ON THE DISSOLUTION VELOCITY OF OXYGEN INTO WATER. PART V.
THE OXIDATION VELOCITY OF SODIUM SULPHITE SOLUTION BY OXYGEN IN THE PRESENCE OF THE MOLECULAR FILM OF FATTY ACID.

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Introduction.

H. Davis and R. Schuler⁽¹⁾ carried out a research on the rate of absorption of the gaseous olefins into sulphuric acid solution and found that the specific absorption coefficient (volume of gas absorbed per second per square centimeter of surface) was not appreciably affected by the agitation of the main body of the liquid. Ethylene was absorbed by concentrated sulphuric acid as rapidly when the acid was quiescent as when it was stirred (without breaking the surface or changing its area) at 400 revolution per minute.

H. Davis and G. Crandall⁽²⁾ studied the rate of the solution gaseous olefines into sulphuric acid solution with an apparatus newly devised, and obtained exactly the same result as that of the above mentioned experiment.

According to Nernst,⁽³⁾ an unstirred stationary liquid layer exists at the upper surface of liquid which is in contact with gas.

Whitman and Keats⁽⁴⁾ extended the theory of Nernst, and proposed an assumption that whenever a liquid and a gas come into contact there exists on the gas side of the interface a layer of gas in which motion by convection is slight compared with that in the main body of the gas, and similarly on the liquid side of the interface there is a surface layer of the liquid which is practically free from mixing by convection.

The theoretical interpretations of the rate of absorption of gaseous olefins by sulphuric acid solution and of the rate of absorption of carbon dioxide by sodium hydroxide solution, given by Davis and Crandall,⁽⁵⁾ are based on the theory of whitman and Keats, the two-film theory.

Davis and Crandall⁽⁵⁾ have made two suppositions; firstly that the reactions take place instantaneously in the liquid film, and secondly that the

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(1) *J. Am. Chem. Soc.*, **52** (1930), 721.
(2) Ibid., **52** (1930), 3757.
(3) *Z. physik. Chem.*, **47** (1904), 52.
(4) *J. Ind. Eng. Chem.*, **14** (1922), 185.
(5) Loc. cit.

upper surface of the liquid film, which is not disturbed by the agitation of the main body of the liquid, is kept at the saturated state with the gas. From these assumptions it is quite easy to see that the velocity of the absorption depends only upon the velocity of diffusion of the gas molecules and that of the molecules of the reacting substances through the stationary liquid film. Davis and Crandall⁽¹⁾ proposed the following equation for the initial rate of absorption of gas into a well-stirred liquid when any irreversible chemical reactions taking place are instantaneous, compared with the rate of solution of the gas.

$$\frac{1}{S}\left(\frac{dn}{dt}\right)_{Initial} = k(c_\infty + c_m) ,$$

where $\frac{1}{S}\left(\frac{dn}{dt}\right)_{Initial}$ is the initial rate of absorption of the gas per unit area of the surface, S the area of the boundary surface, k a constant, c_∞ the saturation concentration of the dissolved gas and c_m the concentration of the reacting solute.

The oxidation of sodium sulphite solution⁽²⁾ by means of oxygen is quite an analogous phenomenon. But from the results of the experiments of the present writers⁽²⁾ it was found that the velocity of the oxidation of sodium sulphite solution does not increase above a certain maximum value, however much the concentration of sodium sulphite be increased.

The above mentioned equation, proposed by Davis and Crandall, will be unsuitable for the interpretation of this phenomenon, and it might be immediately supposed that it would be necessary to make suppositions different from those proposed by Davis and Crandall in order to interprete the velocity of oxidation of sodium sulphite solution.

The following facts were already ascertained by one of the present writers (Miyamoto) experimentally.

(1) The maximum velocities of the oxidation of sodium sulphite, stannous hydroxide and ferrous hydroxide in sodium hydroxide solutions are identical under the comparable conditions.⁽³⁾

(2) The velocities of oxidation of these oxidizable substances do not increase above this maximum value with the increase of the concentration of these substances, as was above mentioned.

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(1) Loc. cit.

