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Absorption of Oxygen in Aqueous Alkaline Solutions of Sodium Dithionite

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The rates of absorption of O_2 into aqueous alkaline solutions of $Na_2S_2O_4$ were measured at 15, 17.5, 25 and 35 °C using a baffled agitated vessel operated batchwise. The experimental results are analyzed with the chemical absorption theory based on the Lévêque model.

The reaction between O_2 and $Na_2S_2O_4$ was found to be zero order with respect to O_2 and first order with respect to $Na_2S_2O_4$ in the low $Na_2S_2O_4$ concentration range below 0.1 g mole/1, and to be half order with respect to O_2 and second order with respect to $Na_2S_2O_4$ in the high $Na_2S_2O_4$ concentration range above 0.1 g mole/1. The reaction rate constants in the low and high $Na_2S_2O_4$ concentration ranges are calculated and correlated as functions of temperature.

1. Introduction

Sharma and his coworkers have shown that the oxidation of $Na_2S_2O_4$ in aqueous alkaline solutions by O_2 can be conveniently employed for the measurement of the interfacial areas in gas-liquid contactors such as packed columns[1], bubble columns[2], mechanically agitated vessels[3], etc. by the chemical method. In order to obtain the reliable data on the interfacial area, it is necessary to know accurately the kinetics of this reaction system. There have been some studies[4~6] on the kinetics of the oxidation of $Na_2S_2O_4$ in aqueous alkaline solutions, but they are contradictory with each other. Morello et al.[4] have reported that the reaction between O_2 and $Na_2S_2O_4$ is zero order with respect to O_2 and first order with respect to $Na_2S_2O_4$. Rinker et al.[5] have found that the reaction is first order with respect to O_2 and half order with respect to $Na_2S_2O_4$. However, Jhaveri and Sharma[6] have shown that the reaction is zero order with respect to O_2 and first order with respect to $Na_2S_2O_4$ for its concentrations below 0.08 g mole/1 and second order with respect to $Na_2S_2O_4$ above 0.08 g mole/1.

Present work was undertaken to clarify the kinetics of the reaction between O_2 and $Na_2S_2O_4$ under alkaline conditions. Experiments on the absorption of O_2 into aqueous $Na_2S_2O_4$ solutions containing NaOH were performed in batch operation using a baffled agitated vessel with a flat gas-liquid interface. The experimental results were analyzed with the chemical absorption theory[7,8] based on the Lévêque model[9].

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2. Chemical Absorption Mechanism

When O_2 is absorbed into aqueous $Na_2S_2O_4$ solutions containing NaOH, the following overall reaction takes place in the liquid phase:

$$O_2 + Na_2S_2O_4 + 2NaOH = Na_2SO_3 + Na_2SO_4 + H_2O. \tag{1}$$
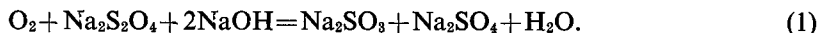
This overall reaction is the same as that used by Jhaveri and Sharma[6], and was confirmed in the present work by means of the analysis of the solutions oxidized in the absorption runs. In the present work, it is assumed that the overall reaction (1) is irreversible and (m, n)th order, i.e., m th order with respect to O_2 and n th order with respect to $Na_2S_2O_4$. Thus, the absorption of O_2 into aqueous $Na_2S_2O_4$ solutions containing NaOH may be treated as a process of absorption accompanied by an irreversible (m, n)th-order reaction represented by reaction (1).

In the previous work[10~12], Hikita et al. showed that the mechanism of liquid-phase mass transfer in the baffled agitated vessel can be described by the Lévêque model[9]. The experimental results obtained in the present work, therefore, are analyzed by using the chemical absorption theory[7,8] based on the Lévêque model.

When the absorption of solute gas A is accompanied by an irreversible chemical reaction, the rate of absorption, N_A, is represented by

$$N_A = \beta k_L{}^* A_i, \tag{2}$$

where $k_L{}^*$ is the liquid-phase mass transfer coefficient, A_i is the interfacial concentration of the dissolved gas, and β is the reaction factor. For absorption with an irreversible (m, n)th-order reaction represented by A+B→Products, the Lévêque model solution for the reaction factor may be approximated by

$$\beta = \gamma\eta + 0.474715/(\gamma\eta)^2 \qquad (\gamma\eta \geq 2.4) \tag{3a}$$

$$\beta = 1 + \sum_{j=1}^{\infty} b_j(\gamma\eta)^{2j} \qquad (\gamma\eta \leq 2.4), \tag{3b}$$

which were originally derived by Hikita et al.[8] for the case of an irreversible second-order reaction. Here $b_1, b_2, \ldots, b_j$ are the numerical constants and are given in tables in references[8,11,13], and γ and η are the dimensionless parameters defined by

$$\gamma = \sqrt{\{2/(m+1)\} k_{m,n} D_A A_i{}^{m-1} B_0{}^n} / k_L{}^* \tag{4}$$

and

$$\eta = \{(\beta_\infty - \beta)/(\beta_\infty - 1)\}^{n/2}, \tag{5}$$

respectively. Further, $k_{m,n}$ is the (m, n)th-order reaction rate constant, B_0 is the bulk concentration of the reactant B, D_A is the liquid-phase diffusivity of the dissolved gas A, and β_∞ is the reaction factor for absorption with an instantaneous reaction and can be obtained from[7,8]

$$\beta_\infty = \Gamma(1/3, \infty)/\Gamma(1/3, \sigma) \tag{6}$$

and

$$\left(\frac{D_B}{D_A}\right)^{2/3} \frac{B_0}{A_i} = \frac{\Gamma(1/3, \infty) - \Gamma(1/3, \sigma D_A/D_B)}{\Gamma(1/3, \sigma)} \exp\left[\sigma\left(\frac{D_A}{D_B} - 1\right)\right], \qquad (7)$$

where D_B is the liquid-phase diffusivity of the reactant B.

