

# Gas Absorption Accompanied by an Irreversible Second-Order Reaction in Turbulent Liquids

Gas absorption accompanied by a second-order irreversible reaction in turbulent liquid films ( $Re > 1,200$ ) is described using the Danckwerts surface renewal theory. The model equations, consisting of two coupled, nonlinear partial differential equations, were solved numerically. Experimental data were obtained for the absorption of carbon dioxide into aqueous sodium hydroxide solutions flowing in a wetted wall column under turbulent flow conditions. The experimental mass transfer coefficients agree to within a mean deviation of 10.3% compared to predictions of the theoretical calculations. For this comparison, the rate of surface renewal was obtained from physical absorption experiments, the liquid viscosity and density were measured, and the reaction rate constant and all other physical properties were obtained from the literature. For the experiments the Reynolds number ranged from 1,400 to 5,300 and  $[OH^-]_b/[CO_2]_s$  varied from 9 to 29.

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## SCOPE

Since gas solubilities in an absorbing liquid are usually very low, it is often the case that the controlling resistance to mass transfer is in the liquid phase. To increase the liquid phase mass transfer coefficient and to increase the capacity of the liquid to absorb, it is desirable to use a liquid in which the absorbed gas will react. Most liquid-phase reactions are second order. However, under certain conditions, the reaction may be considered to be pseudofirst order or instantaneous. In this work, we consider the general case of a second-order reaction.

Gas absorption with second-order irreversible reaction in turbulent liquid films was modeled using the Danckwerts surface renewal theory to describe the turbulent transport. In previous experimental studies of gas absorption in turbulent liquid films in this laboratory, it was found that an eddy diffusivity model could successfully correlate the data. For the case of nonlinear kinetics, as in this study, the eddy diffusivity approach cannot account for the additional term in the time averaged diffusion equation,  $k C_A C_B$ , which arises due to the nonlinear kinetics. This difficulty does not arise in the Danckwerts surface renewal theory.

For physical absorption, the relationship for the mass transfer coefficient is given in terms of the rate of surface renewal as

$$k_c^o = \sqrt{D_A s} \quad (2)$$

Physical absorption measurements of carbon dioxide in water were interpreted using Eq. 2 to determine the surface renewal rate,  $s$ , as a function of Reynolds number. Chemical absorption experiments were carried out for the absorption of carbon dioxide into aqueous sodium hydroxide solutions with turbulent flow in the liquid film ( $Re > 1,200$ ). Experimental conditions were chosen such that the reaction could be considered to be irreversible and of second order. All experiments were conducted in a 0.69-m-long wetted-wall column. The experimental results were compared to theoretical predictions of surface renewal theory. To obtain the theoretical values of the mass transfer coefficient, it was necessary to solve two coupled, nonlinear partial differential equations. These equations were solved numerically using a finite difference procedure.

## CONCLUSIONS AND SIGNIFICANCE

Experimental results agree with the theoretical predictions to within an absolute mean deviation of 10.3% when the reaction rate constant,  $k$ , of Nijssing et al. (1959) is used in the theoretical calculations. If the reaction rate constant reported by Pinsent et al. (1956) is used, the absolute mean deviation becomes 12.7%. None of the parameters for the theoretical pre-

diction are fitted from the experimental chemical absorption data. This relatively good agreement between theory and experiment gives strong support for the application of the surface renewal theory of Danckwerts to modeling of chemical absorption into turbulent liquids.

## INTRODUCTION

The controlling resistance to mass transfer in gas absorption often resides in the liquid phase due to the generally low solubilities of gases in liquids. To increase the liquid-phase mass transfer coefficient and to increase the absorption capacity of the liquid, it is

frequently desirable to add a component to the liquid with which the absorbed gas will react. In this work, we consider gas absorption accompanied by an irreversible second-order reaction in a turbulent liquid. Experimental mass transfer coefficients were measured for the absorption of carbon dioxide into aqueous sodium hydroxide solutions. The hydroxide concentrations were chosen so that the reaction was in a regime where it must be considered to second order rather than pseudofirst order or instantaneous. The contact device used was a 0.69-m-long wetted-wall column with liquid flow

rates set to give Reynolds numbers in the turbulent flow regime ( $Re > 1,200$ ).

