Reaction Kinetics of Oxidation of Sodium Sulfite in Aqueous Solution by Rapid-Mixing Flow Method

By

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Abstract

The homogeneous reaction rate of oxygen and sodium sulfite in an aqueous solution catalyzed by cupric ion was investigated by the rapid-mixing flow method.

The performance of the experimental apparatus was examined and proved to be suitable for the study of the kinetics of gas–liquid reactions.

The rate of reaction was found to be a half order with respect to the initial concentration of oxygen, first order with respect to sulfite, and a quarter order with respect to cupric ion. But in each run, the apparent reaction rate was zero order with respect to oxygen.

1. Introduction

The absorption of oxygen into sodium sulfite solutions is often used in testing the performance of gas–liquid contacting equipment. The results of such investigations are useful, but a theoretical interpretation is difficult without a knowledge of the homogeneous chemical reaction rates of oxidation of sufite with oxygen.

This reaction is catalyzed by many substances effectively,[5] and cobaltous and cupric ions are mainly used as catalysts in many investigations. While many reaction rate data of sulfite oxidation catalyzed by cobaltous ion exist, there are few works[1,4,6] on the reaction catalyzed by cupric ion. Besides, there is poor agreement in the reported results. One of the reasons for such a disagreement may be that the form of copper ion in an aqueous sulfite solution is uncertain, and the concentration of cupric ion which can initiate the chain reaction of sulfite oxidation cannot be determined in the solution. This is because copper ion in the sulfite solution seems

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to exist as cuprous ion[1,4] or to form some complexes.[12]

In this investigation, measurements were made of the homogeneous reaction rate of sodium sulfite and oxygen catalyzed by cupric ion by the rapid–mixing flow method of Hartridge and Roughton.[7] Determination was made of the effect of concentrations of sodium sulfite, oxygen and cupric ion on the reaction rate at 25°C.

The method used was similar to that of Barron et all.[1] Aqueous solutions of oxygen with copper sulfate and sodium sulfite were passed through a rapid mixer, and the extent of reaction was followed by a temperature rise of the reacting stream in a reaction tube following the mixer. The steady–state temperature profile in the reaction tube was determined by a series of thermocouples along the tube.

This method of rate measurement has some remarkable advantages over heterogeneous techniques. Since oxygen is put in the solution before reaction and since mixing by the mixer is completed within a few ten milliseconds, the rate of reaction is in no way limited by an interphase diffusion or mixing. Therefore, data of the solubility and diffusivity of oxygen in the solution are not necessary to analyze for the reaction rate.

2. Experimental Apparatus and Procedure

2.1 Experimental apparatus

Fig. 1 is a diagram of the apparatus. Because of the known sensitivity of the reaction rate to metallic catalysts, no metallic parts were used in any section contacting reactant solutions. Feed tanks, orifices and most parts of the pipe line were
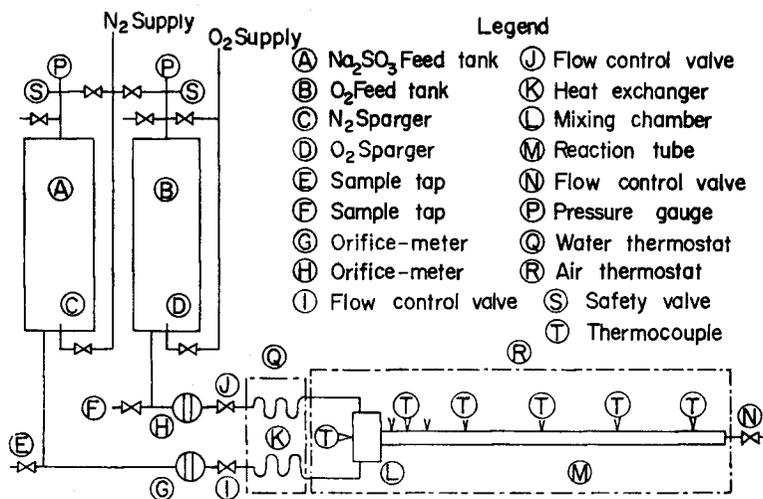
Fig. 1. Schematic diagram of apparatus.

made of vinyl chloride resin.