(2) S, L. Bigelow, *Z. physik. Chem.*, **26** (1898), 493; S. Miyamoto, this Bulletin, **2** (1927), 74; S. Miyamoto and T. Kaya, ibid., **5** (1930), 123; S. Miyamoto, T. Kaya and A. Nakata, ibid., **5** (1930), 229; S. Miyamoto and T. Kaya, ibid., **5** (1930), 321; S. Miyamoto and A. Nakata, ibid., **6** (1931), 9.

(3) S. Miyamoto, this Bulletin, **2** (1927), 74; ibid., **2** (1927), 155; ibid., **3** (1928), 98; ibid., **3** (1928), 137.

(3) The total oxidized quantity of these substances during a definite time interval does not increase by mixing them.⑴

(4) The maximum oxidation velocity of sodium sulphite solution is proportional to the area of the interface of oxygen and the solution.⑵

From these facts one of the present writers (Miyamoto) made the assumption that the maximum velocity of oxidation of sodium sulphite solution will be equivalent to the initial rate of solution of oxygen into water, in the surface of which no free oxygen is present.

This supposition was endorsed by the comparison⑵ of the initial rate of solution of oxygen into water obtained from the result of the direct measurement by several writers⑶ with that calculated from the velocity of oxidation of sodium sulphite solution.

For the theory of the rate of solution of gases into liquids, proposed by one of the present writers⑷ (Miyamoto), a part of which was stated in the previous paper, it is a matter of indifference whether the thin liquid film (the diffusion layer), at the upper surface of the liquid phase, is agitated by the stirring of the main body of the liquid or not. Only the second supposition, proposed by Davis and Crandall, that the upper surface of the liquid film is instantaneously saturated with the gas, seems to be unprobable for the interpretation of the velocity of oxidation of sodium sulphite solution.

If the thin stationary liquid film be really not disturbed by the agitation of the main body of the liquid, as was supposed by several writers, the occurrence of the following phenomenon will be expected.

When the molecules of fatty acid were placed at the upper surface of sodium sulphite solution by a proper method, they occupy a certain area of the surface, undisturbed by the agitation of the main body of the solution, and the velocity of oxidation of sodium sulphite solution, which is equivalent to the initial rate of solution of oxygen under certain conditions, will change as a result of the alteration of the area of the free boundary surface between gas and liquid. Then it will be possible to calculate the effective area of a molecule of fatty acid from the measurement of the velocity of oxidation of sodium sulphite solution in the presence of a measured quantity of fatty acid, as the maximum velocity of the oxidation of sodium sulphite solution was confirmed to be proportional to the area of the boundary surface.

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(1) S. Miyamoto, this Bulletin, **2** (1927), 191; ibid., **4** (1929), 132.

(2) S. Miyamoto and A. Nakata, ibid., **6** (1931) 9.

(3) 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.

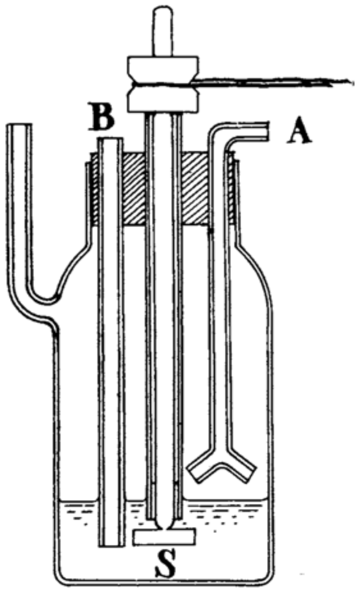
(4) Loc. cit.,

The cross-sections and the length of many organic compounds were obtained from the result of excellent physical experiments by Langmuir⁽¹⁾ and by Adam.⁽²⁾

The present research was carried out with the expectation that the relation between the effective cross-section of the molecule of fatty acid, which will be calculated from the measurement of the velocity of the oxidation of sodium sulphite solution in the presence of the molecules of fatty acid, and the real cross-section obtained from the result of physical experiment will be obtained.

Experimental.

The apparatus, graphically shown in the accompanying figure, was employed as the reacting vessel. The apparatus has nearly the same construction as that employed in the previous research.⁽³⁾ The important difference, which will be seen by the comparison of the present apparatus with that stated in the previous paper, is that the lower end of the tube B is dipped in the solution in the present case.



