Some Aspects on Sodium Sulfite Oxidation in Aqueous Solution

By

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Abstract

The effects of the partial pressure of oxygen and the pH value on the rate of oxidation of sodium sulfite with oxygen in an aqueous solution catalyzed by cobaltous ion were investigated by a gas absorption method at 25°C.

Measurements were made on the solution of 0.3 mol/l of sodium sulfite with 10^{-6} mol/l of cobaltous ion in the region of the pH values from 6 to 13, and in the region of the oxygen partial pressures from 0.1 to 1 atm.

The order of reaction with respect to oxygen was found to be unity when the oxygen partial pressure was higher than 0.17 atm, and two when the oxygen partial pressure was lower than 0.17 atm.

The rate of reaction was very sensitive to the pH value of the solution. The relation between them is very complicated. Hence, it is difficult to find a simple expression to correlate them.

1. Introduction

The absorption of oxygen into sodium sulfite solutions in the presence of cobaltous ion as a catalyst has often been used in studying the mass-transfer characteristics of gas–liquid contacting devices such as packed columns, bubble columns and agitated vessels. For an adequate application of the method, it is necessary to have a knowledge of the kinetics of the homogeneous chemical reaction. Hence the reaction of dissolved oxygen with sodium sulfite has been studied by many investigators. However, there is rather poor agreement in the reported data.

The disagreement among such results seems to be caused by the fact that many factors have effects on the reaction rate and, moreover, may interact upon each other

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because the mechanism of the reaction is very complicated. The concentrations of oxygen and hydrogen ions are the main factors which have a considerable effect on the rate of the reaction.

On this reaction with respect to oxygen, the reaction order has generally been considered to be unity. This has been supported by many experimental results, except a few works[2] which indicated a zero order. Recently, however, many investigators reported that the order of reaction with respect to oxygen was two.

These results can be separated into two groups. One group[6,11,14,16] shows the result that the reaction order with respect to oxygen is two at oxygen partial pressures above 0.2 atm. The other group[1,7,10,17] shows the result that the reaction order with respect to oxygen is two at the oxygen partial pressure around 0.2 atm, while the order is unity at the oxygen partial pressure around 1 atm. Moreover, the latter can be divided into two groups, one[1,7] showing the result that the change of the reaction order with respect to oxygen takes place at a certain limited oxygen pressure range, and the other[10,17] showing the result that the change takes place gradually over a wide oxygen pressure range.

As mentioned above, a definite conclusion on the reaction order with respect to oxygen can not be yet obtained.

About the effect of the concentration of hydrogen ions on the reaction rate, there is also rather poor agreement in the reported data.

Winkelmann[18] and Roxburgh[15] showed that the reaction rate took the maximum value at a certain pH value.

Reith et al.[11] and de Waal et al.[3] stated that the reaction rate increased as the pH value increased in the range from 7.5 to 8.5.

Onda et al.[9] showed that the reaction rate was in proportion to the minus 0.635-th power of the concentration of hydrogen ions in the range from 7.5 to 8.5.

Wesselingh et al.[17] showed that the reaction rate was in proportion to the minus 0.6th power of the concentration of hydrogen ions in the range from 7.5 to 8.5.

Linek et al.[8] expressed the reaction rate by a quadratic equation of pH in the range from 7.8 to 9.1.

Rodionov et al.[14] reported a result similar to that of Linek et al. in the range of pH from 7.8 to 9.2.

As mentioned above, excepting Roxburgh, all previous investigations on the effect of pH dealt with a rather narrow pH range.

In this investigation, the effect of the oxygen concentration and the pH on the reaction rate of sodium sulfite oxidation in an aqueous solution catalyzed by cobaltous ion was studied at 25°C under conditions different from those of previous works.

Kinetic data were obtained from measurements of the rate of absorption of pure

oxygen into an aqueous sodium sulfite solution in a stirred vessel.

The concentration of the solutions used was 0.3 mol/l of sodium sulfite and 10^{-6} mol/l cobaltous chloride, because it was known that the rate of reaction was zero-order with respect to sulfite under this condition.[20] The oxygen concentration in the solution was adjusted by controlling the oxygen pressure in the experimental apparatus.