The reaction tube was made of a glass tube of 0.576cm i. d. and 153cm long with holes for the insertion of thermocouples into the tube. The average cross-sectional area of the reaction tube was 0.2601cm², and the average deviation from the mean value of the area was 0.0021cm² at five cross-sections of the tube. The length of the reaction tube from the mixing chamber to the last thermocouple was 140cm.

The reaction tube was wrapped with approximately a 4cm thickness of fiberglass insulation to minimize heat transfer to the surroundings, and placed in the air bath R, the temperature of which was controlled by a regulator at 25±0.1°C.

The mixing chamber L was made of acrylic resin. Two feed streams entered into the mixing chamber from four ports tangentially to the cross-section of the reaction tube.

Manganin-constantan thermocouples were located in the feed tanks, at thirteen points inside the reaction tube, and at three points outside the tube. The thermocouples were sealed in glass sheaths and inserted in the reaction tube, and then fixed to the tube by epoxy resin.

2.2 Experimental procedure

Before each run, a known quantity of purified water in which a necessary amount of copper sulfate was dissolved was charged to the oxygen feed tank B. Then, adjusting the temperature of the solution to 25°C by an immersion resistance heater, oxygen bubbled through the tank at a certain pressure to produce an oxygen solution of desirable concentration. At the same time, a sodium sulfite solution was charged to the feed tank A, and adjusting the temperature of the solution to 25°C by using a heater, nitrogen gas was forced to bubble through the tank to purge off the oxygen.

After the temperature difference between the two solutions in tanks A and B became less than 0.05°C, the bubbling of the gas was stopped. Then nitrogen and oxygen pressures were applied to tanks A and B, respectively, at 1 to 1.5Kg/cm² higher than the oxygen saturation pressure in tank B. The reactant solutions were allowed to pass through the orifice-meters to the mixing chamber L, where the reaction was initiated.

The flow rates of the two reactant solutions were adjusted to provide the desired ratio of the two streams. Valve J was fully opened when the feed streams flowed. The total flow rate of the mixed solution was controlled by valve N, and the ratio of the two feed streams was controlled by valve I. By a preliminary investigation, it was confirmed that the pressure drop of the stream flowing from the feed tanks to the exhaust valve N was less than 0.5Kg/cm² at the maximum flow rate used in this

experiment. From this result, the desorption of oxygen from the reactant solution in the apparatus was prevented by an application of pressure to the feed tanks and by a flow rate control by valve N as mentioned above.

After a short time, a steady-state temperature profile was established, and temperature measurements were made at a number of points along the tube. Those were made by the No. 0 thermocouple which was set in the mixing chamber and No. 1 to 12 thermocouples which were set in the reaction tube.

Velocities in the reaction tube were such that the Reynolds number was above 5000 in all runs.

The sulfite concentrations of the feed solution and the reaction effluent were determined by iodometry. The oxygen feed solution was analyzed by the Winkler method.[10]

The sodium sulfite used was an anhydrous guaranteed reagent. The copper sulfate used was a guaranteed reagent and recrystallized. The water used was all deionized.

2.3 Analysis of observed data

The experimental data were obtained as the temperature measurements by the thermocouples placed along the reaction tube. The quantity of heat generated by the reaction and therefore the temperature rise along the tube were direct functions of the extent of completion of the reaction. The time of reaction was proportional to the distance along the tube. Consequently, with a knowledge of the flow rate of the reacting stream, the functional relation between the temperature rise and the reaction time was determined.