The reaction factor β is usually represented in a graphical form as a function of γ and β_∞. This graphical representation of the reaction factor is not convenient for the analysis of the experimental data obtained in semi-batch gas-liquid contactors such as agitated vessels or bubble columns, because both values of γ and β_∞ vary
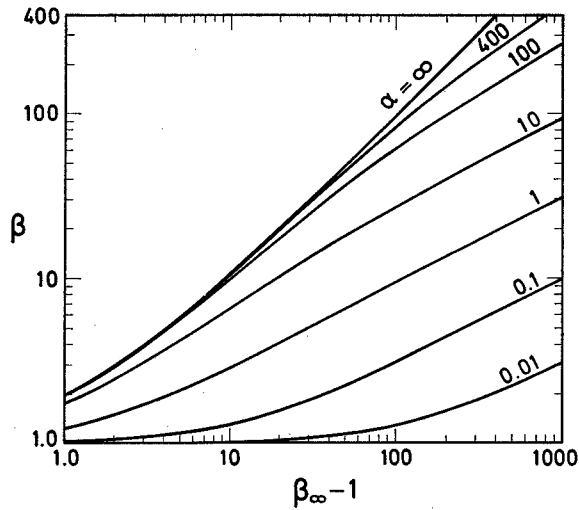
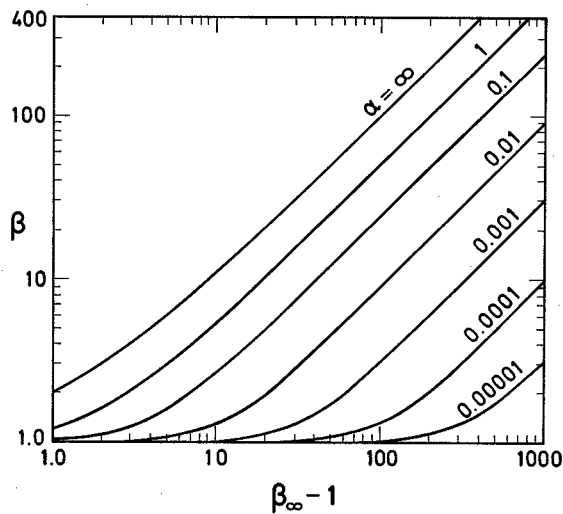Fig. 1. Reaction factor for absorption with an irreversible $(m, 1)$th-order reaction. Lévêque model solution.

Fig. 2. Reaction factor for absorption with an irreversible $(m, 2)$th-order reaction. Lévêque model solution.

with time as the bulk concentration of the liquid-phase reactant, B_0, changes. For such a case, the graphical representation of β against $(\beta_\infty - 1)$ with a new dimensionless quantity α which is independent of B_0 as parameter is very useful, as indicated by Hikita and Ishikawa[14]. According to the Lévêque model, the dimensionless quantity α for absorption with an irreversible (m, n)th-order reaction of the form A+B→Products is given by[14]

$$\alpha = \{2/(m+1)\} k_{m,n} D_A (D_A/D_B)^{2n/3} A_i^{m+n-1}/k_L^{*2} \tag{8a}$$

$$= \gamma^2/\{(D_B/D_A)^{2/3} (B_0/A_i)\}^n. \tag{8b}$$

Figs. 1 and 2 show the values of β for the cases of the $(m, 1)$th-order and $(m, 2)$th-order reactions, respectively, calculated from Eqs. (3)–(8), as functions of $(\beta_\infty - 1)$ with α as parameter. The upper lines for $\alpha = \infty$ in these figures represent the theoretical equation for absorption with an irreversible instantaneous reaction, $\beta = \beta_\infty$.

3. Experimental

3.1 Apparatus and procedure

The agitated vessel was of 12.3 cm I.D. and was the same as that used in the previous work[11,13]. The vessel consisted of acryl resin. Four equally spaced vertical baffles, each one tenth of the vessel diameter in width, were attached to the internal wall of the vessel. The liquid level in the vessel was kept equal to the vessel diameter. The liquid stirrer was an acryl-resin paddle agitator with two flat blades, whose diameter and height were 5.0 cm and 1.5 cm respectively, and was placed at half of the liquid depth. The gas stirrer was an acryl-resin turbine agitator with six flat blades, whose diameter and height were 8.0 cm and 2.0 cm respectively, and was placed in the center of the gas phase in the vessel. The agitated vessel and the main part of the apparatus were kept in a constant temperature room where temperature was maintained constant in the range of 15 to 35°C.