2. Experimental Apparatus and Procedure

Fig. 1 shows a diagram of the apparatus. The main parts of the apparatus were set in an air thermostat regulated at $25\pm0.1\,°C$. The gas absorption vessel A was, moreover, placed in a water thermostat regulated at $25\pm0.1\,°C$ for quick removal of heat generated by the reaction.

The vessel and the impeller are sketched in Fig. 2. The vessel consisted of a glass cylindrical flask of 600 cm^3 with four buffles and a cover with an agitator. The agitator consisted of an impeller with four blades and a stainless steel shaft coated with epoxy resin. The buffles, cover and impeller were made of plastic, so that the sulfite solution did not come in contact with metal in the absorption vessel.

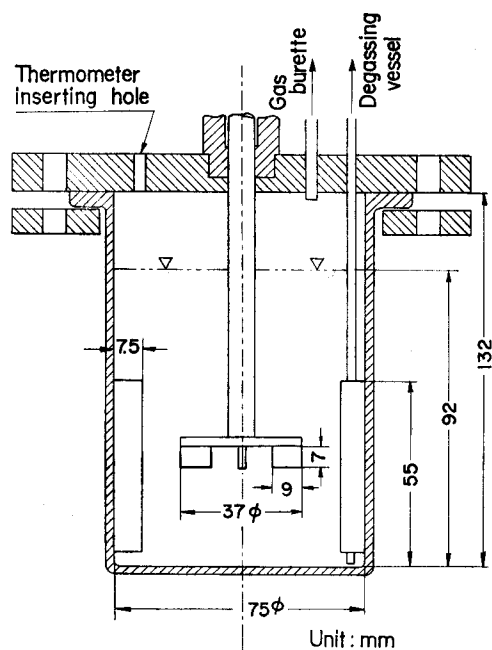|	
Ⓐ Absorption vessel	Ⓔ Water thermostat
Ⓑ Gas burette	Ⓕ O_2 cylinder
Ⓒ Oxygen reservoir	Ⓖ Mercury reservoir
Ⓓ Degassing vessel	Ⓗ Heater
	Ⓚ Cock
	Ⓜ Manometer

Fig. 1. Schematic diagram of apparatus

Fig. 2. Arrangement and dimensions of absorption vessel and stirrer.

The sulfite solution was prepared by an addition of a known quantity of sodium sulfite and cobaltous chloride solution of a definite concentration into de-ionized water so as to make the total volume of the solution to be 3 *l.* In order to study the effect of the **pH**, an aqueous solution of sulfuric acid or sodium hydroxide was further added to the solution to adjust the pH.

The sulfite solution thus prepared was put into the degassing vessel D and evacuated by using an aspirator for several hours. Pure oxygen was charged to all parts of the apparatus, and the oxygen pressure in the apparatus was adjusted at an appropriate value. Then, several hours were allowed for the equilibration of the temperature.

At first in each run, 400 cm³ of the sulfite solution was charged to the absorption vessel A, and the pressure in A was reduced by using a vacuum pump. Then agitation was started, and about one hour was allowed for the equilibration of the temperature and for the saturation of water vapor in the gaseous phase in A under a reduced pressure. Then the absorption vessel A and the oxygen reservoir C were connected by a manipulation of cocks K₃ and K₄, and this moment was identified as the time of the start of absorption.

At 30 seconds after the start, the absorption vessel was cut from the oxygen

reservoir C and connected to the gas burette B by manipulation of the cock K_4. The pressure in A and B was kept automatically at a constant value fixed at the start in each run by reducing the volume of the gaseous phase in the gas burette B by raising the level of the mercury reservoir G_2.

Consequently, the oxygen absorption rate was calculated by measuring the rate at which the surface level of mercury rose in the gas burette.

The impeller was rotated at 96.2 r.p.m. throughout this experiment. At this speed of rotation, a concavity at the center part and ripples were not generated at the surface of the solution.

The analysis and the pH measurement of the solution were done on the samples taken from the degassing vessel just after charging the sulfite solution into the absorption vessel. The sulfite concentration was determined by iodometry. The total salt concentration, which was the total amount of sodium sulfite and sulfate in the sulfite solution, was determined by weighing an anhydrous salt which was evaporated to dryness after having oxidized all the sulfite to sulfate by hydrogen peroxide. The cobaltous chloride concentration was calculated from its amount added to the solution.

All chemicals used were guaranteed reagents.