The experimental method is as follows.

A definite quantity of fatty acid was dissolved in a definite volume of purified, newly distilled benzene, and by means of a calibrated pipette a few drops of the bezene solution of fatty acid was added on the measured quantity of water contained in the vessel, which was placed in a water thermostat. Air, washed by acidified potassium bichromate and sodium hydroxide solutions, was passed at a high velocity through A for about an hour to remove benzene completely from the apparatus. After the benzene has been perfectly evaporated off, oxygen, washed by the above mentioned reagents, was passed into the apparatus at a high velocity through A for about thirty minutes. When the air in the apparatus has been entirely replaced by oxygen, the

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(1) *J. Am. Chem. Soc.*, **39** (1917), 1848.

(2) *Proc. Roy. Soc.*, **99** A (1921), 336; **101** A (1922), 452, 516; **103** A (1923), 676, 687.

(3) S. Miyamoto and A. Nakata, This Bulletin, **6** (1931), 11.

stirrer is put in motion at the rate of about 400 revolutions per minute and the rate of the passage of oxygen was regulated at about 15 liters per hour.

The stop-watch was started when about half the volume of sodium sulphite solution had been added in the vessel through B, the total volume of the solution being made up to 40 c.c. . The quantity of sodium sulphite solution added was determined separately by the usual method of iodometry.

When t-minutes have elapsed, the revolution of the stirrer and the current of oxygen were stopped and nitrogen gas was passed from A in the apparatus at a high velocity to drive the oxygen out as quickly as possible.

The vessel was then taken out and the total quantity of the solution was poured into a known quantity of iodine solution, acidified with hydrochloric acid. After the reacting vessel had been repeatedly washed with distilled water, the excess of iodine was titrated back by means of sodium thiosulphate solution of 0.1000 normal.

Representative results of the experiments are given in Tables 1 and 2.

In the tables, v is the volume of sodium thiosulphate solution of 0.1000 normal, equivalent to the quantity of sodium sulphite remained in

Table 1. (Temp. = 25°C)

No.	Conc. of stearic acid solution moles / liter	Stearic acid solution taken c.c.	S_{acid} cm.^{2}	S_0 cm.^{2}	t min.	v c.c.	k	$\frac{k}{S_0}$
1	0	0	0	26.31	—	—	0.682	0.0259
2	0.879×10^{-4}	0.050	5.60	25.60	0 30	207.69 188.80	0.630	0.0246
3	,,	0.050	5.60	,,	0 30	211.29 190.51	0.693	0.0271
4	,,	0.100	11.20	,,	0 30	203.64 184.01	0.654	0.0255
5	,,	0.200	22.30	,,	0 30	205.25 184.37	0.696	0.0272
6	8.06×10^{-4}	0.050	51.30	,,	0 30	231.18 211.80	0.646	0.0252
7	,,	0.200	205.10	,,	0 30	207.68 188.01	0.656	0.0256
8	43.72×10^{-4}	0.034	189.10	,,	0 30	227.48 208.02	0.649	0.0254
9	,,	0.200	1113·00	,,	0 30	206.50 187.00	0.650	0.0254

Table 2. (Temp. = 25°C)

No.	Conc. of palmitic acid solution moles/liter	Palmitic acid solution taken c.c.	S_{acid} cm.^{2}	S_0 cm.^{2}	t min.	v c.c.	k	$\frac{k}{S}$
1	0	0	0	26.31	—	—	0.682	0.0259
2	1.125×10^{-4}	0.033	4.72	25.5	0 30	232.47 212.22	0.675	0.0265
3	3.707×10^{-4}	,,	15.57	,,	0 30	237.25 217.54	0.657	0.0258
4	8.125×10^{-4}	,,	34.12	,,	0 30	236.28 217.05	0.641	0.0251
5	18.37×10^{-4}	,,	77.14	,,	0 30	236.58 217.51	0.636	0.249
6	41.60×10^{-4}	,,	174.70	,,	0 30	232.09 213.77	0.611	0.0240

the solution, when t-minutes has passed from the moment at which the oxidation had taken place.