Assuming that the reaction tube was an adiabatic tubular reactor and that the flow pattern in the tube was a piston flow, by neglecting the axial heat conduction in the solution flowing in the reactor, we derive the following relation between the change of the oxygen concentration c[mol/l] and the change of the temperature T[°C] of the reacting stream in the reactor.

$$-dc = \frac{1000c_p\rho}{-\Delta H_R}dT \tag{1}$$

Denoting the average flow rate in the reactor by u[cm/sec], the distance from the mixing chamber by z[cm] and the reaction time at the cross-section of z by t[sec], one can express the reaction rate r from Eq. (1) as follows:

$$r = -\frac{dc}{dt} = \frac{1000c_p\rho u}{-\Delta H_R} \cdot \frac{dT}{dz} \tag{2}$$

The heat of reaction for the oxidation of sodium sulfite, ΔH_R, was -131.6 kcal/mol-O_2 consumed, which was calculated from thermodynamic data on standard heats

of formation,[8] because very diluted reactant solutions were used in this work.

If the volumetric flow rate was denoted by $V[cm^3/sec]$, it became $u=3.84\ V$ in this reactor. Substituting these values into Eq. (2), one obtains the following expression.

$$r=0.0292c_p\rho V \cdot \frac{dT}{dz} \tag{3}$$

Eq. (3) was used for analyzing the observed data.

As the specific heat of the reacting solution, $c_p[cal/g \cdot °C]$, the specific heat of the aqueous solution of sodium sulfate[11] was used.

2.4 Investigation of reactor performance

2.4.1 Heat loss from reaction tube wall

Determination of the reaction rate by this apparatus was based on the assumption that no heat was lost from the reaction tube wall. Therefore, it was necessary to examine the heat loss through the tube wall. The completeness of the thermal insulation of the reaction tube was tested by inspecting the difference between temperatures at the mixing chamber and the last thermocouple of the reaction tube when water of 25.5 or 26.0°C was forced to flow in the reaction tube by maintaining the temperature of the air thermostat at 25.0°C. A temperature difference was hardly found in such experiments. Therefore, it was concluded that the heat loss from the reaction tube wall was negligible in analyzing the observed data.

2.4.2 Performance of mixing chamber

The degree of mixing reactant solutions in the mixing chamber had a significant effect on the degree of progress of reaction.

For checking the degree of mixing, hydrochloric acid was made to react with sodium hydroxide in this apparatus. Because the rate constant of this reaction is $1.43 \times 10^{11}\ l/mol \cdot sec$[3] at 25°C, this reaction may be regarded as an instantaneous reaction. Therefore, the degree of completion of this reaction is determined by the degree of mixing the reactant solutions in the reaction tube.

0.1 mol/l solutions of hydrochloric acid and sodium hydroxide were prepared in the feed tanks A and B separately. Then, the reactant solutions were forced to flow through the mixing chamber and down the reaction tube with the velocity of the mixture corresponding to Reynolds number ranging from 5000 to 10000, and the measurement of temperature was made. Fig. 2 shows a plot of temperature along the reaction tube as a function of both the reaction time and the distance along the reaction tube. From Fig. 2, it is clear that the reaction proceeded up to 95% within 2cm
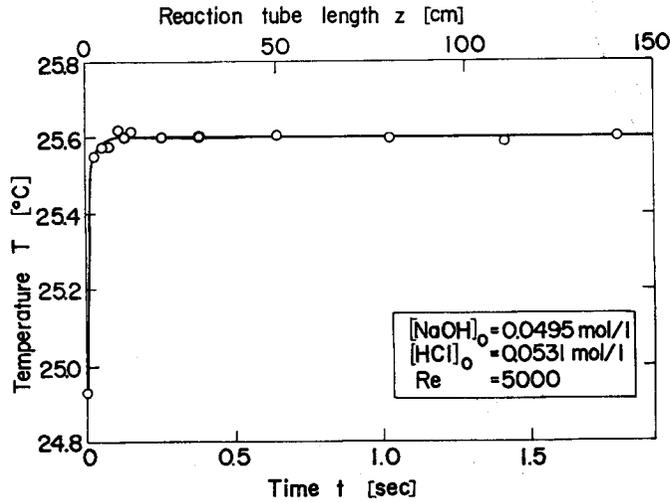
Fig. 2. Check of degree of mixing in mixing chamber.

and completed within 6cm from the mixing chamber.