The following physical properties were used to analyze the observed data. For the saturated water vapor pressure of the sulfite solution at the adjusted value of pH, an estimated value was used. In order to get this estimated value, the sulfite solution used was regarded as a mixture of the sodium sulfite solution of the same molarity as the total salt concentration and sulfuric acid or sodium hydroxide solution. Then, the estimated value of the water vapor pressure was calculated by the method of Robinson and Bower[12] using the saturated vapor pressure of the sodium sulfite solution[19], the sulfuric acid solution and the sodium hydroxide solution.[13]

For the solubility of oxygen in the sulfite solution, the solubility of oxygen in the sodium sulfite solution[19] of the same molarity as the total salt concentration was used because the effect of sulfuric acid or sodium hydroxide on the solubility in the sulfite solution was negligibly small.

3. Results and Discussion

3.1 Absorption without chemical reaction

The rate of absorption of oxygen by water and an aqueous sodium sulfate solution was measured at 25°C for a preliminary test performance of the experimental apparatus.

In this experiment, oxygen was absorbed through a laminar layer at the surface of the liquid phase, and measurement of the absorption rate was continued for a

rather long time. Therefore, the film model was applied as an absorption mechanism.

If the oxygen concentration in the solution in the absorption vessel is expressed by the volume of oxygen absorbed, V_G, which is measured by the gas burette under total pressure in the apparatus, the relation between V_G and t which is time spent after the start of absorption is expressed as follows:

$$k_L At/V_L = \ln\{V_G^*/(V_G^* - V_G)\} \tag{1}$$

The oxygen volume V_G^* which is necessary to saturate the solution in the absorption vessel and measured under total pressure in the apparatus is expressed by use of the solubility of oxygen, L, as follows:

$$V_G^* = LV_L p_{O_2}/P \tag{2}$$

Consequently, by measuring t and V_G and by calculating V_G^* by Eq. (2), one can plot $\ln\{V_G^*/(V_G^* - V_G)\}$ versus t. Such a plot must be a straight line from Eq. (1), and k_L can be obtained from the slope of the straight line. However, in a practical experimental operation, the absorption vessel was connected to the gas reservoir for a limited time at the start of absorption, and after adjusting the pressure in the absorption vessel to the specified value, the absorption vessel was connected to the gas burette and started to measure the oxygen volume in the gas burette. Consequently, it was difficult to obtain k_L by the application of Eq. (1) to the observed data, because it is impossible to measure the gas volume absorbed in the starting period.

Therefore, to eliminate an error in the measurement of the gas volume in the starting period, $(V_{G2} - V_{G1})$ was calculated by applying Eq. (1) to V_{G1}, which described an oxygen volume absorbed until time t and V_{G2}, which in turn, described the volume absorbed until time $2t$. Then, by use of $(V_{G2} - V_{G1})$ the following relation was derived for k_L:

$$k_L = -\frac{V_L}{At}\ln\left(\frac{1 + \sqrt{(1 - 4f)}}{2}\right) \tag{3}$$

where

$$f = (V_{G2} - V_{G1})/V_G^* \tag{4}$$

Because the error in measurement in the starting period was not contained in f, k_L was calculated by Eq. (3) from each pair of data in a run, and the average value of k_L was adopted in each run.

From the results of five runs of absorption of oxygen in water, the average value of k_L was 1.48×10^{-3} cm/sec and the maximum deviation was 2% of the average value.

From the results of four runs of the absorption of oxygen in an aqueous sodium sulfite solution of 0.28 mol/l, the average value of k_L was 1.44×10^{-3} cm/sec and the

maximum deviation was 3% of the average value.

These results demonstrate that the reliability of this experimental apparatus is satisfactory.

3.2 Absorption with chemical reaction

In the case without a gas-film resistance of mass-transfer, the rate of gas absorption accompanied by an irreversible reaction is expressed as follows:

$$\frac{dV_G}{dt} = \frac{k\ell A V_G{}^*}{V_L}$$ (5)

Consequently, by this experimental apparatus, $k\ell$ was easily obtained by measuring the rate of the reduction of the oxygen volume in the gas burette.

