3769.

As was discussed in the previous paper,⑴ the behaviour in this stage will be difficult to be interpreted by the ordinary diffusion layer theories, which are based on the assumption that the boundary surface is instantaneously saturated with gas.

The following equation⑵ was proposed for the rate of solution of gas into liquid by one of the present writers (Miyamoto).

$$\frac{\Delta n}{\Delta t}=N''-N'''_{\ \mathit{moles/sec.}}\,, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where N'' is the number of moles of the gas which enters into the liquid phase per second, N''' the number of moles of the gas which leaves the liquid phase per second, and n the number of moles of the gas in the liquid phase.

When the concentration of the gas in the liquid phase is kept at zero, the equation (1) becomes

$$\left(\frac{\Delta n}{\Delta t}\right)_0=N''_{\ \mathit{moles\ sec.}}\,, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

According to the theory of one of the present writers,⑶

$$\left(\frac{\Delta n}{\Delta t}\right)_0=N''=\frac{60p_{0_2}}{\sqrt{2\pi MRT}}\,e^{-\frac{Mu_0^2}{2RT}}\,S_{\ \mathit{moles/min.}}\,, \quad \ldots\ldots \quad (3)$$

where p_{0_2} is the partial pressure of the gas, M the molecular weight of the gas, R the gas constant, S the area of the boundary surface, and u_0 a constant.

The derivation of this equation is based upon the assumption that among the molecules, which collide with the liquid surface, only those, whose components of velocity at right angles to the surface are greater than a threshold value u_0, are able to enter into the liquid phase.

When the concentration of the gas in the liquid phase is not kept at zero, the rate of the escape of molecules of the gas from the liquid phase should naturally be taken into consideration as was described in the previous paper.⑷

At high concentrations of sodium sulphite solution, the concentration of oxygen at the liquid surface will also be kept at zero by the presence of

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(1) S. Miyamoto, T. Kaya and A. Nakata, this Bulletin, **6** (1931), 133.

(2) S. Miyamoto and A. Nakata, ibid., **6** (1931), 18.

(3) S. Miyamoto and A. Nakata, this Bulletin, **6** (1931), 20.

(4) Ibid.

the sufficient quantity of sodium sulphite reacting with all the molecules of oxygen, which enter into the liquid phase per unit of time, so long as the main body of the liquid is well agitated with a stirrer, and the oxidation velocity of sodium sulphite solution will be equal to the rate of absorption of oxygen by the solution, which will be expressed by the above mentioned equation (3).

As the threshold value u_0 should be considered to depend upon the properties of the boundary surface, it may be expected with a high degree of probability that the value u_0 of pure water and that of the solution will have different values. From the equation (3), it is quite clear that the rate of solution of gases will depend upon the threshold value u_0. When the concentration of sodium sulphite is not very high, the minute difference of the nature of the boundary surface will have no appreciable effect on the value u_0, but at high concentration the threshold value u_0 will be influenced by the change of the nature of the interface. Therefore the present results of experiments may be explained by the assumption that the threshold value u_0 increases with the increase of the concentration of sodium sulphite. At high concentration of sodium sulphite the rate of solution of oxygen decreases in consequence of the increase of the value u_0.

In Tables 3 and 4, the results of the present experiments are given in comparison with the results of the experiments, reported in the previous paper.⁽¹⁾ The agreement will be satisfactory.

In the fifth column of Table 4, the threshold value u_0 at several temperatures, calculated by the equation (3), using the observed values of the rate of solution of oxygen into sodium sulphite solution, are given. The value u_0 was found to be independent of temperature within the region of the present experiments.

The value β given in the fourth column of the table, stands for the ratio of the number of molecules of oxygen which enter into water and the number of molecules of oxygen which collide with the liquid surface per unit of time, and was calculated by

$$\beta = e^{\frac{Mu_0^2}{2RT}} = \frac{1}{60}\,\frac{1}{S}\left(\frac{\Delta n}{\Delta t}\right)_0 \frac{\sqrt{2\pi MRT}}{p_{O_2}}\,.$$

In the last column of the table, the root-mean-square-velocity of oxygen at several temperatures, calculated by

$$\sqrt{\overline{C^2}} = \sqrt{\frac{3RT}{M}}$$

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(1) Loc. cit.

Table 3.

Temp.	Method	S cm².	$\frac{\Delta n}{\Delta t}$ moles per min.	$\frac{1}{60}\frac{1}{S}\frac{\Delta n}{\Delta t}$ moles per sec. per cm².
15°C.	Volume decrease	27.75	0.937×10^{-5}	5.63×10^{-9}
	Iodometry	—	—	5.53×10^{-9}
20°C.	Volume decrease	27.75	1.321×10^{-5}	7.93×10^{-9}
25°C.	Volume decrease	27.75	1.856×10^{-5}	11.14×10^{-9}
	Iodometry	—	—	10.75×10^{-9}
35°C.	Volume decrease	27.75	2.797×10^{-5}	16.81×10^{-9}
	Iodometry	—	—	16.25×10^{-9}

Table 4.

Temp.	p_{O_2} atms.	Method	$\frac{1}{60}\frac{1}{S}\left(\frac{\Delta n}{\Delta t}\right)$ moles per sec. per cm².	β	u_0 cm. per sec.	$\sqrt{\overline{C^2}}$ cm. per sec.
15°C.	0.954	Volume decrease	5.63×10^{-9}	1.278×10^{-8}	1.649×10^{5}	4.737×10^{4}
		Iodometry	5.53×10^{-9}	1.258×10^{-8}	1.650×10^{5}	
20°C.	0.948	Volume decrease	7.93×10^{-9}	1.828×10^{-8}	1.647×10^{5}	4.778×10^{4}
25°C.	0.941	Volume decrease	11.14×10^{-9}	2.773×10^{-8}	1.641×10^{5}	4.818×10^{4}
		Iodometry	10.75×10^{-9}	2.517×10^{-8}	1.646×10^{5}	
35°C.	0.916	Volume decrease	16.81×10^{-9}	4.111×10^{-8}	1.650×10^{5}	4.898×10^{4}
		Iodometry	16.25×10^{-9}	3.974×10^{-8}	1.651×10^{5}	

are given. It follows from the present research that only the molecules of oxygen, whose components of velocity at right angles to the boundary surface are greater than approximately 3.4 times the root-mean-square-velocity, are able to enter into the liquid phase.

Summary.

(1) The rate of solution of oxygen into sodium sulphite solution of various concentrations was observed by the measurements of the decrease of the volume of gas phase at constant temperature and pressure.

(2) At low concentrations of sodium sulphite solution, the rate of solution of oxygen increases as the concentration of sodium sulphite increases. At middle concentrations, the rate of solution is maximum and independent of the concentration of sodium sulphite.

At high concentrations the rate of solution decreases with the increase of the concentration of sodium sulphite.

(3) A theoretical interpretation on the results of the present experiments was given.

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Laboratory of Physical Chemistry,
Hiroshima University, Hiroshima.