Therefore, it was concluded that the degree of mixing in this mixing chamber was remarkably high.

2.4.3 Assumption of piston flow

For the stream in the reaction tube, the piston flow model was assumed. Therefore, the effect of back-mixing on the analysis based on the piston flow model will be analyzed theoretically.

By applying the dispersion model to the stream in the reaction tube, and by assuming that the velocity u is the same at all cross-sections of the reaction tube, the change of concentration c of oxygen along the tube can be expressed as follows:

$$E_z \frac{d^2 c}{dz^2} - u \frac{dc}{dz} - r = 0 \qquad (4)$$

In the case of the first order reaction, the reaction rate is expressed as follows:

$$r = k_r c \qquad (5)$$

By substituting Eq. (5) into Eq. (4), Eq. (4) is transformed into a dimensionless form as follows:

$$\frac{d^2 C}{dZ^2} - Pe_B \frac{dC}{dZ} - N_r \, Pe_B \, C = 0 \qquad (6)$$

where

$$\left.\begin{array}{l} Pe_B = uL/E_z \\ N_r = k_r L/u \\ C = c/c_0 \\ Z = z/L. \end{array}\right\} \tag{7}$$

The boundary conditions are

$$\left.\begin{array}{ll} \dfrac{dC}{dZ} = Pe_B(C_{0+} - 1), & at \ Z = 0 \\[2mm] \dfrac{dC}{dZ} = 0, & at \ Z = 1. \end{array}\right\} \tag{8}$$

The solution[2] of Eq. (6) with these two boundary conditions is

$$C = 2 \exp\left(\frac{Pe_B Z}{2}\right) \times$$

$$\frac{(1+\beta) \exp\left[\dfrac{\beta Pe_B}{2}(1-Z)\right] - (1-\beta) \exp\left[-\dfrac{\beta Pe_B}{2}(1-Z)\right]}{(1+\beta)^2 \exp\left(\dfrac{\beta Pe_B}{2}\right) - (1-\beta)^2 \exp\left(-\dfrac{\beta Pe_B}{2}\right)} \tag{9}$$

where

$$\beta = \left(1 + \frac{4N_r}{Pe_B}\right)^{1/2}. \tag{10}$$

In the piston flow model, the differential equation is

$$dc = -r \ dt. \tag{11}$$

By substituting Eq. (5) into Eq. (11) and integrating Eq. (11) over the whole length of the reaction tube, the solution is

$$C = \exp(-N_r Z). \tag{12}$$
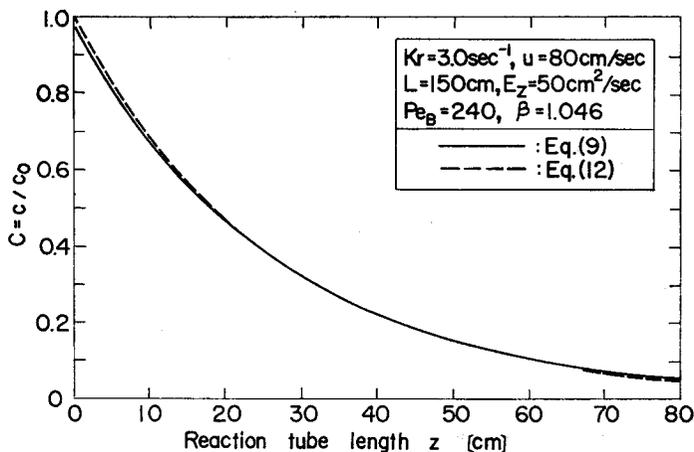
Fig. 3. Comparison between concentration profiles based on dispersion model and piston flow model.

Fig. 3 shows a comparison between concentration profiles in the reaction tube computed by Eq. (9) and Eq. (12).

Similar comparisons of Fig. 3 were made with an axial dispersion coefficient E_z of $50 cm^2/sec^{9)}$ and the first order reaction rate constant k_r ranged from 1 to 10 sec^{-1}. As a result of the calculation based on the two models, the concentration differences were within 2% at the same cross-section.