It is known that the rate of reaction is zero-order with respect to sulfite at the concentrations of sodium sulfite and cobaltous ion used here, and at the oxygen partial pressure of about 1 atm.[20] Therefore, the gas absorption in this experiment is considered as the absorption accompanied by the irreversible m-th order reaction with respect to oxygen only. The following relation was derived[5] for the case mentioned above from the film theory of absorption by assuming the ideal gas law:

$$\frac{dV_G}{dt} = \left(\frac{2}{m+1} k_m D_L\right)^{1/2} \frac{A(L p_{o_2})^{(m+1)/2}}{P(RT)^{(m-1)/2}}$$ (6)

This relation expresses the volumetric absorption rate at the total pressure in the experimental apparatus. By converting the absorption rate to that at an appropriate reference pressure P_0, the following equation is obtained from Eq. (6).

$$\left(\frac{dV_G}{dt}\right)_0 = K p_{o_2}{}^{(m+1)/2}$$ (7)

where

$$K = \left(\frac{2}{m+1} k_m D_L\right)^{1/2} \frac{A L^{(m+1)/2}}{P_0(RT)^{(m-1)/2}}$$ (8)

If m, D_L and L are all constant, K becomes constant from Eq. (8). In this case, a linear relation is obtained from Eq. (7) when the corrected volumetric absorption rates $(dV_G/dt)_0$ are plotted against the oxygen partial pressure in the absorption vessel on log-log graph paper, and m is obtained from the slope of this straight line.

About this reaction, it is also known that the order of reaction with respect to oxygen is unity at the oxygen partial pressure of about 1 atm.[1,7,8,10,11,17] Therefore, at the oxygen partial pressure of 1 atm, the absorption of oxygen in the aqueous sodium sulfite solution used here is the absorption accompanied by an irreversible first-order reaction. In this case, the reaction factor β is expressed by the film theory[4] as follows:

$$\beta = \gamma/\tanh \gamma$$ (9)

where

$$\gamma = (k_r D_L)^{1/2}/k_L \tag{10}$$

In the case of $\gamma > 5$ (or $\beta > 5$), Eq. (9) is approximated by Eq. (11).

$$\beta = \gamma \tag{11}$$

Thus, the reaction rate constant k_r is expressed as follows:

$$k_r = (k_L')^2/D_L \tag{12}$$

If the concentration of sodium sulfite is approximately constant, the value of D_L is considered to be nearly constant, though the pH of the sulfite solution is adjusted by adding acid or alkali. Consequently, when the reaction rate of solution A is different from that of solution B owing to the difference in the pH of A and B, the ratio of the reaction rates is expressed from Eq. (12) as follows:

$$k_{rA}/k_{rB} \cong (k_{LA}')^2/(k_{LB}')^2 \tag{13}$$

Fig. 3 shows the results of some experiments. In this figure, each point represents the average rate of absorption calculated from the oxygen volume absorbed during 5 minutes, the midst of which indicates the time plotted.

Plots similar to Fig. 3 throughout the investigation showed that the rate of absorption was independent of time after the start of absorption.
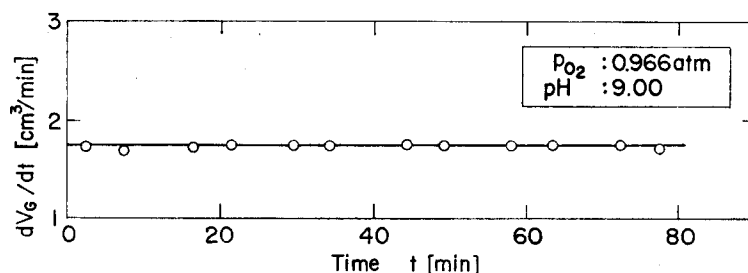

Fig. 3. Rate of absorption of oxygen by aqueous sodium sulfite solution vs absorption time.

3.3 Effect of oxygen concentration

Measurements were made with solutions under oxygen partial pressures ranging from 0.1 to 1 atm without adjusting the pH values. The pH results of the solutions were about 10.1 in all runs.