In previous work on absorption with and without chemical reaction in our laboratory, it was found that an eddy diffusivity model correlated the data very well. However, for the case of a reaction having nonlinear kinetics, the eddy diffusivity model cannot account for the additional terms in the time-averaged diffusion equation which arise from nonlinear kinetics. As an example, consider the case of a second-order reaction. The time-averaged rate of reaction per unit volume for this situation is

$$r = kC_A C_B + k\overline{C'_A C'_B} \quad (1)$$

where  $C_i$  represents the time-mean values of the concentration of species  $i$  and  $C'_i$  represents the concentration fluctuation from the time mean. The eddy diffusivity approach does not allow computation of the term  $\overline{C'_A C'_B}$ . The surface renewal theory does not have this limitation. In this model, it is proposed that a turbulent eddy of fluid is transported to the gas-liquid interface where mass transfer occurs according to penetration theory during its exposure time at the interface. It is assumed that the surface is renewed at a constant rate resulting in a particular distribution of surface ages.

It was found that the physical absorption data of Lamourelle and Sandall (1972) for turbulent liquids is described as well by surface renewal theory as by the eddy diffusivity model. For physical absorption, the mass transfer coefficient according to surface renewal theory is expressed as

$$k_c^o = \sqrt{D_A s} \quad (2)$$

The Lamourelle absorption data gives the rate of surface renewal,  $s$ , as

$$s = 3.19 \times 10^{-5} Re^{1.678} s^{-1} \quad (3)$$

The data of Menez and Sandall (1974) for absorption in turbulent liquids accompanied by a fast first-order reaction can also be correlated by surface renewal theory. For a fast first-order reaction, the chemical absorption mass transfer coefficient as determined by surface renewal theory is given as

$$k_c = \sqrt{D_A (k_1 + s)} \quad (4)$$

The Menez and Sandall data agree with Eq. 4 to within an absolute mean deviation of 1.9% compared to 2.1% for the eddy diffusivity model.

For the case of a second-order reaction, an exact analytical solution for the surface renewal theory has not been obtained. De Coursey (1974), however, has determined an approximate solution which is valid under some reaction conditions. Matherson and Sandall (1978) have solved the model equations numerically, and this technique was used in our work to compare predictions of the surface renewal theory with experimentally determined mass transfer rates.

## THEORY

The physical situation for the absorption of gas A followed by subsequent irreversible reaction with liquid-phase reactant B ( $A + 2B \rightarrow \text{products}$ ) can be represented by a pair of time-dependent diffusion equations:

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} - k C_A C_B \quad (5)$$

$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2} - 2k C_A C_B \quad (6)$$

The initial and boundary conditions are taken to be:

$$\begin{aligned} t = 0 \quad x > 0 \quad C_B &= C_{B_i} \quad C_A = 0 \\ t > 0 \quad x = 0 \quad \frac{\partial C_B}{\partial x} &= 0 \quad C_A = C_{A_o} \\ t > 0 \quad x \rightarrow \infty \quad C_B &= C_{B_i} \quad C_A = 0 \end{aligned} \quad (7)$$

Matherson (1977) solved Eqs. 5 and 6 with boundary conditions given by Eq. 7 using the Crank-Nicolson finite-difference procedure. The program developed by Matherson was used in this work. The numerical results obtained for the rate of absorption were integrated according to the Danckwerts surface renewal theory to obtain the enhancement factor

$$E(s) = \frac{1}{C_{A_o} \sqrt{D_A s}} \int_0^\infty s e^{-st} R(t) dt \quad (8)$$

where  $R(t)$  is the rate of absorption per unit area.