Therefore, it was concluded that the analysis of the observed data based on the piston flow model was accurate enough for practical purposes.

3. Results and Discussion

Fig. 4 shows an example of a plot of temperature as a function of distance from the mixing chamber or time of reaction in reaction rate measurements. Plots similar to Fig. 4 throughout the investigation showed that the temperature increased almost linearly with the reaction time up to the point where the oxygen was completely consumed. Beyond that point, the temperature of the solution was essentially constant.

The symbols used in Fig. 4, $[O_2]_0$, $[Na_2SO_3]_0$ and $[CuSO_4]$ describe the oxygen concentration at the start of reaction, the sodium sulfite concentration at the start of reaction and the copper sulfate concentration respectively, and all represent the values of the solution in the reaction tube.

In this work, the ratio of concentration of sodium sulfite to that of oxygen ranged from 4 to 10 at the start of the reaction in each run. Therefore, the shape of the temperature–time plots was mainly determined by the reaction order of oxygen, because the change of sulfite concentration was very small throughout the reaction
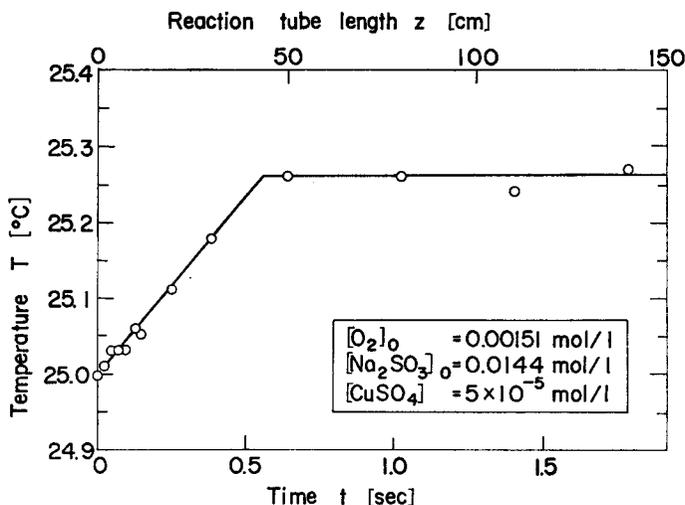
Fig. 4. Plot of temperature against reaction time in reaction tube.

in each run. Under these conditions, the almost linear relationship of the tempera-ture–time plots indicates that the reaction rate is apparently independent of the oxygen concentration. This agrees with the result of Barron et al.[1]

In Fig. 4, the relation between the temperature and the reaction time was approximated by a straight line in the temperature rising section, and the reaction rate r was obtained from the slope of the straight line by Eq. (3). This reaction rate was taken as that at the average concentration, or the logarithmic mean value of the initial and final concentration of sulfite in the reacting solution.

Though the temperature of the reacting solution increased by a few tenths of a degree in each run, the effect of the temperature rise on the reaction rate was neglected. This was because the increment of the reaction rate accompanied by a temperature increase of a few tenths of a degree was estimated at only a few per cent by using the activation energy of 18.3 kcal/mol.[1]

To confirm the order of reaction with respect to oxygen, this reaction was assumed to be the first–order with respect to sulfite. Of the data with 10^{-5} mol/l copper sulfate, the value of the reaction rate r divided by the average concentration of sodium sulfite $[Na_2 SO_3]$ was plotted against the initial oxygen concentration $[O_2]_0$ on a log–log graph paper in Fig. 5. From this figure, it is obvious that the reaction rate is in proportion to the square root of the initial oxygen concentration. This result contradicts the result in Fig. 3. This strange behavior may be caused by the fact that this reaction is a very complicated chain reaction, and affected strongly by the experimental conditions. It is difficult to explain this behavior clearly, because the mechanism of the reaction is not yet clarified.