Absorption rates $(dV_G/dt)_0$ were calculated on the basis of P_0 as 1 atm from the results at the various oxygen partial pressures. Fig. 4 shows a plot of $(dV_G/dt)_0$ versus oxygen partial pressure. From this figure, it is clear that this plot gives essentially two straight lines intersecting each other at the oxygen partial pressure of
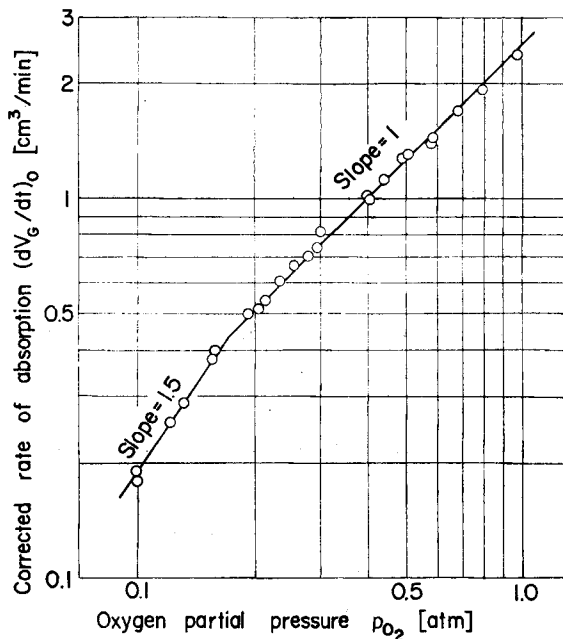
Fig. 4. Effect of oxygen partial pressure on corrected rate
of absorption of oxygen.

about 0.17 atm. The slopes of the lines are unity for the oxygen partial pressures above 0.17 atm and three halves for the oxygen partial pressures below 0.17 atm.

Because the concentration of sodium sulfite in the solutions were approximately constant throughout the investigation, D_L and L of oxygen in the sulfite solutions were almost constant, respectively. When Eq. (7) is applied to the lines in Fig. 4, K is constant for each line. Under these conditions, the values of m can be determined by Eq. (7) from the slope of the lines. As a result, the values of m were determined as unity at the oxygen partial pressures above 0.17 atm and two at those below 0.17 atm.

From Fig. 4, it is also obvious that the reaction order changes rather suddenly in the very limited pressure range of oxygen around 0.17 atm.

In similar results of the previous investigation,[1,7] the oxygen pressure at the change of the reaction order was higher than that of the present work, that is 0.8 atm or above. The reason for this discrepancy may be the difference in experimental conditions, especially the concentration of a catalyst.

3.4 Effect of pH

Measurements were made with solutions of pH ranging from 6 to 13 and at the

oxygen partial pressure of about 1 atm. The pH of the solutions decreased gradually as the reaction proceeded by the oxidation of sulfite to sulfate. In the experiment, however, the pH value at the start of each run was used as that in the run, because the lowering of the pH of the sulfite solution was rather slight, that is within 0.05, in each run.

The values of k_l calculated by Eq. (5) were plotted against the pH value in Fig. 5. From this figure, it is obvious that the β's were larger than 8 in all runs. Then the ratio of k_r to $k_{r\mathrm{max}}$ was calculated by Eq. (13), $k_{r\mathrm{max}}$ being the reaction rate constant corresponding to the maximum value of k_l in the experiment.

Fig. 6 shows the plot of $k_r/k_{r\mathrm{max}}$ versus pH. The plot has a shape like a bell which has a peak at pH=9.6. It is unsymmetrical, and shows that the effect of the pH on the reaction rate is complicated.

Among previous studies concerning this effect, Roxburgh[15] investigated the effect of pH on k_l in a rather wide range of pH and found the existence of a peak value in k_l. The comparison between the result of this work and that of Roxburgh in the case of a cobalt catalyst was made in Fig. 7. Because the experimental conditions were different from each other, the ratios of k_l to $k_{l\mathrm{max}}$ in each investigation were plotted against pH respectively in Fig. 7.
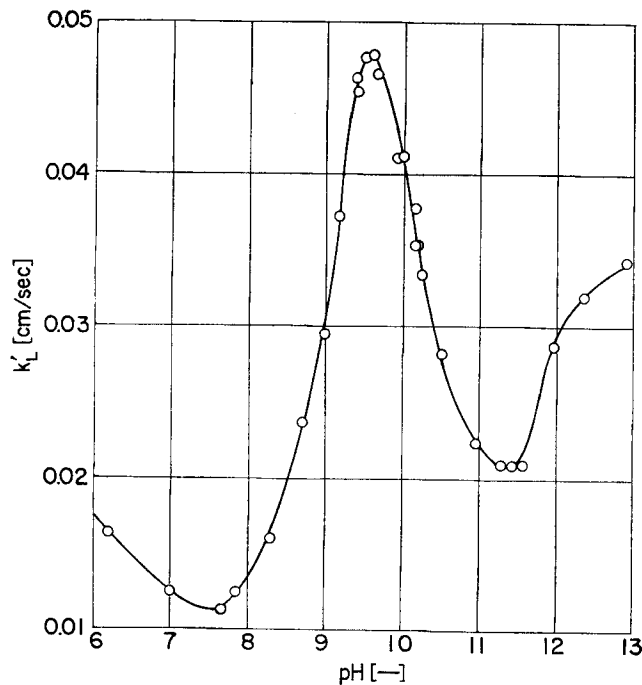