Due to the upper limit of infinity for the integral in Eq. 8, it is necessary to split the integral into two parts, so that for the first part, for  $0 \leq t \leq \tau_o$ , the integrand may be determined from the numerical solution of the differential equations. For the second part,  $\tau_o \leq t < \infty$ , the asymptotic expression of Pearson (1963) may be used for  $R(t)$  in the integrand. In this case, the second integral may be evaluated exactly.  $\tau_o$  is taken to be sufficiently large so that the numerical calculations for  $R(\tau_o)$  agree with the asymptotic solution of Pearson.

## EXPERIMENTAL APPARATUS AND PROCEDURES

The apparatus is the same that is used by others in this laboratory (Lamourelle and Sandall, 1972) with some modifications to assure precise control of temperature, Figure 1. The apparatus consists mainly of a long wetted-wall column. The liquid stream passes through a distributor, and the film is formed on the outside of a 0.0159-m (5/8-in.) outside diameter stainless-steel pipe. The gas stream flows cocurrently with the liquid stream in the annulus between this pipe and a 0.0762-m (3-in.) diameter glass pipe.

The column length could be varied by adjustment of the liquid receiver. In this work, all experiments were carried out using a liquid film length of 0.69 m (27-in.). The liquid level inside the column was adjusted by a valve on the outlet liquid stream that controlled the outflow from the column. The gas stream was controlled by a regulating valve and heated to the atmospheric temperature by passing through a long steel coil. The partial pressure of  $\text{CO}_2$  was approximately 1 atm for all runs. The gas was not saturated with water vapor before introduction into the column, and this results in some evaporative cooling at the gas-liquid interface. However, for the flow rates used in this work, evaporative cooling may be shown to have a negligible effect on the interface temperature. The pressure in the column was measured by a manometer containing a fluid having a specific gravity 1.75. Liquid flow rate was measured by a flowmeter and controlled by a valve on the bypass of the circulating pump. The liquid temperature was measured at the inlet and the outlet by means of two mercury ther-

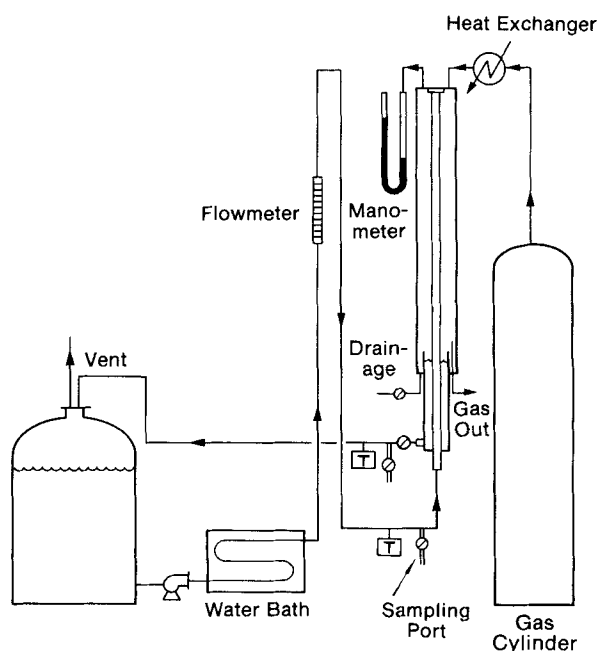


Figure 1. Experimental apparatus.

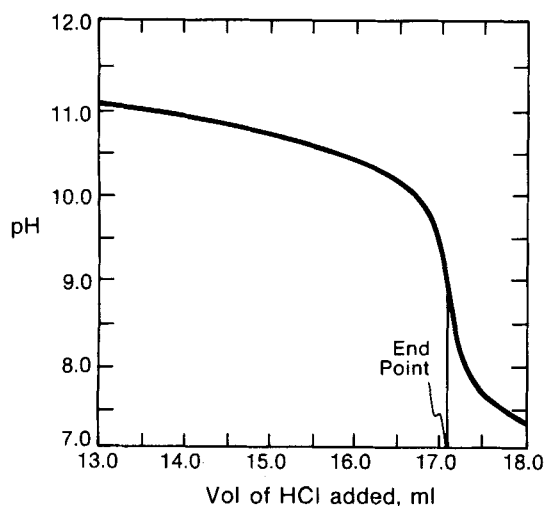


Figure 2. Titration curve for NaOH with 0.25 N HCl.

monitors and controlled by means of a controlled temperature water bath. All runs were carried out at a temperature at 25°C.