The values k, given in the third column of the tables, were calculated according to the equation.

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

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

The values of S_{acid}, given in the 4th column of the tables, stand for the area, which would be occupied by the molecules of fatty acid added, if they formed a monomolecular film, and the values were calculated in the following manner.

According to the investigations of Langmuir⁽¹⁾ and Adam,⁽²⁾ when a few drops of benzene solution of fatty acid was placed on the surface of water, the molecules of fatty acid are arranged not indiscriminately but perpendicular to the surface and parallel to each other after the benzene has been evaporated off.

If the thin stationary layer at the surface of the solution be not disturbed by the agitation of the main body of the solution with a stirrer, the orientation of the molecules of fatty acid will take place during the present observation in exactly the same way as in the case of quiescent water. From

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(1) Loc. cit.

(2) Loc. cit.

this assumption the values S_{acid} were calculated from the quantity of fatty acid solution taken and the area of the cross-section of each molecule, for which 21×10^{-16} cm²., obtained by Adam,⁽¹⁾ was adopted for stearic acid and palmitic acid.

The area of the boundary surface between liquid and gas in the absence of the molecules of fatty acid was calculated by exactly the same process, as that stated in the previous paper,⁽²⁾ and the value is given as S in the 5th column of the tables.

The value of k in the absence of the molecules of fatty acid, given in the tables, is the value already obtained in the previous experiment.⁽³⁾

As will be seen in the tables, the difference between the value of k observed in the absence of fatty acid and that observed in the presence of fatty acid lies in the range of experimental error, and it may be described that the presence of the molecules of fatty acid has virtually no effect on the oxidation velocity of sodium sulphite solution, which will be equivalent to the rate of solution of oxygen into water, which is free from oxygen, under the condition of the present experiments.

Discussion.

The molecules of these fatty acids employed will form a monomolecular or multimolecular film on the upper surface of the liquid after the complete evaporation of benzene. In the case of the experiments Nos. 2–5 in Table 1 and Nos. 2–3 in Table 2, a part of the boundary surface is covered with the monomolecular film, and in the case of the experiments Nos. 6–9 in Table 1 and Nos. 4–6 in Table 2, the total area of the boundary surface is occupied by the multimolecular film of the fatty acid.

According to the experiments of Adam,⁽⁴⁾ the molecules of these fatty acids have the following magnitude.

	Cross section.		Length.
	Head. cm².	Chain. cm².	cm.
Palmitic acid.	25.1×10^{-16}	21.0×10^{-16}	23.7×10^{-8}
Stearic acid.	25.1×10^{-16}	21.0×10^{-16}	26.2×10^{-8}

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(1) Loc. cit.
(2) Loc. cit.
(3) Loc. cit.
(4) Loc. cit.

The calculation of the thickness of the assumed stationary liquid film⁽¹⁾ was carried out by Brunner⁽²⁾ and by Davis and Crandall,⁽³⁾ and was based upon the assumption that the rate of solution of gases into liquids is no other than the velocity of diffusion of the gas molecules through the stationary liquid film at the interface. According to these writers, the thickness of the stationary liquid film is about 2×10^{-3}—2×10^{-2} cm., which naturally depends upon the rate of revolution of the stirrer in the main body of the liquid.

If the assumption, that a stationary film exists at the interface, be acceptable, the multimolecular film of fatty acid, whose thickness is a minute portion of that of the stationary film, will occupy the area of the upper surface of the interface during the measurements of the present experiments, undisturbed by the agitation of the main body of the liquid. From this consideration it will quite be probable to expect that the presence of the multimolecular film of fatty acids at the upper surface will have some effect on the rates of solution of gases into liquids.

The result of the present experiments was contrary to this expectation, and it will be difficult to interprete the present result by the ordinary theory, which is based upon the supposition of the presence of a stationary liquid film.