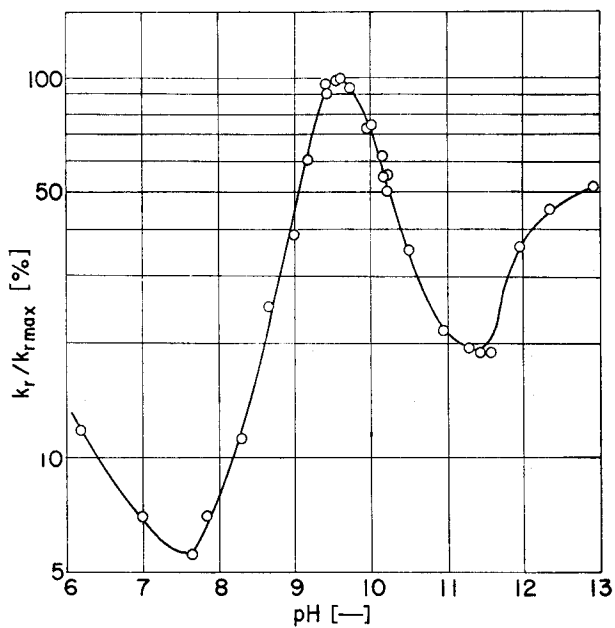Fig. 5. Effect of pH value on liquid-film mass transfer coefficient.

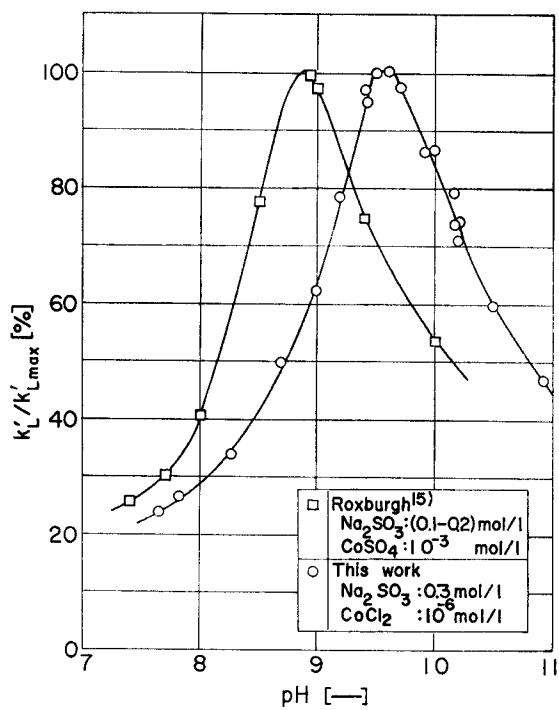Fig. 6. Effect of pH value on reaction rate constant.

Fig. 7. Comparison of experimental result with result by Roxburgh.

Fig. 7 shows that the relations between kl and pH are almost the same in both experiments though their experimental conditions are different from each other to a certain extent, as indicated in the figure. The difference of pH values corresponding to kl_{max} in each plot may be caused by different concentrations of sulfite and cobaltous ion used in each investigation.

The disagreement among the results of the effect of pH on the reaction rate by previous investigators[8,9,14,17] is naturally caused by the difference of the range of pH values and concentrations of sulfite and cobaltous ions. Consequently, when we utilize the correlations between the reaction rate and the pH proposed by previous investigators, it is necessary to examine the experimental conditions used to obtain those correlations.