In the case of chemical absorption, circulation of the solution was necessary to avoid consumption of large amounts of the solution.

A falling ball viscometer was used to measure viscosities of the inlet and the outlet streams for each run. Solution densities were determined using hydrometers.

Wet chemistry analysis was carried out using a highly sensitive (0.01 mL, 0.01 pH) automatic titrometer.

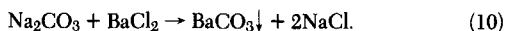
To test the equipment, experiments were conducted for the case of physical absorption of carbon dioxide in water. In operating the apparatus, the valve on the bypass of the pump was adjusted to give the required flow rate. When the flow rate and temperature of water were steady (about 15 min) carbon dioxide gas was introduced into the column. Samples were taken after 20 min using a 50-mL syringe taking care to avoid absorption and desorption of carbon dioxide. The samples were analyzed for carbon dioxide using a wet chemistry method. Sodium hydroxide and barium chloride were added to the sample to transform the absorbed carbon dioxide into barium carbonate according to the reaction



The excess amount of sodium hydroxide was titrated with a standard hydrochloric acid (0.1 N) with the endpoint being determined by plotting pH vs. the volume of hydrochloric acid added.

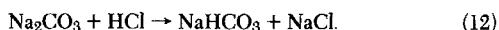
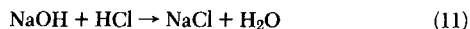
For chemical absorption, the method of operation was the same as for physical absorption. The solution used was sodium hydroxide having a concentration range 0.3–0.5 gmol/L. Samples were taken by means of two ports at the inlet and the outlet. A wet chemistry method was used to determine carbon dioxide absorbed as:

(i) A part of the sample was treated with an excess amount of barium chloride to precipitate carbon ions without affecting sodium hydroxide present in the sample as:



Then the sodium hydroxide left in this part was titrated with a standard hydrochloric acid (0.25 N). pH was plotted against volume of hydrochloric acid added to determine the endpoint, Figure 2.

(ii) Another part of the sample was titrated directly with hydrochloric acid (0.25 N) to determine sodium hydroxide concentration plus half carbonate concentration according to:



The endpoint of the reaction was determined by plotting pH against volume of hydrochloric acid added. The difference in volumes of hydrochloric acid consumed in (i) and (ii) is equivalent to half of the carbonate concentration in the sample. The difference between the carbonate in the inlet and the outlet samples represents the amount of carbonate formed due to reaction during the absorption process, and this is equivalent to the carbon dioxide absorbed.

## EXPERIMENTAL RESULTS AND DISCUSSION

Several initial runs were made for the physical absorption of carbon dioxide into turbulent water as a check on the experimental procedure. Mass

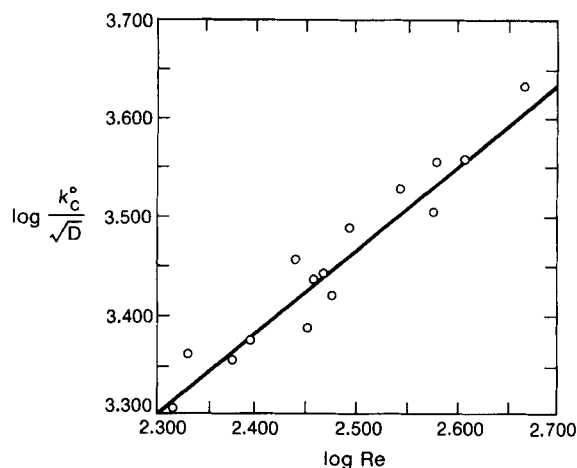


Figure 3. Physical absorption mass transfer coefficients compared to correlation of Lamourelle and Sandall.

