THERMAL ANALYSIS OF THE OXIDATION OF SULPHITES. (I)

The Oxidation of Acid Sulphite by Iodate.

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Among the oxidation reaction of sulphurous acid in aqueous solution hitherto investigated, the oxidation by iodic acid is one of the reactions whose initial parts are so interesting to mention. In the reaction between sulphurous acid and iodic acid in dilute aqueous solution, when the latter is in excess, a certain time elapses before iodine appears. This reaction is what is called the Landolt reaction[1] which is famous for its having an induction period. And such a phenomenon as this is called "Landolt effect." Many studies[2] on the very reaction have been made since Landolt, and the reaction mechanism[1,2] ascertained is as follows:

$$IO_3^- + 3SO_3^{--} \rightarrow I^- + 3SO_4^{--} \qquad \text{(slow)} \qquad (1)$$

$$IO_3^- + 6H^+ + 5I^- \rightarrow 3I_2 + 3H_2O \qquad \text{(measurably rapid)} \qquad (2)$$

$$3I_2 + 3SO_3^{--} + 3H_2O \rightarrow 6I^- + 6H^+ + 3SO_4^{--}. \qquad \text{(instantaneous)} \qquad (3)$$

This mechanism is commenced with the first reaction (1) The iodine ions formed become iodine molecules according to reaction (2); the molecules are, however, soon reduced to the iodine ions according to reaction (3). The iodine ions thus formed taking part successively in reaction (2), the rate of disappearance of sulphurous acid becomes larger and larger. As soon as sulphurous acid is exhausted, only reaction (2) begins to proceed and at this instant iodine appears. While these three reactions—(1), (2) and (3)—are proceeding simultaneously, equation (1) is stoichiometrically established, because reaction (2) plus reaction (3) makes reaction (1). The rate-determining reactions at the induction period are reactions (1) and (2), and according to the researches[3]~[5] hitherto made, the velocity equations of these two reactions (1) and (2) are respectively

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[1] H. Landolt, *Ber. Dtsch. chem. Ges.*, **19**, 1317 (1886); **20**, 745 (1887).

[2] e.g. J. Eggert, *Z. Elektrochem.*, **23**, 8 (1917); A. Skrabal, *ibid.*, **28**, 224 (1922); J. Eggert u. L. Pfeffermann, *Z. anorg. Chem.*, **139**, 310 (1924).

[3] A. Thiel u. E. Meyer, *Z. anorg. Chem.*, **137**, 125 (1924).

[4] A. Skrabal u. A. Zahorka, *Z. Elektrochem.*, **33**, 42 (1927).

[5] S. Dushman, *J. Phys. Chem.*, **8**, 453 (1904); E. Abel u. F. Stadler, *Z. physik. Chem.*, **122**, 49 (1926).

as follows:

$$\frac{-d[IO_3^-]}{dt}=x_1[IO_3^-][SO_3^{--}][H^+], \tag{4}$$

$$\frac{-d[IO_3^-]}{dt}=x_2[IO_3^-][I^-]^2[H^+]^2, \tag{5}$$

where x_1 and x_2 are constants.

Of these two, reaction (1) as an isolated reaction has not been studied so much.[3),4)] By Prof. S. Horiba's thermal analysis,[6)] which had been successfully applied to the reactions in solution,[7)] the author investigated the Landolt introducing reaction (1) and tried to see whether the velocity equation (4) was right.

Sulphurous acid has three different types, such as SO_2, HSO_3^- and SO_3^{--} according to the hydrogen ion concentration of the reaction system, but when $pH=4\sim5$, it may be said that only HSO_3^- exists[4)]. Even in such a simple case, it has been reported that the same mechanism and velocity equation as those for SO_3^{--} are established,[4)] and so the present experiment was carried out on solutions of $pH=4\sim5$.

Experimental.

Materials.

All the reactants used were the chemicals "für Analyse" of Kahlbaum and Merck. The water employed for the preparation and dilution of the solutions was what had been redistilled in the tin flask and was free from carbon dioxide.

(1) Acid sodium sulphite. About 0.09 mol/*L* solution prepared by weighing was titrated by the standard iodine solution. This solution was kept with nitrogen in a flask holding about 5 litres for fear of its autoxidation by the air, and was taken out by the pressure of nitrogen compressed by alkaline pyrogallol solution. Though no acid was added to it for the protection from its decomposition, yet its change of the titre was so little as about 7% 1 month after it was prepared. The concentration was accurately measured every time the experiment was carried out.

(2) Potassium iodate. 0.03 mol/*l.* solution prepared by weighing was titrated as usual with the standard thiosulphate solution by the method of iodometry.

(3) Acetic acid. Diluting pure glacial acetic acid (99~100%) 0.9 mol/*l.* solution was prepared and titrated with the standard barium hydroxide.

(4) Sodium acetate. The salt which had fully been dried was accurately weighed and 0.9 mol/*l.* solution prepared.

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6) S. Horiba and T. Ichikawa, *Rev. Phys. Chem.*, **1**, 145 (1927); T. Ichikawa, *Z. Physik. Chem.*, (B), **10**, 299 (1930).

7) S. Horiba, *Rev. Phys. Chem.*, **11**, 189 (1937); T. Kōsaki, *ibid.*, **12**, 21 (1938).

Thermal analysis, procedure and apparatus.

The principle of the thermal analysis can be represented by this:

$$\frac{dT}{dt}-\frac{dT'}{dt}=\frac{Q}{W}\frac{dx}{dt}, \tag{6}$$

where $\frac{dT}{dt}$ denotes the observed value of the temperature change in a reaction system, $\frac{dT'}{dt}$ the cooling velocity due to the temperature difference between a reaction system and its surroundings, Q the reaction heat, W the water equivalent of the reaction system, and $\frac{dx}{dt}$ the reaction velocity. In the present case when the cooling confirms to Newton's law, the cooling velocity is

$$-\frac{dT'}{dt}=K\Delta T', \tag{7}$$

where K is the cooling constant and $\Delta T'$ the temperature difference between the reaction system and its surroundings.

From the observed value of $-\frac{dT''}{dt}$, the natural cooling of the reaction system, K can be calculated; hence W, the water equivalent of the reaction system, by calculating $\frac{dT'}{dt}$ with a constant supply of a known amount of heat to the reaction system. From K and W, the reaction heat Q can be easily obtained thus: let T_0 represent the temperature in the reaction system at the time t_0 and T_a represent that at the time t_a as the reaction proceeds. If "a" mols of the reaction product are produced, the reaction heat for 1 mol is given by the following expression which has been derived from equations (6) and (7):

$$Q=\frac{W}{a}\left\{\int_{t_0}^{t_a}dT+K\int_{t_0}^{t_a}\Delta T dt\right\}$$

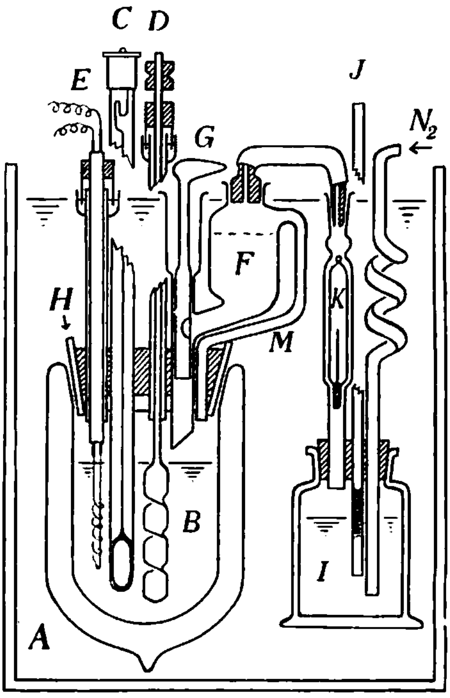
$$=\frac{W}{a}\left\{(T_a-T_0)+KS\right\}, \tag{8}$$

where S is the area of the integrated graph surrounded with the cuive showing the relation between $\Delta T'$ and t.

The temperature rise per unit time $\frac{dT}{dt}$ was calculated by means of a calorimeter which is shown in Fig. 1.