The reason why the reaction rate has a maximum value at a certain value of pH has been explained as follows: the reaction rate increases with an increasing pH. However, when the pH exceeds a certain value, cobaltous ion precipitates as an inactive cobaltous hydroxide, and the concentration of cobaltous ion decreases, forcing the reaction rate to decrease.

However, it does not sufficiently clarify the effect of pH on the reaction rate by only the above mentioned explanation, because no precipitation was found at the highest pH in this experiment. In a certain pH range higher than that corresponding to the peak, the reaction rate increased with an increasing pH as seen in Fig. 7.

3.5 Preparation of the solution without adjustment of pH

In this work, it was not possible to find any difference between the pH value to make the reaction rate to maximum and the pH of the solution prepared without any adjustment of pH. The pH of the solution of 0.3 mol/l sodium sulfite with 10^{-6} mol/l cobaltous ion was within a range of 9.75 and 10.2; and the reagent of anhydrous sodium sulfite has a possibility of containing a trace of alkali. Taking this into account, it is considered that the pH corresponding to kr_{max} is very close to the pH of a solution prepared by dissolving pure sodium sulfite and a cobalt compound into water without adding any acid or alkali.

4. Conclusion

The effect of the oxygen concentration and the pH on the rate of oxidation of sodium sulfite in 0.3 mol/l aqueous sulfite solution catalyzed by 10^{-6} mol/l cobaltous chloride was investigated by a gas absorption method at 25°C.

To investigate the effect of the pH, measurements were made with solutions of pH ranging from 6 to 13 at an oxygen pressure of about 1 atm. For studying the effect of the oxygen concentration, measurements were made with solutions without

adjusting the pH under oxygen partial pressures ranging from 0.1 to 1 atm.

Under the conditions in this work, it was found that:

(1) the order of reaction with respect to oxygen was unity at oxygen partial pressures above 0.17 atm and two at those below 0.17 atm,

(2) the change of this reaction order arose in the very limited pressure range of oxygen around 0.17 atm,

(3) the rate of reaction was influenced by the variation of the pH of the solution significantly,

(4) the relation between the reaction rate and the pH was very complicated, and could not be correlated by a simple expression,

(5) the reaction rate and the pH are correlated by a rather simple expression in only a limited pH range, and the correlations of the effect of the pH proposed by previous investigators, therefore, cannot be extrapolated out of the pH range used to get them, and

(6) the value of the pH corresponding to the maximum reaction rate may be very near to the pH of the solution without adjustment of the pH.

Nomenclature

A : gas–liquid interfacial area $\hspace{4em}$ [cm^2]

D_L : diffusion coefficient of gas in liquid $\hspace{2em}$ [cm^2/sec]

f : parameter defined by Eq. (4) $\hspace{4em}$ [—]

K : parameter defined by Eq. (8) $\hspace{2em}$ [cm^3/atm$^{(m+1)/2}$ · sec]

k_L : liquid-phase mass transfer coefficient $\hspace{2em}$ [cm/sec]

k_L' : liquid-phase mass transfer coefficient with reaction $\hspace{2em}$ [cm/sec]

k_m : mth-order reaction rate constant $\hspace{2em}$ [$l^{(m-1)}$/mol$^{(m-1)}$ · sec]

k_r : first-order reaction rate constant $\hspace{3em}$ [1/sec]

L : Ostwald coefficient of oxygen at 25°C and 1 atm. $\hspace{2em}$ [—]

m : order of reaction for gas $\hspace{4em}$ [—]

P : total pressure in absorption vessel $\hspace{3em}$ [atm]

p_{O_2} : partial pressure of oxygen $\hspace{4em}$ [atm]

R : gas constant $\hspace{4em}$ [atm · l/mol · K]

T : temperature $\hspace{5em}$ [°C or K]

t : absorption time $\hspace{4em}$ [sec or min]

V_G : volume of gas absorbed in liquid $\hspace{3em}$ [cm^3]

V_G^* : volume of gas required to saturate V_L of liquid $\hspace{2em}$ [cm^3]

V_L : volume of liquid phase $\hspace{4em}$ [cm^3]

β : reaction factor $\hspace{5em}$ [—]

γ : parameter defined by Eq. (10) $\hspace{3em}$ [—]

<Subscripts>

A,B : specified pH value

max : maximum value

0　　: reference state

1　　: time t

2　　: time 2t

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