The absorbing liquids used were aqueous $Na_2S_2O_4$ solutions of concentrations from 0.014 to 0.83 g mole/1 containing NaOH of various concentrations. In these solutions, 0.001 g mole/1 EDTA-2Na was added to suppress the further oxidation of Na_2SO_3 produced by the oxidation of $Na_2S_2O_4$. In some experimental runs, Na_2SO_4 was added to the absorbents to change the ionic strength of the solution. The gas phase in most of the experiments was pure O_2 saturated with water vapour. A few experiments were carried out by using the mixtures of O_2 and N_2 as gas phase. In pure O_2 runs, the gas phase in the vessel was not agitated. In dilute O_2 runs, however, the gas stirrer was driven at a constant speed of 500 rpm. The stirring speeds of the liquid stirrer were 100 and 200 rpm.

All the experiments were carried out in batch operation with respect to the liquid. The rate of absorption of O_2 was obtained from the graphical differentiation of the curve of the amount of O_2 absorbed vs. time. The amount of O_2 absorbed into the

Table 1. Experimental conditions and physical properties of systems used

Run no.	Initial conc., g mole/1				p_A atm	Temp. °C	N_L rpm	$A_i \times 10^4$ g mole/1	$D_A \times 10^5$ cm²/sec	D_B/D_A ——	$k_L^* \times 10^3$ cm/sec
	B_0	H_0	E_0	F_0							
1	0.0145	0.497	0.0035	0.0035	0.969	25	100	10.2	2.23	0.364	1.54
2	0.0140	0.496	0.0040	0.0040	0.969	25	200	10.2	2.23	0.364	2.50
3	0.0494	0.488	0.0133	0.0133	0.983	15	200	11.5	1.67	0.360	1.88
4	0.0563	0.500	0.0068	0.0068	0.945	35	200	7.66	2.82	0.350	3.15
5	0.0781	0.498	0.0115	0.0115	0.969	25	100	9.46	2.19	0.354	1.51
6	0.0786	0.499	0.0110	0.0110	0.969	25	200	9.46	2.19	0.354	2.45
7	0.0750	0.492	0.0146	0.0146	0.590	25	200	5.76	2.19	0.354	2.45
8	0.0788	0.499	0.0109	0.0109	0.200	25	200	1.95	2.19	0.354	2.45
9	0.165	0.500	0.0176	0.0176	0.969	25	100	8.63	2.13	0.349	1.47
10	0.153	0.489	0.0262	0.0262	0.969	25	200	8.63	2.13	0.349	2.39
11	0.325	0.400	0.0376	0.0376	0.969	25	200	7.17	2.02	0.343	2.26
12	0.340	0.500	0.0303	0.0303	0.600	25	200	4.44	2.02	0.344	2.04
13	0.349	0.500	0.0257	0.0257	0.231	25	200	1.71	2.02	0.344	2.04
14	0.377	0.461	0.0714	0.0714	0.969	25	200	6.51	1.96	0.339	2.20
15	0.384	0.475	0.0645	0.0645	0.983	15	200	7.32	1.49	0.340	1.68
16	0.338	0.384	0.110	0.110	0.945	35	200	6.08	2.50	0.337	2.79
17	0.386	0.979	0.0625	0.0625	0.969	25	200	5.32	1.79	0.342	1.98
18	0.385	0.977	0.230	0.0634	0.969	25	200	4.57	1.70	0.346	1.86
19	0.388	0.984	0.393	0.0597	0.969	25	200	3.91	1.60	0.346	1.73
20	0.571	0.652	0.572	0.272	0.969	25	200	2.70	1.37	0.345	1.45
21	0.792	0.714	0.266	0.266	0.969	25	100	2.83	1.40	0.338	0.938
22	0.771	0.672	0.287	0.287	0.969	25	200	2.83	1.40	0.337	1.53
23	0.825	0.781	0.232	0.232	0.400	25	200	1.16	1.40	0.336	1.53
24	0.747	0.624	0.310	0.310	0.980	17.5	100	2.87	1.14	0.343	0.764
25	0.830	0.791	0.227	0.227	0.945	35	100	2.87	1.78	0.330	1.20

solution was determined as a function of time by measuring the decrease in volume of O_2 by a soap-film meter. The contents of $Na_2S_2O_4$, Na_2SO_3, Na_2SO_4 and NaOH in the solution were determined by the conventional analytical methods. Three separate analyses were made on three separate samples. These were: (1) iodometric titration to determine the sum of the concentrations of $Na_2S_2O_4$ and Na_2SO_3; (2) iodometric titration to determine only the concentration of $Na_2S_2O_4$ and neutralimetric titration to determine the concentration of NaOH; (3) gravimetric analysis to determine the concentration of Na_2SO_4.

The experimental conditions are given in Table 1.