To determine the effect of the catalyst concentration on the reaction rate, the reaction rate divided by the average concentration of sodium sulfite and by the
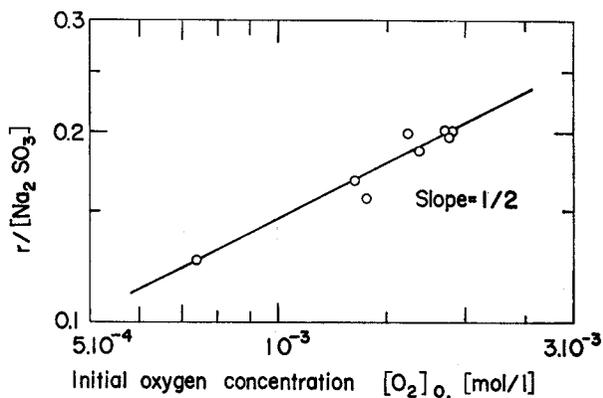
Fig. 5. Effect of initial oxygen concentration on reaction rate.
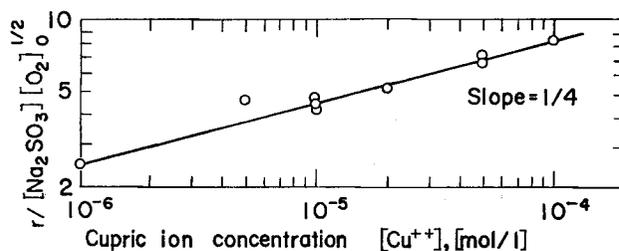
Fig. 6. Effect of catalyst concentration on reaction rate.

square root of the initial oxygen concentration was plotted against the catalyst concentration in Fig. 6. In this work, the concentration of copper sulfate was regarded as the same as that of cupric ion, because all of the copper was considered to have a form of cupric ion in the solution at the start of reaction. From Fig. 6, the order of reaction with respect to cupric ion was found to be a quarter.

Lastly, the order of reaction with respect to sodium sulfite was examined. Fig. 7 shows a plot of the reaction rate divided by the square root of the initial oxygen concentration and by the fourth root of the cupric ion concentration versus the average sulfite concentration. From Fig. 7, the order of reaction with respect to sulfite was found to be one; and it was confirmed that the previous assumption of the first–order dependence of the reaction on sulfite concentration was reasonable.

As a result, the rate of this reaction is correlated by the following expression:
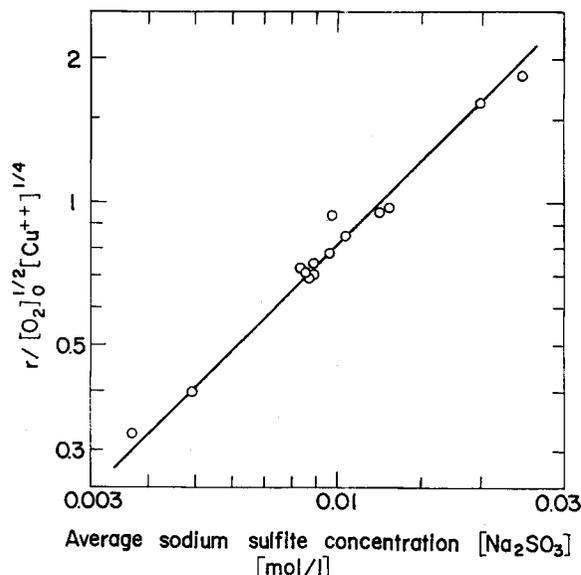
Fig. 7. Effect of sodium sulfite concentration on reaction rate.

$$-\frac{d[O_2]}{dt} = 81[Cu^{++}]^{1/4}[O_2]_0^{1/2}[Na_2SO_3] \qquad (13)$$

Eq. (13) is applicable to the following concentration range:

[Na_2SO_3] : 0.0037~0.025 mol/l

[O_2]_0   : 0.00074~0.0028 mol/l

[Cu^{++}]   : 10^{-6}~10^{-4} mol/l

([Cu^{++}] describes the concentration of cupric ion.)