A is a thermostat of 25±0.002°C.; B a glass Dewar vessel which is capable of holding about 200 c.c. solution; C is a normal. Beckmann thermometer; D a glass stirrer rotating 280±20 times per minute; E is a heater with platinum wire resistance which is movable up and down; F a glass vessel with a ground glass lid holding about 50 c.c. solution, which is connected with B by a leading tube M; G a cock

Fig. 1.



attached to F and by turning it about 130° the solution in F flows into B; H a ground glass mantle inserted in the upper part of B, having a rubber stopper under which a paraffin-soaked thin cork plate is attached; I the flask which holds alkaline pyrogallol solution to be used for the purification of nitrogen to expell the air on the B and F solutions; J the manometer to measure the rate of flow of nitrogen; K a normal thermometer (graduated into a tenth of a degree), by which the temperature of nitrogen is ascertained to be equal to that of the thermostat.

When B holding 100 c.c. of mixed aqueous solution of potassium iodate, acetic acid and sodium acetate is heated to almost the same temperature as that of the thermostat by E, it is raised upwards and on 50 c.c. of acid sodium sulphite solution held in F purified nitrogen is made to flow for 20～30 minutes at such a speed as not to lower the temperature of the solution.[8] The gas flows out from the place made air tight with liquid paraffin through F, M and B. 1 hour later, the F solution is mixed with the B solution.[9] At the same time, the reading of Beckmann thermometer being tapped automatically is made together with the time reading by a stop watch. It takes 2.0～2.2 seconds to drop out the whole of the F solution and, according to a test with a coloured solution and water, both solutions are mixed instantaneously. Therefore, the author assumed that the reaction started at the moment the F solution was dropped in.

Values of the cooling constants and the water equivalent.

The resistance of the platinum wire E for electric heating was measured preliminarily by means of a potentiometer and a standard 1 ohm resistance under the same condition as in the calculation of the water equivalent and found to be 2.019 ohm. Similarly, the accuracy of the ammeter used for reading the electric current to the heater was confirmed. The values of W, the water equivalent, and K, the cooling constant,[10] obtained thus are given in Table 1.[11]

Here it is to be noted that a platinum wire is dipped in 150 c.c. of the solution in the case of the calculation of the water equivalent, but not in the course of the reaction. Therefore it is no wonder that this caused the difference between the cooling constants for both cases; K_w and K_r in Table 1 correspond to those for the calculations of the water equivalent and the reaction velocity respectively. And the exact water equivalent for the reaction is to

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[8] Skrabal and Zahorka (*loc. cit*) carried out this experiment in the air and observed the autoxidation of acid sulphite when the reaction was slow, especially at the later part of the reaction. They recommended that the reaction should be made in the atmosphere of inert gas. Accordingly, the present author relieved himself of the trouble of passing nitrogen when the reaction was supposed to take place relatively rapidly.

[9] It was preliminarily ascertained that the change of the titre of acid sulphite in the vessel F during the procedure was so small as to be neglected.

[10] When the cooling is corrected using the value of K according to equation (7), the temperature of the surroundings of the reaction system should be taken to be 0.017°～0.019°C., higher than the temperature of the thermostat. For the cooling is caused by some other method than that of conduction and also affected by the heat of stirring.

[11] When room temperature was higher than 25°C., the wind by an electric fan was made to blow on the surface of the thermostat for cooling and the thermostat was heated by a microburner.

Table 1.

150 c.c. solution and water (25°C.)

Expt. No.	i (amp.)	K_w' (min.$^{-1}$)	K_r' (min.$^{-1}$)	$\frac{dT}{dt}+K_w'\Delta T$ (°C./min.)	W (cal.)	N.B.
I, 1	0.500	0.01173	0.01123	0.04371	165.60	The same pure water
2	0.496	"	"	0.04304	165.50	
3	0.400	"	"	0.02794	165.81	
4	0.300	"	"	0.01569	166.11	
II, 5	0.400	0.01179	0.01131	0.02785	166.33	Pure water
III, 6	0.300	0.01184	0.01138	0.01571	165.85	
IV, 7	0.400	0.01174	0.01123	0.02798	165.57	The same solution of KIO_3, HAc & NaAc
8	0.300	"	"	0.01570	165.94	
V, 9	0.400	0.01178	——	0.02802	165.34	Solution after reaction
VI, 10	0.300	0.01181	——	0.01573	165.69	

Mean values: $K_w'=0.01178$; $K_r'=0.01130$; $W=165.8$

be given by deducting that of the platinum wire from the value of W in Table 1. As the water equivalent of the latter, however, is only 0.02 (cal.), the value of W, in practice, is given by the above-mentioned mean value: 165.8 (cal.).

Theoretical.

(a) Thermal analysis of the second order reaction.

As already mentioned, when iodic acid is in excess of sulphurous acid, the Landolt effect appears, and the reaction becomes so much complicated that it is now a little difficult to deal with it thermo-analytically. An interesting question is whether or not the introducing reaction (1) can be isolated when the quantities of iodic acid and sulphurous acid are almost equal, or when sulphurous acid is in excess of iodic acid. In order to solve this question, when the hydrogen ion concentration is fixed by a buffer solution of acetic acid and acetate having excessive concentrations for the other reactants, the reaction must be dealt with as a second order reaction with respect to iodic and sulphurous acids.

In this case it is possible that, the concentration of one reactant being made to be more than 10 times as high as that of the other, the velocity constant of the second order reaction is calculated from that of a pseudo-unimolecular reaction as done by Y. Nakanishi[12] in his thermo-analytical study of the reaction between chromic acid and oxalic acid. This method, however, can not be generally applied in the present case. Therefore, it is desirable for us to have a new

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[12] Y. Nakanishi, *Rev. Phys. Chem. Japan* (*Japanese edition*), 9, 95 (1934).

thermo-analytical method to be applied for the second order reaction, except that for the first order reaction which has already been used.

The author's thermal analysis of the second order reaction will be mentioned below.

(1) When the concentrations of two reactants are equal, we have

$$\frac{dx}{dt}=k_2(a-x)^2, \tag{9}$$

where k_2 is the velocity constant of the second order reaction, and a the initial concentration of the reactants. Being integrated, this becomes

$$k_2=\frac{1}{t}\cdot\frac{x}{a(a-x)}. \tag{10}$$

Hence

$$x=\frac{k_2a^2t}{k_2at+1}. \tag{11}$$

Substituting (11) in (9), we have

$$\frac{dx}{dt}=k_2\left(\frac{a}{k_2at+1}\right)^2. \tag{12}$$

Then, substituting this in our fundamental formula (6), we have

$$\frac{d\theta}{dt}=\frac{Qk_2}{W}\left(\frac{a}{k_2at+1}\right)^2, \tag{13}$$

where $\frac{d\theta}{dt}$ is what has been obtained by adding $K\Delta T$, the correction for the cooling, to $\frac{dT}{dt}$. Taking the roots of both sides of equation (13) and then their reciprocals, this becomes

$$\frac{1}{\sqrt{\frac{d\theta}{dt}}}=\sqrt{\frac{Wk_2}{Q}}\cdot t+\frac{1}{a}\sqrt{\frac{W}{Qk_2}}. \tag{14}$$

Accordingly, if the reaction is of the second order, plotting the directly observed value of $1\Big/\sqrt{\frac{d\theta}{dt}}$ for the time t, a straight line will be obtained. The slope of the line thus obtained is given by $\sqrt{Wk_2/Q}$, and the length of the ordinate at $t=0$ by $\frac{1}{a}\sqrt{W/Qk_2}$. Let S and I represent this slope and its intercept respectively, then the following relations will hold:

$$k_2=\frac{S}{I\times a}=\frac{S^2\times Q}{W}=\frac{W}{I^2\times Q\times a^2} \tag{15}$$

and

$$Q=\frac{W}{S\times I\times a}. \tag{16}$$

Consequently, the values of the velocity constant k_2 and the reaction heat Q can be easily calculated.