3.2 Results

The experimental results are shown in Fig. 3, where the absorption rate of O_2, N_A, is plotted against the concentration of $Na_2S_2O_4$, B_0, on logarithmic coordinates. Runs (1, 2), (5, 6) and (9, 10) shown in the figure indicate that the liquid-phase stirring speed, N_L, has a considerable effect on the absorption rate. The extent of this effect, however, is less than that observed in the experimental runs on the ab-
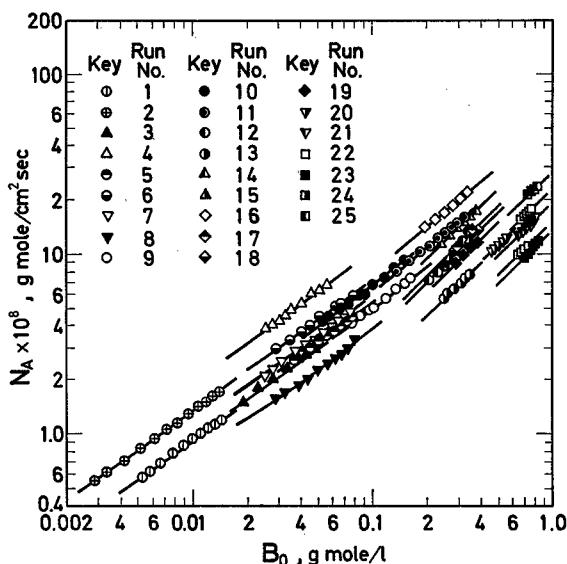
Fig. 3.   Absorption rate of O_2 into aqueous alkaline $Na_2S_2O_4$ solutions.

sorption with an irreversible instantaneous reaction[12], and this means that the absorption of O_2 into aqueous $Na_2S_2O_4$ solutions containing NaOH may take place in the intermediate regime between the pseudo m th-order reaction regime and the instantaneous reaction regime.   Furthermore, Fig. 3 indicates that the slopes of the lines for the data points in the high $Na_2S_2O_4$ concentration range above 0.1 g mole/1 are greater than those in the low $Na_2S_2O_4$ concentration range below 0.1 g mole/1, suggesting that the kinetics of the reaction between O_2 and $Na_2S_2O_4$ depends on the range of $Na_2S_2O_4$ concentration.

4. Analysis and Discussion

4.1 Prediction of physical properties

In order to analyze the experimental results, it is necessary to know the values of the physical properties of the O_2-$Na_2S_2O_4$ system, such as A_i, D_A, D_B, etc.

When O_2 reacts with $Na_2S_2O_4$ irreversibly and instantaneously in an aqueous alkaline solution, an aqueous solution containing Na_2SO_4 ($2Na^+ + SO_4^{2-}$), Na_2SO_3 ($2Na^+ + SO_3^{2-}$) and NaOH ($Na^+ + OH^-$) of uniform concentrations exists in the region between the gas-liquid interface and the reaction plane.   According to the Lévêque model, these uniform concentrations of SO_4^{2-}, SO_3^{2-} and OH^- ions, E_i, F_i and H_i respectively, are approximately given by the following equations[12,13]:

$$E_i = E_0 + (D_B/D_E)^{2/3} B_0 \qquad (9)$$

$$F_i = F_0 + (D_B/D_F)^{2/3} B_0 \qquad (10)$$

$$H_i = H_0 - 2(D_B/D_H)^{2/3} B_0 , \qquad (11)$$

where B_0, E_0, F_0 and H_0 are the bulk concentrations of $S_2O_4^{2-}$, SO_4^{2-}, SO_3^{2-} and OH^- ions, respectively, and D_B, D_E, D_F and D_H are the effective diffusivities of $S_2O_4^{2-}$, SO_4^{2-}, SO_3^{2-} and OH^- ions, respectively. Therefore, when the absorption of O_2 takes place in the instantaneous irreversible reaction regime, the physical solubility and the liquid-phase diffusivity of O_2 in this solution should be taken as the values of A_i and D_A, respectively. On the other hand, when the absorption of O_2 occurs in the irreversible pseudo m th-order reaction regime, the concentrations of $S_2O_4^{2-}$, SO_4^{2-}, SO_3^{2-} and OH^- ions are constant throughout the liquid phase at the values in the bulk of the liquid, B_0, E_0, F_0 and H_0, respectively. In this case, therefore, the physical solubility and the liquid-phase diffusivity of O_2 in the solution of the same composition as that of the bulk liquid should be used as the values of A_i and D_A, respectively.

Under the experimental conditions used in the present work, the absorption of O_2 into aqueous $Na_2S_2O_4$ solution containing NaOH is considered to take place in the intermediate regime between the instantaneous reaction regime and the pseudo m th-order reaction regime. However, the values of the physical solubility and the liquid-phase diffusivity predicted at the two limiting cases of the instantaneous reaction regime and the pseudo m th-order reaction regime differ from each other by only 10.0% and 6.4%, respectively, then the arithmetic means of the values predicted at the two limiting reaction regimes were used in the present work.