In regard to the order of reaction with respect to sulfite, the result of this work agrees with that of Fuller et al.[4] But as regards the effects of the other factors on the reaction rate, the results of this work are different from those of previous works.[1,4,6] The causes of such disagreement may be that (1) the concentration of sulfite used in this work was similar to that of Fuller et al.[4], but very different from those of Barron et al.[1] and Greenhalgh et al.[6] which ranged from 0.05 to 0.5 mol/l, (2) the experimental method used here was different from those of Fuller et al. and Greenhalgh et al. which were gas absorption methods, and (3) there was appreciable difference among the methods of estimating the concentration of cupric ion as a catalyst.

4. Conclusion

The homogeneous reaction rate of oxygen and sodium sulfite in an aqueous solution catalyzed by copper sulfate was investigated by the rapid-mixing flow method at 25°C. Copper sulfate was always added to the oxygen feed solution to change all copper into cupric ion.

As a result, it was pointed out that (1) although the order of reaction with respect to oxygen was apparently zero in each run, the rate of reaction was dependent on the oxygen concentration at the start of the reaction, and (2) all data obtained in the present work were correlated by Eq. (13).

The results of this investigation did not agree with those of previous works except in a few points. This may be due to a difference among experimental methods and conditions used by the different investigators.

Nomenclature

C = dimensionless concentration (= c/c_0)   [—]

C_{0+} = dimensionless concentration just within entrance of the reaction
          tube   [—]

c = concentration of oxygen in solution   [mol/l]

c_p = specific heat of solution   [cal/g·°C]

d = diameter of reaction tube   [cm]

E_z	= dispersion coefficient	[cm^2/sec]
ΔH_R	= heat of reaction	[cal/mol]
k_r	= first-order reaction rate constant	[sec^{-1}]
L	= reaction tube length	[cm]
N_r	= $k_r L/u$	[—]
Re	= Reynolds number $(=du\rho/\mu)$	[—]
Pe_B	= Peclet number $(=uL/E_z)$	[—]
r	= reaction rate	[mol/l·sec]
T	= temperature	[°C]
t	= reaction time	[sec]
u	= average linear flow rate	[cm/sec]
V	= volumetric flow rate	[cm^3/sec]
Z	= dimensionless distance $(=z/L)$	[—]
z	= distance from mixing chamber in reaction tube	[cm]
β	= defined by Eq. (10)	[—]
ρ	= density of solution	[g/cm^3]
μ	= viscosity of solution	[g/cm·sec]

$\langle$Subscript$\rangle$

0   = value at entrance of reaction tube

References

1) Barron, C. H. and H. A. O'Hern : Chem. Eng. Sci., **21**, 397 (1966).
2) Danckwerts, P. V. : Chem. Eng. Sci., **2**, 1 (1953).
3) Ertl, G. and H. Gerischer : Z. Elektrochem., **66**, 560 (1962).
4) Fuller, E. C. and R. H. Crist : J. Am. Chem. Soc., **63**, 1644 (1941).
5) "Gmelins Handbuch der anorganischen Chemie", Schwefel, Teil B. Lieferung 3, 8 Auflage, p. 1293, Verlag Chemie, Weinheim (1963).
6) Greenhalgh, S. H., W. J. McManamey, and K. E. Porter : Chem. Eng. Sci., **30**, 155 (1975).
7) Hartridge, H. and F. J. W. Roughton : Proc. R. Soc. London, A **104**, 376, 395 (1923).
8) Hougen, O. A., K. M. Watson, and R. A. Ragatz : "Chemical Process Principles", Part 1, 2nd ed., p. 317, John Wiley and Sons, Inc., New York (1954).
9) Levenspiel, O. : "Chemical Reaction Engineering", p. 276, John Wiley and Sons, Inc., New York (1964).
10) Nippon Kagaku Kai : "Jikken Kagaku Koza", Vol. 15-II, p. 348, Maruzen, Tokyo (1958)
11) Timmermans, J. : "Physico-Chemical Constants of Binary Systems", Vol. 3, p. 437, Interscience Publishers, Inc., New York (1960).
12) Vepřek-Šiška, J. and S. Luňák : Z. Naturforsch. B **29**, 689 (1974).