If $\frac{d\theta}{dt}$ at t_1 and that at t_2 are represented by $\left(\frac{d\theta}{dt}\right)_1$ and $\left(\frac{d\theta}{dt}\right)_2$ respectively, equation (14) becomes

$$\sqrt{k_2}\cdot\sqrt{\frac{W}{Q}}=\frac{1}{t_2-t_1}\left\{\frac{1}{\sqrt{\left(\frac{d\theta}{dt}\right)_2}}-\frac{1}{\sqrt{\left(\frac{d\theta}{dt}\right)_1}}\right\}. \tag{17}$$

(2) When the concentrations of two reactants are different from each other, we have

$$\frac{dx}{dt}=k_2(a-x)(b-x), \tag{18}$$

where a and b are the initial concentrations of the two reactants. Being integrated, this becomes

$$k_2=\frac{1}{t}\cdot\frac{1}{a-b}\ \ln\frac{b(a-x)}{a(b-x)};$$

hence

$$x=\frac{ab\{e^{k_2t(a-b)}-1\}}{ae^{k_2t(a-b)}-b}. \tag{19}$$

Substituting this in equation (18), we have

$$\frac{dx}{dt}=k_2ab(a-b)^2\cdot\frac{e^{k_2t(a-b)}}{\{ae^{k_2t(a-b)}-b\}^2}. \tag{20}$$

Then, substituting this in equation (6), we have

$$\frac{d\theta}{dt}=\frac{Q}{W}\cdot k_2ab(a-b)^2\cdot\frac{e^{k_2t(a-b)}}{\{ae^{k_2t(a-b)}-b\}^2}. \tag{21}$$

In this case, even if equation (21) is transformed, such a simple relation as equation (14) will not be obtained. Accordingly, the curve of $\frac{d\theta}{dt}\sim t$ directly observed, by using the value of k_2 obtained from equation (15) when $a=b$, and that of Q from equation (16) or equation (8) or from the thermochemical data, should be verified in the whole course of the reaction.

(b) Comparison of the formula of the second order reaction with that of the first order reaction.

The formula of the first order reaction[7] is this:

$$\ln\left(\frac{d\theta}{dt}\right)=\ln\frac{Qk_1a}{W}-k_1t, \tag{22}$$

where k_1 is the velocity constant of the first order reaction and a the initial concentration of a reactant.

Let us compare equation (22) with (14). In the former, the velocity constant can be simply obtained merely from the linear slope expressing the relation between $\log\left(\frac{d\theta}{dt}\right)$ and t, but not in the latter as seen from equation (15). As to the latter, in the calculation of k_2 we have an advantage of being able to adopt any one of the three terms in the right hand side of equation (15) according to the combination of two or three reliable values from S, I, Q and a. In the adoption of I, however, attention should be paid to the fact that the numerical values of the intercept would considerably depend upon the measurement of the start of the reaction or $t=0$, analogous to the case of chemical analysis. As to the thermal analysis, the time when the reaction starts is determined relatively accurately by observing the rise of temperature by means of a Beckmann thermometer, and the time lag caused by the thermometer can be checked by extrapolating the observed curve of $\Delta T \sim t$. Therefore, the present method of using the intercept is comparatively satisfactory as will be seen later from the value of k_2. When the reaction heat is known or calculated accurately, it is better for us to calculate k_2 from equation (17) taking any time after the start of the reaction to be zero, as the case of chemical analysis.

It is well known that the velocity constant of the first order reaction is independent of the concentration, while that of the second order reaction depends on the unit of the concentration. Accordingly, in the case of the first order reaction, if the number of gram mols of the reacting substances present in the whole capacity of the reaction system is substituted, for example, in "a" in equation (22), the velocity constant and the reaction heat for 1 gram mol can be directly obtained. In the case of the second order reaction, in order to obtain the velocity constant indicated by the unit of gram mol per litre and the reaction heat for 1 gram mol directly from equation (14) and others as in the above case, the whole capacity of the reaction system must be 1 litre and so only the value of W corresponding to this should be used. Accordingly, when the capacity is not 1 litre, for instance, a c.c., for the above-mentioned purpose, what the multiplication of the observed water equivalent by the numerical value of $\frac{1000}{a}$ gives must always be used.

Results.

In the Landolt introducing reaction:

$$IO_3^- + 3HSO_3^- + 3Ac^- \rightarrow I^- + 3SO_4^{--} + 3HAc, \qquad (23)$$

the ratio of the molar concentration of potassium iodate to that of acid sodium sulphite should be 1 : 3, or it should be "equivalent concentration". If 1 mol of acid sodium sulphite is used for 1 mol of potassium iodate, the Landolt effect will apppear because of excess in potassium iodate.

The concentrations of acetic acid and sodium acetate, which were employed in order to fix the pH of the reaction system to 4~5 and to keep the hydrogen ion concentration constant in the course of the reaction, were made to be amply high for those of potassium iodate and acid sodium sulphite. This procedure might be enough to prevent the ionic strength of the solution from varying in the reaction system during the reaction, as seen from the above-mentioned stoichiometric equation: (23).

Whether the reaction (23) proceeds according to the second order reaction or not is the immediate question. To this the present author intended to apply the thermal analysis of the second order reaction. This intention is attained best in the case when the concentrations of potassium iodate and acid sodium sulphite are equivalent to each other. Therefore, the experimental results obtained are divided into two cases: (I) when the concentrations of the two reactants are equivalent and (II) when those are not equivalent. To the former case, equation (9) is to be applied, and to the latter, equation (18). And if the molar concentration of potassium iodate be substituted in the "a" of equations (9) and (18), then one third of the molar concentration of acid sodium sulphite in "b" of equation (18). Hence, in the following descriptions, the cases (I) and (II) will be mentioned simply as the case: $a=b$ and the case: $a\neq b$ respectively.

(I) The case when the concentrations of potassium iodate and acid sodium sulphite are equivalent.

(a) When the concentrations of potassium iodate and acid sodium sulphite are fixed aud hydrogen ion concentration is varied.

Experiments were carried out[13] on the solutions, whose concentrations are given in Table 2, taken out by means of calibrated pipettes from stock solutions. The whole capacity of the reaction system was 150 c.c.

One of the results obtained on the experiments in Table 2, e.g. on Expt. 4, is given in Table 3.

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[13] The vessel (F in Fig. 1) holding 50 c.c. of the solution was preliminarily washed with the same solution as was used in the experiment. In the experiment, 0.05 c.c. of this solution being dropped in the Dewar vessel at a certain time after the start of the measurement, it was received by a small removable dish lest the water equivalent should be changed during the reaction. Therefore, the amount of the solution was preliminarily increased by 0.05 c.c.

Table 2.

Expt. No.	Solution in Dewar vessel before mixed (Total volume 100 c.c.)				Solution to be added (Total volume 50 c.c.)	
	KIO_3 0.03 mol/*l.*	HAc 0.9 mol/*l.*	NaAc 0.9 mol/*l.*	H_2O	$NaHSO_3$ ca. 0.09 mol/*l.*	H_2O
1	10 c.c.	10 c.c.	20 c.c.	60 c.c.	13.72 c.c.	36.28 c.c.
2	10	20	20	50	13.74	36.26
3	10	30	20	40	13.72	36.28
4	10	40	20	30	13.72	36.28

Table 3.
(Expt. 4 in Table 2.)

T (°C.)	t (min · sec)	T (°C.)	t (min · sec)	T (°C.)	t (min · sec)	T (°C.)	t (min · sec)	T (°C.)	t (min · sec)
3.763	0	3.850	38	3.950	2 · 29	4.000	7 · 00	3.990	26 · 00
”	3	860	43	960	53	003	8	983	29
770	6	870	49	970	3 · 26	006	9	978	32
780	10	880	56	975	46	007	10	969	36
790	14	890	1 · 5	978	4 · 00	008	12	962	40
800	17	900	14	983	30	008	14	951	46
810	21	910	24	988	5 · 00	007	16	942	50
820	25	920	37	992	30	006	18	932	56
830	29	930	50	996	6 · 00	002	20	921	62
840	34	940	2 · 9	998	30	3.997	23	912	68

Using the observed values as in Table 3, the curves obtained by plotting ΔT for t with respect to Expts. 1, 2, 3 and 4 are shown in Fig. 2.[14]

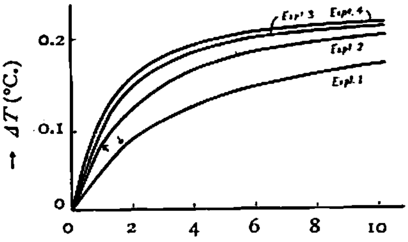

Fig. 2.—Influence of [H+].