The physical solubility of O_2 in aqueous solutions containing $Na_2S_2O_4$, Na_2SO_4, Na_2SO_3 and NaOH was calculated from the following equation proposed by Danckwerts and Gillham[15] for the solubility in mixed electrolyte solutions:

$$\log(A_i/A_{iw}) = -(k_{sB}I_B + k_{sE}I_E + k_{sF}I_F + k_{sH}I_H), \qquad (12)$$

where A_i and A_{iw} are the physical solubilities in the solution and in water, respectively, and k_{sB}, k_{sE}, k_{sF} and k_{sH} are the salting-out parameters for $Na_2S_2O_4$, Na_2SO_4, Na_2SO_3 and NaOH, respectively, whose ionic strengths are I_B, I_E, I_F and I_H. The salting-out parameter k_s is expressed as the sum of the contributions owing to the positive and negative ions present and the dissolved gas[16]:

$$k_s = i_+ + i_- + i_g . \qquad (13)$$

The values of i for Na^+, SO_4^{2-} and OH^- ions and the values of i_g for O_2 at various temperatures were obtained from the data of van Krevelen and Hoftijzer[16], and the value of i_- for SO_3^{2-} ions was taken from the data of Hikita et al.[17] to be equal to -0.005 1/g ion. The value of i_- for $S_2O_4^{2-}$ ions was assumed to be the same as that for SO_4^{2-} ions, as suggested by Jhaveri and Sharma[6]. The estimated values of k_s for $Na_2S_2O_4$, Na_2SO_4, Na_2SO_3 and NaOH are given in Table 2. The value of A_{iw} was calculated from the partial pressure of O_2 in gas phase by use of the Henry's law constant obtained from the data of Morrison and Billett[18], assuming that the gas-phase resistance to mass transfer is negligible. (The gas-phase resistance was calculated by using the empirical formula obtained in the previous work[13] and

Table 2. Values of salting-out parameters for Na₂S₂O₄, Na₂SO₄, Na₂SO₃ and NaOH

Temp. °C	k_{sB} (Na₂S₂O₄) 1/g ion	k_{sE} (Na₂SO₄) 1/g ion	k_{sF} (Na₂SO₃) 1/g ion	k_{sH} (NaOH) 1/g ion
15	0.148	0.148	0.122	0.188
17.5	0.145	0.145	0.119	0.185
25	0.134	0.134	0.108	0.174
35	0.120	0.120	0.094	0.160

was found to be less than 1.6% of the total resistance.) The values of the Henry's law constant at 15, 25 and 35°C were taken as 657, 789 and 912 atml/g mole, respectively.

The liquid-phase diffusivity of O₂ in aqueous solutions containing Na₂S₂O₄, Na₂SO₄, Na₂SO₃ and NaOH was estimated from the following equation proposed by Hikita et al.[19] which is the extension of the method of Ratcliff and Holdcroft[20] to the mixed electrolyte solutions:

$$D_A/D_{Aw} = 1 - (\kappa_B C_B + \kappa_E C_E + \kappa_F C_F + \kappa_H C_H), \tag{14}$$

where D_{Aw} is the liquid-phase diffusivity of O₂ in water, and κ_B, κ_E, κ_F and κ_H are the constants for Na₂S₂O₄, Na₂SO₄, Na₂SO₃ and NaOH solutions whose concentrations are C_B, C_E, C_F and C_H and were found from viscosity data to be 0.204, 0.232, 0.250 and 0.138 1/g mole, respectively, being independent of temperature. The values of D_{Aw} at various temperatures were predicted from the value of 2.41×10^{-5} cm²/sec[21] obtained at 25°C, by correcting for temperature and viscosity of water, according to the well-known Stokes-Einstein relation.

The ratios of the effective diffusivity of S₂O₄²⁻ ions to those of SO₄²⁻, SO₃²⁻ and OH⁻ ions and to the liquid-phase diffusivity of O₂, i.e., D_B/D_E, D_B/D_F, D_B/D_H and D_B/D_A, respectively, were assumed to be equal to those at infinite dilution or in water. The effective diffusivities of S₂O₄²⁻, SO₄²⁻, SO₃²⁻ and OH⁻ ions at infinite dilution were estimated by the method of Vinograd and McBain[22], using the values of the ionic conductance for these ionic species reported in the literature[23].

The values of the liquid-phase mass transfer coefficient k_L^* were calculated from the following empirical equation which was obtained in the previous work[10]:

$$\frac{k_L^* l}{D_A} = 0.322 \left(\frac{d_L^2 N_L \rho_L}{\mu_L}\right)^{0.7} \left(\frac{\mu_L}{\rho_L D_A}\right)^{1/3}, \tag{15}$$

where l is the vessel diameter, d_L is the diameter of the liquid stirrer, ρ_L and μ_L are the density and viscosity of the liquid, respectively. The density and viscosity of the solutions were determined experimentally.

The physical properties such as A_i, D_A, k_L^*, etc. changed due to the variation in the composition of the solution as the absorption proceeded. However, the changes in the physical properties during each run were small (less than 6.4%),

then the arithmetic means of the values predicted at the beginning and the end of the run were used. These predicted values of the physical properties are listed in Table 1.