transfer coefficients for these runs were calculated from an integrated material balance as

$$k_c^o = \frac{q}{L} \cdot \frac{R}{R + d} \ln \frac{C_{A_o} - C_{A_1}}{C_{A_o} - C_{A_2}} \quad (13)$$

In Eq. 13,  $q$ ,  $R$ ,  $L$ ,  $C_{A_1}$  and  $C_{A_2}$  were measured. The surface concentration of  $\text{CO}_2$  in water,  $C_{A_o}$ , was calculated using Henry's law

$$C_{A_o} = \frac{P_A}{H^o} \quad (14)$$

where  $H^o$  is given as a function of temperature by Danckwerts and Sharma (1966)

$$\log_{10} H^o = \frac{1,140}{T} - 5.3 \quad (15)$$

The film thickness,  $d$ , was obtained from the correlation of Brötz (1954)

$$d = 0.0672 \left( \frac{\mu^2}{g} \right)^{1/3} \text{Re}^{2/3} \quad (16)$$

The physical absorption data are compared with the correlation of Lamourelle and Sandall (1973), Eq. 3, Figure 3. The data show an absolute mean deviation of 4.95% from Eq. 2. For this comparison, the diffusivity of  $\text{CO}_2$  in water at 25°C was taken to be  $1.98 \times 10^{-9} \text{ m}^2/\text{s}$  (Perez and Sandall, 1973).

Chemical absorption runs were made for turbulent flow for the absorption of  $\text{CO}_2$  into aqueous NaOH solutions. An integrated material balance in this case gives

$$k_c = \frac{q}{2L} \cdot \frac{R}{R + d} \cdot \frac{C_{B_1} - C_{B_2}}{C_{A_o}} \quad (17)$$

To calculate the mass transfer coefficient,  $q$ ,  $L$ ,  $R$ ,  $C_{B_1}$  and  $C_{B_2}$  were measured.  $C_{A_o}$  is given by Henry's law, but in the case of chemical absorption Henry's constant was corrected for the presence of the electrolyte according to the method given by Danckwerts (1970).

A total of 85 chemical absorption runs were made for the hydroxide concentration range 0.3 to 0.5 gmol/L and for Reynolds numbers varying from 1,400 to 5,300. The sodium hydroxide concentrations used were chosen so that the chemical reaction could be considered to be in the second-order regime. Danckwerts and Sharma (1966) give two limiting criteria for conditions under which a second-order reaction may be considered to be either pseudofirst order or instantaneous. These criteria are

$$\text{For pseudofirst order: } \sqrt{D_A k C_{B_b}} \leq \frac{1}{2} k_c^o \left( 1 + \frac{C_{B_b}}{2C_{A_o}} \right) \quad (18)$$

$$\text{For instantaneous reaction: } \sqrt{D_A k C_{B_b}} \geq 10 k_c^o \left( 1 + \frac{C_{B_b}}{2C_{A_o}} \right) \quad (19)$$

Thus to ensure second-order reaction conditions, hydroxide concentrations were chosen to satisfy the following inequalities

$$\frac{1}{2} k_c^o \left( 1 + \frac{C_{B_b}}{2C_{A_o}} \right) < \sqrt{D_A k C_{B_b}} < 10 k_c^o \left( 1 + \frac{C_{B_b}}{2C_{A_o}} \right) \quad (20)$$

Figure 5 compares the experimental enhancement factors defined as

$$E = \frac{k_c}{k_c^o} \quad (21)$$

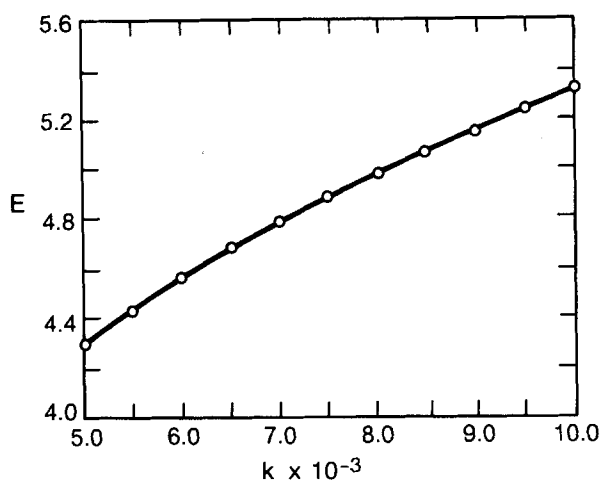


Figure 4. Effect of reaction rate constant on the enhancement factor.