The values of $\frac{d\theta}{dt}$ and $1\Big/\sqrt{\frac{d\theta}{dt}}$ of Expt. 4 calculated from $\frac{dT}{dt}$, which has been obtained from the tangent of the curve of $\Delta T \sim t$, are given in Table 4.

The value of $\sqrt{k_2}\cdot\sqrt{\frac{W}{Q}}$ tabulated in the last column of Table 4 having been calculated according to equation (17), it is satisfactorily constant for the whole course of the reaction. The linear relation was obtained between $1\Big/\sqrt{\frac{d\theta}{dt}}$ and t, as predicted from equation (14), as shown in Fig. 3 with respect to Table 4 and in Fig. 4 with respect to all the experiments of Table 2. (Some deviation from the line at the intial part will be discussed in section (III)).

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[14] The mark in the figure will be explained later.

Table 4.
(Expt. 4 in Table 2)

t (min.)	ΔT (°C.)	$\frac{dT}{dt}$ (°C./min.)	$\frac{d\theta}{dt}$ (°C./min.)	$1/\sqrt{\frac{d\theta}{dt}}$	$\sqrt{k_2}\cdot\sqrt{\frac{W}{Q}}$
1/6	0.015	0.1519	0.15188	2.57	
2/6	0.043	0.1547	0.15499	2.54	
3/6	0.067	0.1329	0.13347	2.74	
4/6	0.089	0.1256	0.12641	2.82	
5/6	0.107	0.0858	0.08682	3.39	
1	0.120	0.0738	0.07496	3.65	—
8/6	0.142	0.0594	0.06081	4.06	(1.23)
10/6	0.158	0.0421	0.04369	4.80	(1.73)
2	0.171	0.0350	0.03674	5.22	1.57
2.5	0.186	0.0262	0.02811	5.96	1.54
3	0.198	0.0197	0.02175	6.78	1.54
3.5	0.206	0.0156	0.01774	7.51	1.54
4	0.214	0.0127	0.01493	8.18	1.51
5	0.224	0.0083	0.01059	9.72	1.52
6	0.231	0.0057	0.00812	11.10	1.49
7	0.236	0.0038	0.00628	12.62	1.50
8	0.239	0.0021	0.00460	14.75	1.59

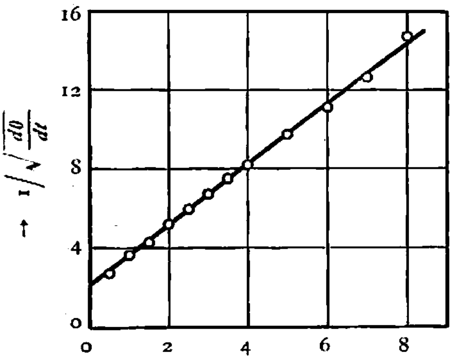

Fig. 3.—Expt. 4.

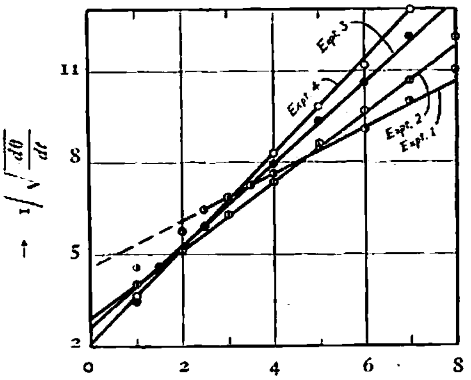

Fig. 4.—Influence of [H+].

Using the values of the slope S and the intercept I for each line obtained from Fig. 4, the velocity constant k_2 was calculated by the three different formulae of equation (15) and the reaction heat Q was calculated by equations (8) and (16). In order to obtain k_2 having the unit of mol per litre and to calculate Q corresponding to 1 mol of potassium iodate, the following precautions have been taken. (i) The concentrations of the reactants in Table 2 are converted to mol per litre; (ii) in "a" of equations (8), (15) and (16), the molar concentration of potassium iodate is substituted; (iii) for the water equivalent W to be used in the calculations of Q and k_2, the value, $165.8 \times 1000/150 = 1105$, is taken instead of 165.8 which has been preliminarily obtained for the true water equivalent W (Table 1).

The values of k_2 and Q thus calculated are tabulated in Table 5, where "Q_g" denotes the reaction heat calculated by equation (8) and the value of Q_g for each experiment was used, for convenience, in the calculation of the corresponding k_2 when the reaction heat Q is necessary.

Table 5.

Expt. No.	Conc. of reacting substances (mol/litre)				Q (Kcal.)		k_2 (mol/litre; min.)			Time lag (sec.)	Atmosphere
	$NaHSO_3$	KIO_3	HAc	NaAc	Q_g	$\frac{W}{S \cdot I \cdot a}$	$\frac{S}{I \cdot a}$	$\frac{S^2 \cdot Q}{W}$	$\frac{W}{I^2 \cdot Q \cdot a^2}$		
1	0.006	0.002	0.06	0.12	156.3	157.5	83 (83)	82	83	3	nitrogen
2	0.006	0.002	0.12	0.12	159.8	165.6	185(189)	178	191	4	"
3	0.006	0.002	0.18	0.12	160.1	156.1	247(251)	254	241	1.5	"
4	0.006	0.002	0.24	0.12	156.2	163.1	349(362)	334	364	3	"

As seen from Table 5, though the methods of calculating the value of Q and of k_2 are thermo-analytically different from one another, these values are in good agreement.[15]

That the reaction takes place stoichiometrically according to equation (23) is justified by the good agreement of the observed values of the reaction heat with the value of 159.6 Kcal. obtained by calculation from the thermochemical data.[16]

Assuming that the reaction is proportional to the first power of the hydrogen ion concentration, when the values of k_2 of each experiment obtained, for example, from the expression "$S/I \cdot a$" were divided by the integers, 2, 3 or 4 to make it equal to the pH value of Expt. 1, those of Expts. 1, 2, 3 and 4 were found to be 82.7, 92.3, 82.5 and 87.1 respectively, and 86.2 as the mean value. From these results it is evident that the reaction is proportional to the hydrogen ion concentration $[H^+]$. It follows, therefore, that the velocity equation (4) of Skrabal and Zahorka is valid.

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15) As to the value of the intercept (I) in equations (15) and (16), of course, it is corrected by the time lag (See the 5th column.) which has been taken to be the mean value between the observed value and the value obtained by extrapolation of the $\Delta T \sim t$ curve. The values in parenthesis are what have not been corrected, but it is seen that there is little difference between those values and the corrected ones.

16) Bichowski & Rossini, *Thermochemistry of Chemical Substances* (1936).

(b) Influence of dilution.

In the case when each solution of the reactants is diluted in equal proportion, the ratio of the concentration of acetic acid to that of sodium acetate being made to be constant, the experimental results obtained are given in Table 6,[17] the $\Delta T \sim t$ curve in Fig. 5, and the linear relation of $1\Big/\sqrt{\frac{d\theta}{dt}} \sim t$ in Fig. 6.[18]

Table 6.

Expt. No.	Conc. of reacting substances (mol/litre)				Q (Kcal.)		k_2 (mol/litre ; min.)			Time lag (sec.)	Atmosphere
	$NaHSO_3$	KIO_3	HAc	NaAc	Q_g	$\frac{W}{S \cdot I \cdot a}$	$\frac{S}{I \cdot a}$	$\frac{S^2 \cdot Q}{W}$	$\frac{W}{I^2 \cdot Q \cdot a^2}$		
5	0.012	0.004	0.12*	0.12	163.6	163.0	199	199	199	9	air
6	0.009	0.003	0.09*	0.09	165.2	163.2	154	154	154	8	,,
7	0.006	0.002	0.06*	0.06	156.3	151.9	86	88	84	13	,,
8	0.003	0.001	0.03	0.03	129.2	124.2	53	55	51	5	nitrogen
2	0.006	0.002	0.12	0.12	159.8	165.6	185	178	191	4	,,

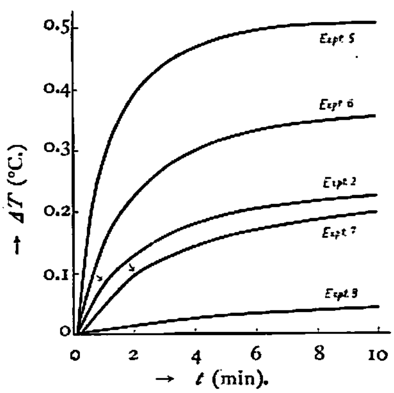

Fig. 5.—Influence of dilution.