4.2 Analysis of experimental data

All the experimental results were presented as a log-log plot of β against $(\beta_\infty - 1)$, as suggested by Hikita and Ishikawa[14]. The reaction factor β was calculated from the measured value of absorption rate, N_A, using the values of A_i, D_A and k_L^* predicted by the methods described above. The value of β_∞, the reaction factor for
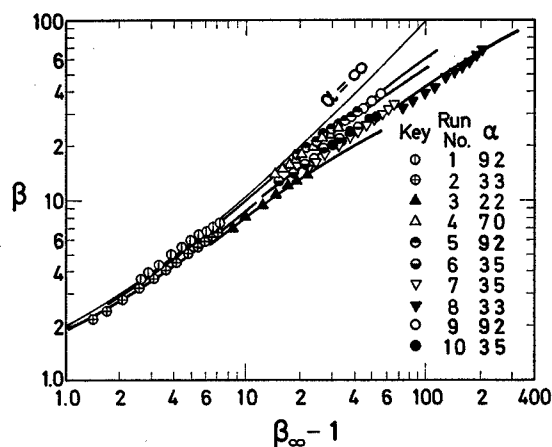
Fig. 4. Reaction factor for absorption of O_2 into aqueous alkaline $Na_2S_2O_4$ solutions. $B_0 < 0.1$ g mole/l.
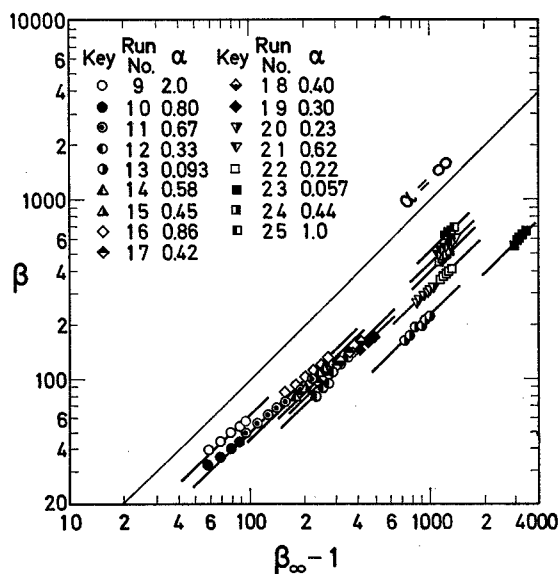
Fig. 5. Reaction factor for absorption of O_2 into aqueous alkaline $Na_2S_2O_4$ solutions. $B_0 > 0.1$ g mole/l.

the case of irreversible instantaneous reaction, was calculated from the theoretical Eqs. (6) and (7).

Figs. 4 and 5 show the experimental results obtained with the $Na_2S_2O_4$ solutions of the concentrations below and above 0.1 g mole/1, respectively. For runs 9 and 10, the data points obtained in the low $Na_2S_2O_4$ concentration range below 0.1 g mole/1 are shown in Fig. 4, and those obtained in the high $Na_2S_2O_4$ concentration range are given in Fig. 5. The solid lines in Figs. 4 and 5 are the theoretical lines for absorption accompanied by an irreversible $(m, 1)$th-order reaction and by an irreversible $(m, 2)$th-order reaction, respectively, and were calculated from Eqs. (3) and (5)–(8), taking the numerical values shown on the graphs as the dimensionless parameter α. As can be seen in these figures, the experimental data points are in good agreement with the theoretical lines. This indicates that the reaction is first order with respect to $Na_2S_2O_4$ in the low concentration range and second order with respect to $Na_2S_2O_4$ in the high concentration range. This result is in agreement with that obtained by Jhaveri and Sharma[6], who have found that the reaction order with respect to $Na_2S_2O_4$ changes from one to two when the $Na_2S_2O_4$ concentration exceeds 0.08 g mole/1.

The reaction order with respect to O_2 was determined from a plot of the value of $\alpha(k_L^*)^2$ against the interfacial concentration of dissolved O_2, A_i, on logarithmic coordinates. As can be seen from Eq. (8), the following relation holds between the values of $\alpha(k_L^*)^2$ and A_i:

$$\alpha(k_L^*)^2 \propto A_i^{m+n-1}. \qquad (16)$$

Thus, the log-log plot of $\alpha(k_L^*)^2$ against A_i would be a straight line with a slope of $(m+n-1)$, from which the value of m can be determined if the value of n is known.
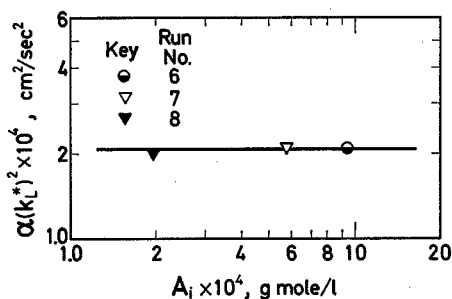

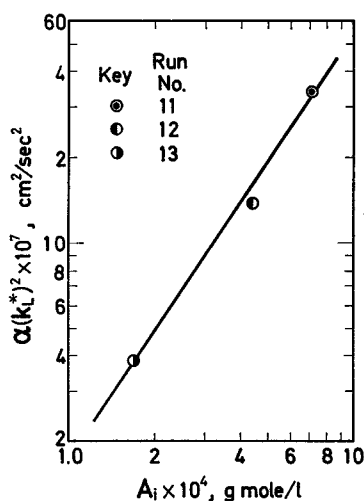Fig. 6. log-log plot of $\alpha(k_L^*)^2$ vs. A_i at 25°C. I=0.85 g ion/1, B_0<0.1 g mole/1.

Fig. 7. log-log plot of $\alpha(k_L^*)^2$ vs. A_i at 25°C. I=1.90 g ion/1, B_0>0.1 g mole/1.