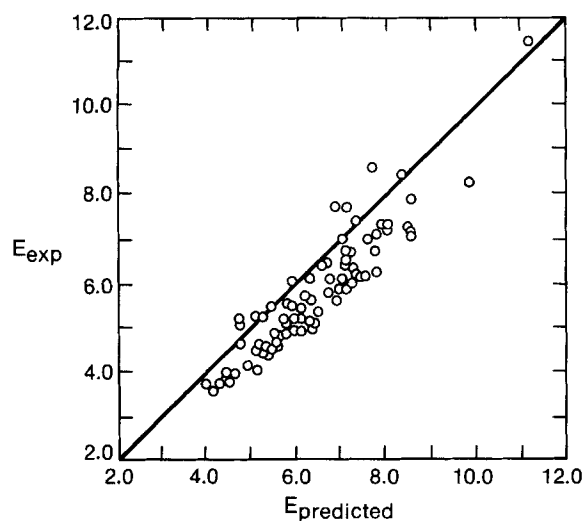


Figure 5. Experimental enhancement factors compared to theoretical prediction of surface renewal theory.

with the enhancement factors predicted from surface renewal theory. The experimental value of the enhancement factor was calculated using the experimental results for the chemical absorption mass transfer coefficient,  $k_c$ , and using Eq. 2 to calculate the physical absorption mass transfer coefficient,  $k_c^o$ . For the theoretical calculations, the diffusion coefficient for carbon dioxide was corrected for the effect of reactants in solution by application of the Stokes-Einstein equation using measured solution viscosities. The ratio  $D_{OH^-}/D_{CO_2}$  was taken as 1.67 as given by Nijssing et al. (1959). The rate of surface renewal,  $s$ , was taken from Eq. 3. Since there is a wide range of reaction rate constant values as obtained by different researchers, two values which bound upper and lower limits of available data were used. At 20°C, the reaction rate constant ranges from 4,700–5,900  $l \text{ gmol}^{-1} \text{ s}^{-1}$ . The lower and upper values were obtained by Nijssing et al. (1959) and Pinsent et al. (1956), respectively. The reaction rate constant dependency on temperature, as given by Pinsent et al., is

$$\log_{10} k = 13.635 - \frac{2,895}{T}, T \text{ in K} \quad (22)$$

since activation energy for the reaction is constant, the lower value of the reaction rate constant can be given by

$$\log_{10} k = 13.548 - \frac{2,895}{T}, T \text{ in K} \quad (23)$$

If the effect of ionic strength is taken into account as given by Nijssing et al. to be equal to 0.131, the above equations become, respectively

$$\log_{10} k = 13.635 - \frac{2,895}{T} + 0.131 \quad (24)$$

$$\log_{10} k = 13.548 - \frac{2,895}{T} + 0.131 \quad (25)$$

The effect of reaction rate constant on enhancement factor for one of the runs is shown in Figure 4. The reaction rate constant for the calculations, Figure 5, was obtained by Eq. 25. The absolute mean deviation between experimental and predicted enhancement factor is 10.3%. If Eq. 24 is used for the theoretical calculations, the mean deviation becomes 12.7%. Since none of the parameters for the theoretical predictions are determined from the experimental chemical absorption data, this relatively good agreement between theory and experiment indicates that the surface renewal model satisfactorily describes the turbulent transport for the case of absorption with an irreversible second-order reaction.