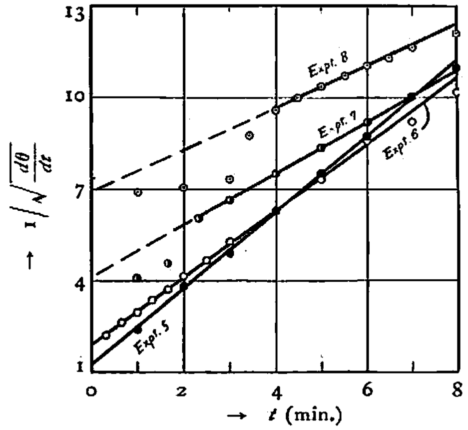

Fig. 6.—Expt. 8; $\left[\left(1\Big/\sqrt{\frac{d\theta}{dt}}\right)-6\right] \sim t$.

As seen in Table 6, the values of Q and k_2 of each experiment are in good agreement with each other. (See the same row.) The values of k_2 are considerably different from one another in different experiments, except those of Expts. 2 and 5. This difference is ascribed to the salt effect as will be explained later.

If the calculated value of $\frac{d\theta}{dt}$ (Table 7) is plotted for t according to equation (13), for example, using the values of Q and k_2 in Table 6 for the observed curve

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[17] The concentrations of acetic acid used in the experiments indicated by * are 1.153 times as large as those given in the table. Accordingly, the observed value obtained being divided by 1.153, from the results of the preceding section (a), the value of k_2 was obtained.

[18] There is some abnormality at the initial part of the reaction in Expts. 7 and 8.

of $\frac{d\theta}{dt} \sim t$ of Expt. 6, taking the correction of the time lag (8 seconds) into consideration, both the calculated and observed values agree well with each other for the whole course of the reaction as seen in Fig. 7.

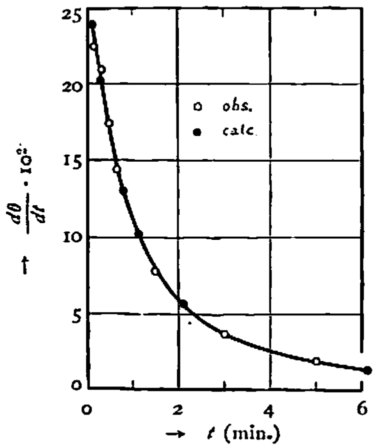

Fig. 7.—Expt. 6.

(c) Salt effect.

As described in the preceding section (b), the deviation of the velocity constant k_2 in Table 6 is chiefly caused by the salt effect of sodium acetate in the solution.

Skrabal and Zahorka[4] carried out the same experiment as Expt. 8 (Table 6) at 25°C. by chemical analysis and found the value of k_2 to be 29. This value of his is remarkably different from the present author's—53. Considering that the difference might be due to the decomposition of acid sodium sulphite in stock, the following two experiments were performed: (1) the case when acid sodium sulphite solution of almost the same concentration as before was employed immediately after its preparation; (2) the case when sodium chloride was added as a neutral salt to the solution of the former case. The results obtained are given

Table 7.
(Expt. 6 in Table 6)

t (min.)	ΔT (°C.)	$\frac{d\theta}{dt}$ (obs.) (°C./min.)	$1/\sqrt{\frac{d\theta}{dt}}$	$\sqrt{k_2}\cdot\sqrt{\frac{W}{Q}}$	$\frac{d\theta}{dt}$ (calc.) (°C./min.)
0	0	0			0.2390
1/6	0.008	0.22523	2.11	—	0.2017
2/6	0.044	0.20954	2.19	(0.48)	
3/6	0.077	0.17391	2.40	0.87	0.1491
4/6	0.104	0.14412	2.63	1.06	0.1302
5/6	0.126	0.12856	2.79	0.82	
1	0.147	0.11490	2.95	1.01	0.1018
8/6	0.181	0.08889	3.35	1.07	0.0818
10/6	0.206	0.07226	3.72	1.07	0.0671
2	0.227	0.05800	4.16	1.12	0.0561
2.5	0.252	0.04609	4.66	1.09	
3	0.271	0.03620	5.26	1.11	0.0354
4	0.298	0.02631	6.24	1.08	0.0244
5	0.317	0.01882	7.31	1.08	
6	0.330	0.01367	8.66	1.12	0.0136
7	0.380	0.01187	9.21	1.04	0.0107

in Table 8, the $\Delta T \sim t$ curve for each in Fig. 8 and the linear relation of $1 \Big/ \sqrt{\frac{d\theta}{dt}} \sim t$ in Fig. 9.

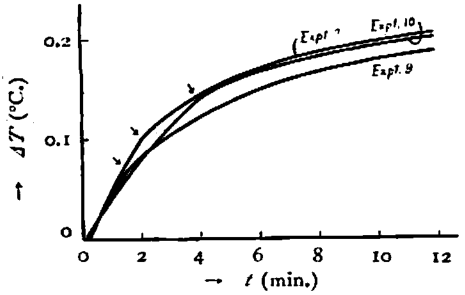

Fig. 8.—Salt effect.

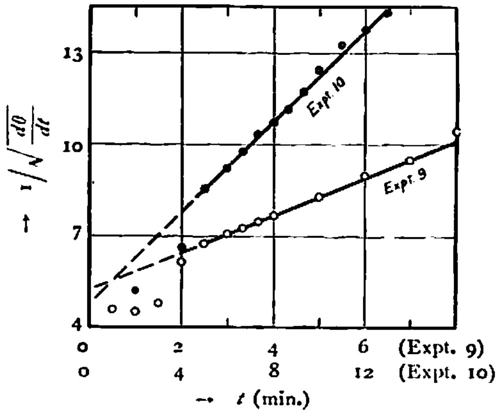

Fig. 9.—Salt effect.

Table 8.

Expt. No.	Conc. of reacting substances (mol/litre)					Q (Kcal.)		k_2 (mol/litre; min.)		Time lag (sec.)	Atmosphere
	$NaHSO_3$	KIO_3	HAc	NaAc	NaCl	Q_θ	$\frac{W}{S \cdot I \cdot a}$	$\frac{S}{I \cdot a}$	$\frac{S^2 \cdot Q}{W}$		
7	0.006 (old)	0.002	0.06*	0.06	—	156.3	151.9	86	88	13	air
9	0.006 (new)	0.002	0.06	0.06	—	162.0	172.6	57	54	5	nitrogen
10	0.006 (new)	0.002	0.06	0.06	0.06	154.3	155.1	77	79	4	air

For comparison, the author studied the same reaction as that of Expt. 9 (Table 8) by chemical analysis,[19] and the results obtained are given in Table 9, which agree considerably well with those obtained by the thermal analysis.

It is evident from Tables 8 and 6 that the reaction is affected positively by

Table 9.

Thermal analysis (Expt. 9; nitrogen)						Chemical analysis (Expt. 11; air)		
t (min.)	ΔT (°C.)	$\frac{d\theta}{dt}$ (°C./min.)	$\frac{1}{\sqrt{\frac{d\theta}{dt}}}$	$\sqrt{k_2} \cdot \sqrt{\frac{W}{Q}}$	k_2	t (min.)	Conc. of iodate $(a-x)$ (mol/litre)	k_2
3	0.107	0.02023	7.03	—	—	1	0.001566	—
4	0.124	0.01714	7.64	0.61	55	2	0.001435	58
5	0.139	0.01432	8.36	0.67	66	3.5	0.001229	70
6	0.151	0.01247	8.96	0.64	60	6.5	0.001029	61
7	0.161	0.01117	9.46	0.61	55	10	0.000902	52
8	0.170	0.00934	10.35	0.66	64	16	0.000763	46

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19) The analytical method is the same as used by Skrabal and Zahorka (*loc. cit.*); the reaction was made in a measuring cylinder which was open to the air and dipped in a thermostat at 25°C.