In Fig. 6, the values of α in the low $Na_2S_2O_4$ concentration range, obtained at 25°C and at an ionic strength of about 0.85 g ion/1, are shown as a log-log plot of $\alpha(k_L^*)^2$ against A_i. The slope of the straight line in this figure is zero, and this indicates that the reaction order with respect to O_2, m, is equal to zero, because the value of n is unity. In Fig. 7, on the other hand, the values of α in the high $Na_2S_2O_4$ concentration range, obtained at 25°C and at an ionic strength of about 1.9 g ion/1, are shown as a log-log plot of $\alpha(k_L^*)^2$ against A_i. As can be seen in this figure, data points are well correlated by a straight line with a slope of 1.5. This implies that the value of m is equal to 1/2, since the value of n is two.

Thus, it was found that the reaction is zero order with respect to O_2 and first order with respect to $Na_2S_2O_4$ in the low $Na_2S_2O_4$ concentration range below 0.1 g mole/1, and half order with respect to O_2 and second order with respect to $Na_2S_2O_4$ in the high $Na_2S_2O_4$ concentration range above 0.1 g mole/1.

The values of the rate constants for the (0, 1)th-order reaction and the (1/2, 2)th-order reaction, $k_{0,1}$ and $k_{1/2,2}$, respectively, were calculated using Eq. (8) from the observed values of α.

The effect of ionic strength of the solution on the reaction rate constant is shown in Figs. 8 and 9. These figures indicate that both the rate constants, $k_{0,1}$ and $k_{1/2,2}$,
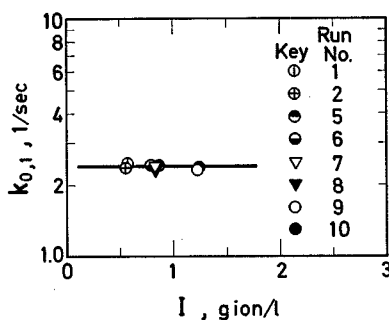

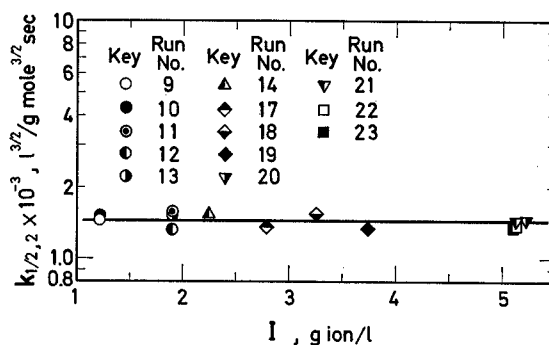Fig. 8.   Effect of ionic strength on (0, 1)th-order reaction rate constant at 25°C. $B_0 < 0.1$ g mole/1.

Fig. 9.   Effect of ionic strength on (1/2, 2)th-order reaction rate constant at 25°C. $B_0 > 0.1$ g mole/1.
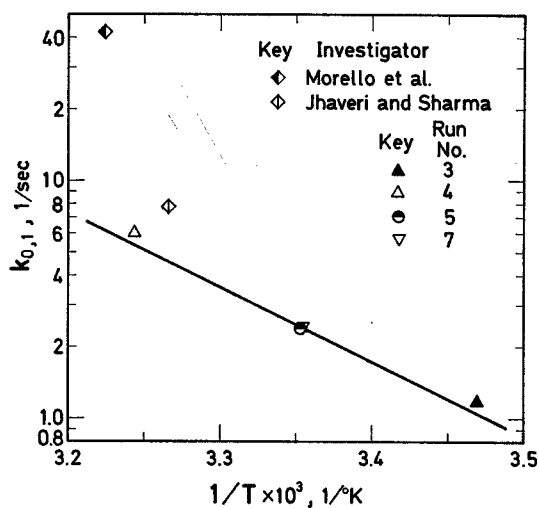
Fig. 10. Arrhenius plot of (0, 1)th-order reaction rate constant.
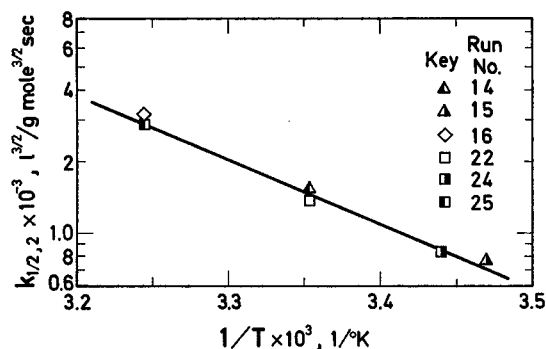$B_0 < 0.1$ g mole/l.

Fig. 11. Arrhenius plot of (1/2, 2)th-order reaction rate constant.
$B_0 > 0.1$ g mole/l.

are constant in the range of ionic strength studied.   The effect of temperature on the rate constant is shown in Figs. 10 and 11 as the Arrhenius plots.   The activation energies for the (0, 1)th-order reaction and the (1/2, 2)th-order reaction were found to be 14400 and 12300 cal/g mole, respectively.   All the values of $k_{0,1}$ and $k_{1/2,2}$ obtained in the present work were correlated empirically by

$$\log k_{0,1} = 10.94 - 3150/T \qquad (B_0 < 0.1 \text{ g mole/l}) \qquad (17)$$

$$\log k_{1/2,2} = 12.18 - 2690/T \qquad (B_0 > 0.1 \text{ g mole/l}) \qquad (18)$$

with the average deviation of 4.8% and 6.7%, respectively.