One of the present writers (Miyamoto) has an opinion that it will be very probable to interprete the process of solution of gases into liquids by the assumption that among the molecules which collide with the liquid surface only those molecules, whose components of velocity at right angles to the boundary surface are greater than a threshold value u_0, are able to enter into the the liquid phase. According to this supposition, the rate of solution will be expressed by

$$D_0 = N''S - N'''S\,,$$

where N'' is the number of the molecules which enter into the liquid phase through the unit area of the boundary surface per unit of time, N''' the number of the molecules which leave the liquid phase through the unit area of the boundary surface per unit of time and S the area of the boundary surface.

So long as the concentration of the gas in the liquid phase is maintained at zero, the rate of solution is given by

$$D_0 = N''S\,,$$

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(1) Nernst, *Z. physik. Chem.*, **47** (1904), 52; Whitman and Keats, *J. Ind. Eng. Chem.*, **14** (1922), 185.

(2) *Z. physik. Chem.*, **47** (1904), 99.

(3) *J. Am. Chem. Soc.*, **52** (1930), 3760.

N''' being zero under this condition.

As was stated in the previous paper,⁽¹⁾ the oxidation velocity of sodium sulphite solution of proper concentration is equivalent to the value D_0, when the main body of the liquid is well agitated with a stirrer.

According to this theory of the rate of solution of gas into liquid, it is quite enough for the interpretation of the result of the present experiments if only one of the following assumptions be satisfied.

(1) The value u_0 does not differ whether the molecules of fatty acids are present or not.

(2) The liquid film at the interface is not stationary and the molecules of fatty acids are covered with the solution when the main body of the solution is agitated.

The present writers consider that the first assumption will be inadequate to be adopted.

If the second supposition be satisfied, the total area of the boundary surface is not altered by the addition of fatty acids, and the concentration of oxygen at the upper surface will be kept at zero by the presence of the sufficient quantity of sodium sulphite to react with all of the molecules of oxygen which enter into the liquid phase, so long as the main body of the liquid is well agitated with a stirrer.

It is then quite clear that the presence of the molecules of fatty acids will have no effect on the velocity of the oxidation of sodium sulphite solution, which is equivalent to the initial rate of solution of oxygen into water, D_0, under the present conditions.

For this interpretation it is of no use to investigate whether the molecules of fatty acids, covered with the solution, remain in the upper layer of the liquid or go down into the main body of the liquid during the experiments.

From the discussion, above stated, it seems that the supposition of the existence of the stationary liquid film of proper thickness, proposed by several writers, the diffusion theory, will be unfavourable to the interpretation of the result of the present experiments.

As the conclusion of the present research it will be possible only to describe that the thickness of the stationary liquid film, if it exist, should be smaller than the length of the molecule of palmitic acid, 23.7×10^{-8} cm., when the main body of the liquid is well agitated with a stirrer.

Although the present research failed to produce the expected result, the phenomenon observed will be one of the important experimental facts,

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(1) Loc. cit.

which will be employed for the discussion of the process of solution of gasses into liquids.

As a result of the present research, it can be said that, under the conditions of the study on the rate of oxidation of sodium sulphite solution, carried out by Miyamoto and his collaborators, stationary liquid film does not exist at the boundary surface, and therefore the results of the experiments can not be interpreted by the classical theory, based upon the assumption that the phenomenon is the rate of diffusion through a stationary film at the interface.

Summary.

(1) The monomolecular or multimolecular films of stearic acid or of palmitic acid were formed at the upper surface of sodium sulphite solution, and the velocity of the oxidation of sodium sulphite solution was studied, the main body of the solution being well agitated with a stirrer of special construction. It was confirmed that the velocity of the oxidation of sodium sulphite solution by oxygen, observed in the presence of the molecules of these fatty acids, and that observed in the absence of the molecules of the fatty acids, are almost identical under the conditions above described.

(2) A short discussion on the result of the present experiments was made.

The assumption, that a stationary liquid layer is present at the interface between gas and liquid, seems to be unfavourable to the interpretation of the phenomenon observed by the present writers. It was stated that the assumption, that the molecules of fatty acid at the upper surface of the liquid will also be agitated by the stirring of the main body of the liquid and covered with the solution, has great probability for the interpretation of the result of the present experiments.

(3) The mechanism of solution of gas into liquid was shortly discussed.

A part of the opinion of one of the present writers (Miyomoto) on the rate of solution of gases into liquids was described.

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