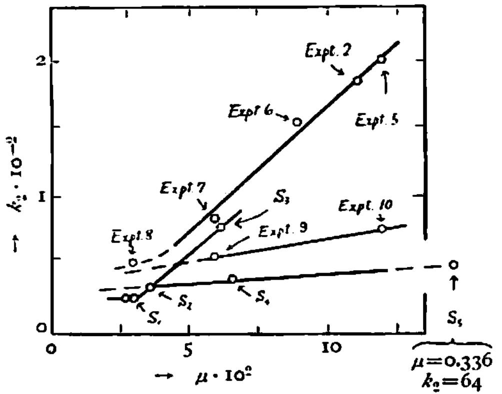

Fig. 10.—Dependence of the velocity constant upon the ionic strength.

the salt effect. Plotting the velocity constant k_2 of each experiment for the ionic strength μ[20] of each reaction system, such a straight line as shown in Fig. 10 was obtained. The results of Skrabal and Zahorka are also shown in Fig. 10 for comparison.[21]

In this figure, the straight line of $k_2 \sim \mu$ obtained by the author agrees well with that of Skrabal and Zahorka in its inclination, especially in the case of no addition of sodium chloride.

(II) The case when the concentrations of potassium iodate and acid sodium sulphite are not equivalent.

When the concentration of one reacting substance is very large as compared with that of the other, that is, n times ($n > 10$) as large, the thermal analysis is most easily applicable. In this case, the reaction proceeds according to a pseudo-unimolecular reaction, so that the equation of thermal analysis of the first order reaction (22) is applicable and the velocity constant k_1 is obtained; hence the value of k_2 by dividing the value of k_1 by $n \times a$.

Therefore, the experiment was carried out on the concentration of acid sodium sulphite 10 times as high as that of Expt. 8 in Table 6. The $\Delta T \sim t$ curve is shown in Fig. 13. (See below.) Plotting $\log\left(\frac{d\theta}{dt}\right)$ for t, a straight line was obtained for the relatively initial part of the reaction as shown in Fig. 11. The values of Q and k_2 calculated from this are given in Table 10.

In other words, if the salt effect is taken into account, the value of k_2 of Expt. 12 calculated by the equation of the thermal analysis of the first order reaction agrees well with that of k_2 by the equation of the second order reaction.

The phenomenon that the reaction does not proceed according to the first

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[20] $\mu = \Sigma 1/2\, mz^2$, where m is the molar concentration of the ion and z its valence. Assuming, for simplicity, that acetic acid does not dissociate, sodium acetate dissociates by 86% and all the others dissociate completely, the calculation was made. If the dissolution of the acid sulphite solution in stock is taken into consideration, the point in Fig. 10 will be removed slightly to the right in parallel with the abscissa.

[21] S_1, S_2, S_3, S_4 and S_5 indicate Expts. 1, 8, 9, 10 and 11 in Table 8 of Skrabal and Zahorka (*loc. cit.*) respectively. Of these, S_3 is what has been obtained by doubling the value of k_2 in Expt. 9 to convert its pH value into the same as the others.

Table 10.

Expt. No.	Conc. of reacting substances (mol/litre)				Q (Kcal.)		k_2 (mol/litre: min.)	Time lag (sec.)	Atmosphere
	$NaHSO_3$	KIO_3	HAc	NaAc	Q_g	$\frac{eI \cdot W}{S \cdot a}$	$\frac{k_1}{10 \cdot a}$		
12	0.030	0.001	0.03	0.03	234.0	227.8	65	1.5	air
						$\frac{W}{S \cdot I \cdot a}$	$\frac{S}{I \cdot a}$		
8	0.003	0.001	0.03	0.03	129.2	124.2	58	5	nitrogen

order reaction from about $t=2$ (min.) in Fig. 11 is also seen in the $\frac{d\theta}{dt} \sim t$ curve of Fig. 12.

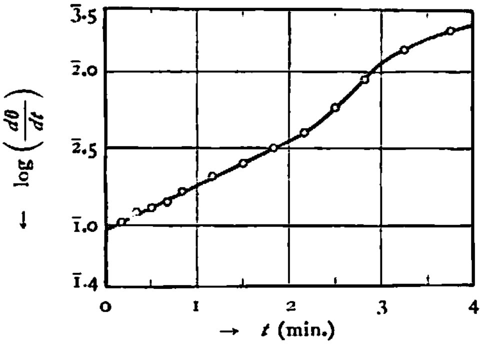

Fig. 11.—Expt. 12 (Pseudo-unimolecular).

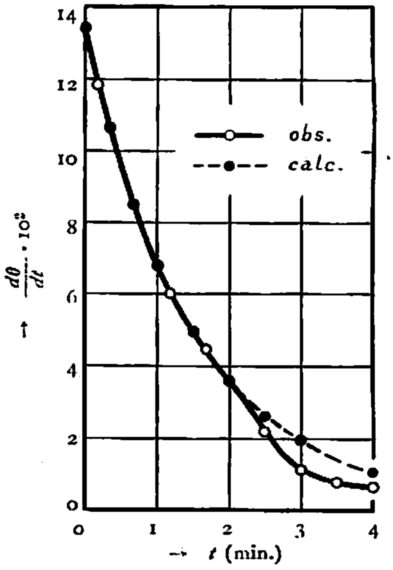

Fig. 12.—Expt. 12 (Pseudo-unimolecular).

In regard to this Expt. 12, using the values of k_2 and Q_g in Table 10, the value of $\frac{d\theta}{dt}$ for t calculated from the equation of the thermal analysis (21) for $a \neq b$ are given in Table 11.

Comparing this result with the observed $\frac{d\theta}{dt} \sim t$ curve, it is seen, as shown in Fig. 12, that the observed curve coincides well with the theoretical one at the initial part of the reaction.

Using this reliable equation (21), other cases where the concentrations of the two reactants are not equivalent were examined. The experiments under the condition: $a \neq b$ are tabulated in Table 12 and the $\Delta T \sim t$ curves are shown in Fig. 13. The value of k_2 corresponding to the ionic strength μ of the reaction medium for each experiment was obtained from Fig. 10. Using this value of k_2 and Q_g calculated by the graphical integration of the $\Delta T \sim t$ curve, the observed

Table 11.

(Expt. 12 in Table 10)

t (min.)	ΔT (°C.)	$\frac{d\theta}{dt}$ (obs.) (°C./min.)	$\log\left(\frac{d\theta}{dt}\right)$	$k_1 \cdot 10^2$ (min.$^{-1}$)	$\frac{d\theta}{dt}$ (calc.) (°C./min.)
0	0	0			0.1336
1/6	0.027	0.11816	$\bar{1}.0724$	—	
2/6	0.046	0.10208	$\bar{1}.0089$	(87.7)	0.1063
3/6	0.062	0.09506	$\bar{2}.9780$	65.4	
4/6	0.077	0.08809	9449	58.8	0.0848
5/6	0.091	0.07505	8754	68.2	
1	0.103	0.06866	8367	65.3	0.0684
8/6	0.122	0.05452	7366	66.5	
0.5	0.131	0.04996	6986	64.7	0.0493
10/6	0.139	0.04447	6481	65.3	
2	0.141	0·03595	5557	65.1	0.0357
2.5	0.165	0.02203	3430	72.3	
3	0.173	0.01140	0569	83.0	0.0196
3.5	0.177	0.00798	$\bar{3}.9020$	81.5	
4	0.179	0.00653	8149	76.3	0.0107

Table 12.