4.3   Comparison with previous results

As stated above, the kinetics of the oxidation of $Na_2S_2O_4$ has been studied by Morello et al.[4], Rinker et al.[5], and Jhaveri and Sharma.[6]   Morello et al.[4] measured

the rate of reaction between O_2 and $Na_2S_2O_4$ in aqueous alkaline solutions at 37 °C by using a modified rapid-mixing method[24] in the range of $Na_2S_2O_4$ concentration from 8×10^{-5} to 4.75×10^{-4} g mole/l, and found that the reaction is (0, 1)th order. Rinker et al.[5] measured the rate of this reaction at temperatures of 30 to 60 °C using a gas-sparged agitated vessel in the $Na_2S_2O_4$ concentration range from 0.005 to 0.02 g mole/l and found that the reaction is (1, 1/2)th order. Jhaveri and Sharma[6] studied the kinetics of this reaction by measuring the absorption of O_2 into aqueous alkaline $Na_2S_2O_4$ solutions of concentrations from 0.017 to 0.29 g mole/l at 33 °C in an agitated vessel with a flat gas-liquid interface, a liquid-jet column and a packed column, and analyzed the experimental results with the chemical absorption theory based on the surface renewal model[25]. They found that the reaction is (0, 1)th order when the $Na_2S_2O_4$ concentration is less than 0.08 g mole/l, and (0, 2)th order when the $Na_2S_2O_4$ concentration is greater than 0.08 g mole/l. The results obtained by Morello et al.[4], and Jhaveri and Sharma[6] concerning the order of the reaction in the low $Na_2S_2O_4$ concentration range are in agreement with that obtained in the present work. However, the result of Rinker et al.[5] does not agree with the present result. The values of the (0, 1)th-order reaction rate constant, $k_{0,1}$, obtained by Morello et al.[4] at 37 °C and by Jhaveri and Sharma[6] at 33 °C are also shown in Fig. 10 for comparison with the present data. The $k_{0,1}$ value of Jhaveri and Sharma is in approximate agreement with the present data. However, the $k_{0,1}$ value of Morello et al. exceeds the present data by a factor of 5.9. The reason for this enormously high $k_{0,1}$ value is not clear.

At high $Na_2S_2O_4$ concentrations above 0.08 g mole/l, the kinetics of the reaction has been reported only by Jhaveri and Sharma[6]. The order of the reaction obtained by Jhaveri and Sharma is (0, 2) and the reaction order with respect to O_2 is different from that found in the high $Na_2S_2O_4$ concentration range in the present work.

Notation

A_i, A_{iw} : interfacial concentrations or physical solubilities of O_2 in solution and in water, g mole/l

b_j : coefficient in Eq. (3b), —

B_0 : concentration of $Na_2S_2O_4$ or $S_2O_4^{2-}$ ions in bulk of solution, g mole/l

C : concentration of electrolyte in solution, g mole/l

d_L : diameter of liquid stirrer, cm

D_A, D_{Aw} : liquid-phase diffusivities of O_2 in solution and in water, cm^2/sec

D_B : effective diffusivity of $S_2O_4^{2-}$ ions in solution, cm^2/sec

D_E, D_F, D_H : effective diffusivities of SO_4^{2-}, SO_3^{2-}, OH^- ions in solution, cm^2/sec

E_i, F_i, H_i : interfacial concentrations of SO_4^{2-}, SO_3^{2-}, OH^- ions, g mole/l

E_0, F_0, H_0 : concentrations of SO_4^{2-}, SO_3^{2-}, OH^- ions in bulk of solution, g mole/l

i_+, i_-, i_g : contributions of positive ions, negative ions, solute gas to salting-out parameter, 1/g ion

I	: ionic strength of solution, g ion/1
$k_L{}^*$	: liquid-phase mass transfer coefficient, cm/sec
$k_{m,n}$	: (m, n)th-order reaction rate constant, $(1/\text{g mole})^{m+n-1}/\text{sec}$
k_s	: salting-out parameter, 1/g ion
l	: diameter of agitated vessel, cm
m, n	: orders of reaction with respect to O_2 and $Na_2S_2O_4$, —
N_A	: absorption rate of O_2, g mole/cm² sec
N_L	: liquid-phase stirring speed, rev./sec or rpm
p_A	: partial pressure of O_2, atm
T	: absolute temperature, °K

Greek letters

α	: dimensionless parameter defined by Eq. (8), —
β	: reaction factor defined by Eq. (2), —
β_∞	: reaction factor for absorption accompanied by an irreversible instantaneous reaction, —
γ	: dimensionless parameter defined by Eq. (4), —
$\Gamma(m, n)$	: incomplete gamma function, $\int_0^n t^{m-1} \exp(-t)\, dt$, —
η	: dimensionless parameter defined by Eq. (5), —
κ	: coefficient in Eq. (14), 1/g mole
μ_L	: viscosity of solution, g/cm sec
ρ_L	: density of solution, g/cm³
σ	: dimensionless parameter defined by Eq. (7), —

Subscripts

B	: $Na_2S_2O_4$
E	: Na_2SO_4
F	: Na_2SO_3
H	: $NaOH$

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