Expt. No.	Conc. of reacting substances (mol/litre)				Q (Kcal.)	Time lag (sec.)	Atmosphere	Variation of conc.
	$NaHSO_3$	KIO_3	HAc	NaAc	Q_g			
13	0.006	0.004	0.06*	0.06	163.7	8	nitrogen	④
14	0.006	0.003	0.06*	0.06	170.8	7	air	③
(7)	0.006	0.002	0.06*	0.06	156.3	13	,,	② (6)
15	0.006	0.001	0.06	0.06	180.1	7	nitrogen	①
16	0.012	0.002	0.06*	0.06	204.0	8	,,	(12)
(8)	0.003	0.001	0.03	0.03	129.2	5	,,	(3)
12	0.030	0.001	0.03	0.03	234.0	1.5	air	(30)

$\frac{d\theta}{dt}\sim t$ curve obtained from Fig. 13 was verified by equation (21). The coincidence of the theoretical $\frac{d\theta}{dt}\sim t$ curve with the observed one is, however, not so good as already seen in Fig. 12 and 7. This shows, as will be explained below, that a new reaction which would prevent the reaction from proceeding duly according to the second order reaction has taken place.

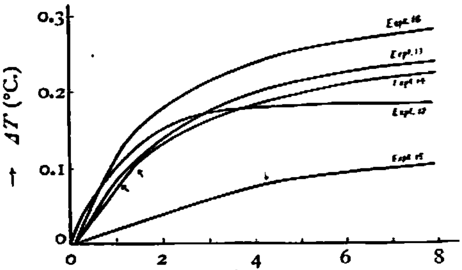

Fig. 13.—[$NaHSO_3$] and [KIO_3] are not equivalent.

(III) The abnormality of the initial part of the reaction.

In most of the $\Delta T \sim t$ curves shown in Figs. 2, 5, 8, and 13, there is a break at the initial part of the reaction,[22] which has been marked with an arrow-like notation. Accordingly, in the case when $a=b$, the linear relation between $1\Big/\sqrt{\frac{d\theta}{dt}}$ and t is always of such a type as Fig. 14 having some deviation in the earlier period; in the case when $a \neq b$, abnormality is found in the $\frac{d\theta}{dt} \sim t$ curve as in Fig. 15. In the latter case, the observed curve is above the theoretical one at the initial part and at the later part[23] slightly below it.

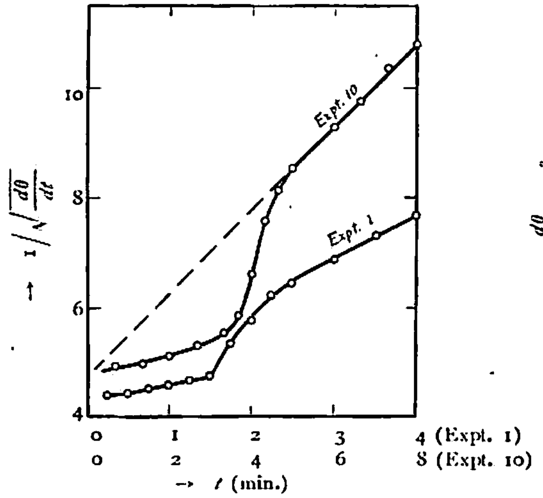

Fig. 14.

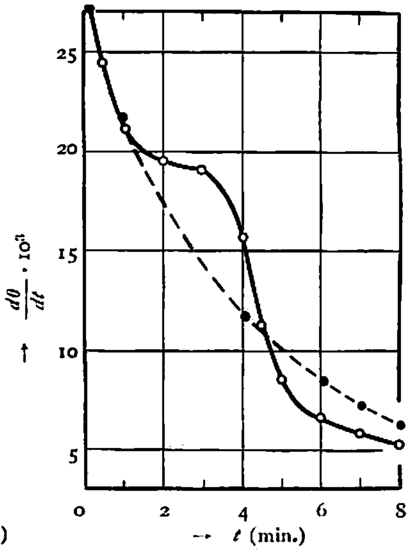

Fig. 15.—Expt. 15.
(○ : obs.; ● : calc.)

A tendency found in the experimental result obtained by chemical analysis using another reaction vessel which was open to the air (Table 9)—the velocity constant becomes smaller towards the end of the reaction—was also noticed in that obtained by chemical analysis made under almost the same conditions (including the reaction vessel but not the atmosphere[24] only) as the thermo-analytical

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[22] In the case of such electrical heating as to make almost the same rise of temperature $\frac{dT}{dt}$ as in the reaction, this break does not appear, so that it seems to be due to the reaction itself and not to the Beckmann thermometer.

[23] But when $a=b$, the both curves nearly agree with each other at the later part, which is supposed to be partially due to the fact that the calculated values of k_2 and Q_g are more accurate than in the case: $a \neq b$.

[24] The thermo-analytical experiment was carried out in nitrogen and the experiment by chemical analysis in the air.

experiment (Table 13). The rise of temperature being measured each time the same reaction was made to proceed, it was ensured that the initial part of the reaction had undoubtedly the peculiarity mentioned above, the degree of which, however, was more or less different in each experiment.

The remarkable changes of this phenomenon of the initial part caused by systematic variation in the conditions of the reaction are shown in Figs. 16~19: the changes made by the variations in iodate, acid sulphite and hydrogen ion concentrations in Figs. 16, 17 and 18 respectively; the change by addition of sodium chloride in Fig. 19.

Table 13.
(Expt. 17; air) (Cf. Expt. 1)

t (min.)	Conc. of iodate $(a-x)$ (mol/litre)	k_2
1.5	0.001677	—
2	0.001503	138
3	0.001321	107
4.5	0.001181	84
6	0.001078	74
11	0.000811	67

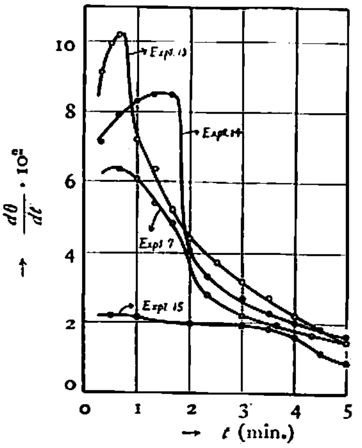

Fig. 16.—Variation of $[KIO_3]$.

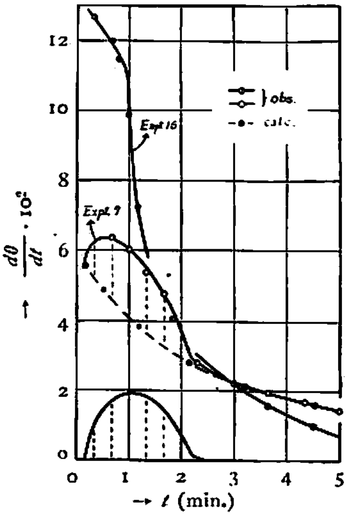

Fig. 17.—Variation of $[NaHSO_3]$.

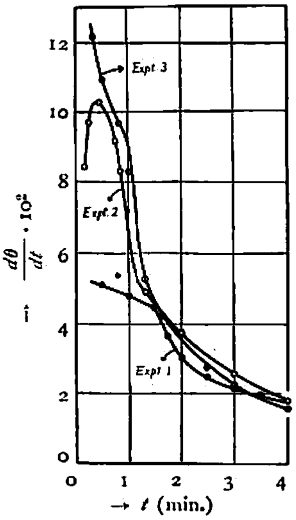

Fig. 18.—Variation of $[H^+]$.

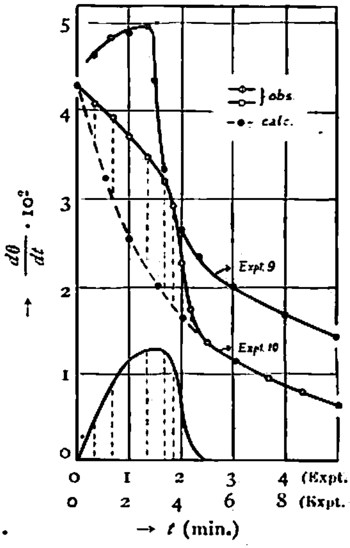

Fig. 19.—Effect of NaCl.

Discussion.

From the above-mentioned results the following conclusions are drawn with ease when $a \fallingdotseq b$.

(1) The values of Q_g from equation (8) and Q from equation (16) are almost equal to that obtained from thermochemical data. It follows that the reaction actually taking place·is stoichiometrically that represented by equation (23) or (1), at least when the both concentrations are equivalent, which may be true even when these concentrations are slightly different.

(2) The observed linear relation between $1\Big/\sqrt{\frac{d\theta}{dt}}$ and t and the influence of $[H^+]$ on k_2 confirm that the following velocity equation:

$$\frac{-d[IO_3^-]}{dt}=\varkappa[IO_3^-][HSO_3^-][H^+]$$

is undoubtedly established when $a=b$, and probably even when $a \fallingdotseq b$.

(3) That the Landolt introducing reaction (1) has been isolated in the present experiments is justified by the facts that a straight line was obtained for the relation between $1\Big/\sqrt{\frac{d\theta}{dt}}$ and t in the main part of the reaction and, the salt effect being taken into consideration, the value of k_2 obtained from this line agrees with that obtained by Skrabal and Zahorka.

It may be said, therefore, the main aim of the present research has been attained. Then, how the abnormality noticed at the initial part is to be explained will be the next subject to handle.

In the case of a slow reaction, it is seen from some experimental results obtained by titration that the iodate ions which should have been exhausted remain as they are, though a few, in the reaction system after the reaction has finished. This is, as Skrabal and Zahorka said, ascribed to a partial oxidation of acid sulphite due to the oxygen present in the reaction vessel. In fact, when the concentration of acid sulphite is too high for that of iodate, the reaction heats calculated from equation (8) are large in amount as compared with that in the case when the concentrations of acid sulphite and iodate are equivalent, and in Expts. 12 and 14 where the reaction vessels were open to the air, it is seen from the calculation of the reaction heat Q_g by equation (8) that heat is being generated continuously in. a little amount even when the reaction seems to have finished. This may be also ascribed to the oxidation of acid sulphite in the presence of oxygen.

From the fact that in some cases the observed $\frac{d\theta}{dt}\sim t$ curve coincides quite well with its theoretical curve at the later part where the phenomenon in question has disappeared rapidly and completely, plotting the difference between the observed $\frac{d\theta}{dt}$ and the theoretical one corresponding to each time at the initial part for t, the curve (mountain-like) shown below in Fig. 17 or 19 was obtained, which is the $\frac{d\theta}{dt} \sim t$ curve only for the phenomenon in the initial part.

Assuming that this $\frac{d\theta}{dt} \sim t$ curve is ascribed to the oxidation of acid sulphite by dissolved oxygen in the solution containing the reacting substances, the amount of heat evolved only by the phenomenon in question can be calculated by the graphical integration of the corresponding $\frac{d\theta}{dt} \sim t$ curve just described and by the same water equivalent. As far as the order is concerned, the number of gram mols of the decomposed acid sulphite calculated, using the heat of oxidation 65.0 kcal.[25] for 1 mol of acid sulphite, is comparable with those of the oxygen present at 100°C. in water, and this amount of oxygen is always found to be sufficient for the above-mentioned decomposition of acid sulphite. Accordingly, it is supposed that in the present experiments the actual amount of the dissolved oxygen as is capable of taking part in the rapid oxidation may be, in fact, smaller than the above-mentioned amount.

The number of gram mols of iodate remaining until after the reaction is a third of that of acid sulphite thus calculated, so that the corrected reaction heat Q_r for 1 mol of iodate can be accurately calculated by the following expression:

$$Q_r = \frac{(\text{Total amount of heat}) - (\text{Amount of heat due to autoxidation})}{(\text{No. of mols of iodate initial}) - (\text{No. of mols of iodate remaining})}.$$

The results obtained are given in Table 14.

Table 14.

Expt. No.	Comparison between sulphite and oxygen (mol/litre)		Amount of heat (cal./litre)		Amount of iodate (mol/litre)		Reaction heat (Kcal.)	
	decomposed sulphite	dissolved oxygen	total	due to autoxidation	initial	remaining	corrected (Q_c)	not corrected (Q_g)
1	0.0003430	0.0006895	312.59	22.29	0.002	0.0001143	154.0	156.3
2	0.0002507	0.0006901	319.60	16.29	0.002	0.0000836	158.3	159.8
7	0.0004855	0.0007062	312.92	31.56	0.002	0.0001618	153.1	156.5
9	0.0005165	0.0007589	324.19	40.23	0.002	0.0001722	155.4	162.1
10	0.0006868	0.0007589	308.61	44.65	0.002	0.0002289	149.0	154.3

As seen in Table 14, the value of Q_c is nearly equal to that obtained

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[25] This value is what has been obtained by calculation using the thermochemical data of Bichowski and Rossini (*loc. cit.*), with respect to the following reaction:

$$HSO_3^- + \frac{1}{2}O_2\,(aq.) + Ac^- \rightarrow SO_4^{--} + HAc.$$

thermochemically i.e. 159.6 kcal., and not so different from the value of Q_g which has not been thus corrected.

Again, that the phenomenon in question is caused by the oxidation of acid sulphite by oxygen is supported by the following facts: (i) the value of the velocity constant k_2 obtained by chemical analysis becomes smaller as time elapses; (ii) the amount of the decomposed acid sulphite when nitrogen is substituted for the air (Expt. 1) is smaller than when the reaction vessel is open to the air (Expt. 17); (iii) when the concentrations of acid sulphite and iodate at the instant when the initial part of the reaction has ended are calculated, and $\frac{d\theta}{dt}$ is plotted for t taking these concentrations for new initial ones, the curve thus obtained will become more equal to the observed $\frac{d\theta}{dt}\sim t$ curve than the theoretical one with no correction.

Assuming that the phenomenon in question appears because the oxidation of acid sulphite takes place as a side reaction of the reaction between acid sulphite and iodate, this side reaction is one of the autocatalytic reactions and ends rapidly in each experiment as seen from the $\frac{d\theta}{dt}\sim t$ curve shown at the lower part of Fig. 17 or 19 and also from Figs. 16~19. Moreover, the reaction velocity of this side reaction is nearly proportional to the concentrations of iodate, acid sulphite and hydrogen ion, and the higher these concentrations are, the shorter duration of the phenomenon.

From these considerations it seems most probable that the oxidation of acid sulphite[26] by oxygen is accelerated by a catalytic action of the iodide ion, the product of the reaction between acid sulphite and iodate. According to A. Berg,[27] for each concentration of sulphurous acid there is a limiting proportion of hydroiodic acid which has no influence on the oxidation, but the hydroiodic acid has a retarding or accelerating effect according as it is present in proportions greater or less than this limit. Consequently, if the iodide ion has an accelerating effect, the fact that the phenomenon at the initial part of the reaction ends rapidly will be satisfactorily explained, for the amount of oxygen to be contained in the reaction system and to participate in the reaction is limited. This consideration, however, will be confirmed by further thermo-analytical research on the effect of the hydroiodic acid for the oxidation of sulphites by oxygen.

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26) It has been preliminarily ascertained that the very rapid oxidation does not generally take place without adding any catalyst in a sulphite solution of such concentration as dealt with by the author.

27) A. Berg, *Bull. Soc. Chim.*, (3) 23, 499 (1900); *Compt. Rend.*, 138, 907 (1904).

Summary.

(1) By the method of thermal analysis the ionic reaction between acid sulphite and iodate in aqueous solution, in the case when the latter is not so much in excess of the former, has been studied at $pH=4\sim5$ in the atmosphere of nitrogen or the air.

(2) A formula of the thermal analysis for the second order reaction has been proposed and applied to the above-mentioned reaction.

(3) That the following velocity equation derived from chemical analysis by Skrabal and Zahorka is applicable to the very reaction has been thermo-analytically ascertained:

$$\frac{-d[IO_3^-]}{dt}=\kappa[IO_3^-][HSO_3^-][H^+].$$

(4) For the heat of reaction of the following reaction:

$$IO_3^- + 3HSO_3^- + 3Ac^- \longrightarrow I^- + 3SO_4^{--} + 3HAc$$

in a buffer solution of acetic acid and acetate, a value nearly equal to 159.6 kcal. calculated from thermochemical data has been obtained.

(5) It has been found that at the initial part of the very reaction there occurs some phenomenon to prevent the reaction from proceeding according to the second order reaction when pH is constant.

(6) The author has assumed that the phenomenon at the initial part is caused by the oxidation of a part of acid sulphite by the oxygen present in the solution where the principal reaction proceeds, and interpreted that the rapid disappearance of the phenomenon is due to the autocatalytic acceleration of the oxidation of acid sulphite by the iodide ion, the reaction product.

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