## NOTATION

$C_A$	= concentration of gas A in liquid, kmol/m <sup>3</sup>
$C_{A_0}$	= concentration of A at interface, kmol/m <sup>3</sup>
$C_{A_b}$	= bulk liquid concentration of A, kmol/m <sup>3</sup>
$C_{A_1}$	= concentration of A in liquid inlet, kmol/m <sup>3</sup>
$C_{A_2}$	= concentration of A in liquid outlet, kmol/m <sup>3</sup>
$C_A$	= fluctuating concentration of A, kmol/m <sup>3</sup>
$C_B$	= concentration of liquid-phase reactant, kmol/m <sup>3</sup>
$C_{B_b}$	= bulk liquid concentration of B, kmol/m <sup>3</sup>
$C_{B_i}$	= initial liquid concentration of B, kmol/m <sup>3</sup>
$C_B$	= fluctuating concentration of B, kmol/m <sup>3</sup>
$C_{B_1}$	= concentration of B in liquid inlet, kmol/m <sup>3</sup>
$C_{B_2}$	= concentration of B in liquid outlet, kmol/m <sup>3</sup>
$d$	= film thickness, m
$D_A$	= diffusion coefficient of B, m <sup>2</sup> /s
$E$	= enhancement factor = $k_c/k_c^o$
$g$	= acceleration of gravity, m/s <sup>2</sup>
$H^o$	= Henry's law constant for pure water, kPa·m <sup>3</sup> /kmol
$k$	= second-order rate constant, m <sup>3</sup> /gmol·s
$k_1$	= first-order rate constant, s <sup>-1</sup>
$k_c$	= chemical absorption mass transfer coefficient, m/s = $R(t)/C_{A_0}$
$k_c^o$	= physical absorption mass transfer coefficient, m/s = $R(t)/(C_{A_0} - C_{A_b})$
$L$	= film length, m
$P_A$	= partial pressure of A, kPa
$q$	= volumetric flow per wetted perimeter, m <sup>2</sup> /s
$r$	= rate of reaction per unit volume, kmol/m <sup>3</sup> ·s
$R$	= radius of wetted-wall column, m
$R(t)$	= rate of absorption per unit surface area, kmol/s·m <sup>2</sup>
$Re$	= Reynolds number = $\frac{4q}{\nu}$
$s$	= rate of surface renewal, s <sup>-1</sup>
$t$	= time, s
$T$	= temperature, K
$x$	= distance from free surface, m
$\nu$	= kinematic viscosity, m <sup>2</sup> /s
$\tau_o$	= time at which large time asymptotic solution applies, s

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# Unified Treatment of Structural Effects in Fluid-Solid Reactions

By considering reaction and diffusion through a product layer and concomitant movement of pore and reaction surfaces, a general rate equation is derived for fluid-solid reactions. Application to the random pore model extends the prior results (Bhatia and Perlmutter, 1980, 1981a) to account for nonlinear concentration gradients in the product layer, by assuming that the product is deposited as overlapping cylindrical annulae. For the Petersen (1957) model, new results are derived which account for product layer diffusion. A comparison of numerical conversion-time predictions from the grain model (Szekely et al., 1976), the Petersen model, and the random pore models suggests that they are more strongly affected by the representation of the reaction surface than by that of the pore surface. The model is applied to the data of Borgwardt (1970) on the SO<sub>2</sub>-lime reaction, and the results are compared with a previous interpretation using a linear concentration gradient approximation.

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## SCOPE

For fluid-solid chemical reactions, a general rate equation is derived which treats the various existing models (Petersen, 1957; Szekely et al., 1976; Bhatia and Perlmutter, 1980, 1981a) in a single unified analytical framework involving the simultaneous motion of pore and reaction surfaces. The distinction among the different models is made in terms of only the several representations of these motion.

Prior representations of the motion of the pore surface have on occasion yielded inconsistent results. Thus, for example, expanding grain models (Georgakis et al., 1979) predict an ever-increasing pore surface area in spite of a decrease in pore

volume. The random pore model developed by Bhatia and Perlmutter (1981a) considers the pore and reaction surface areas to be equal, an approximation which, of necessity, is less accurate at high conversions. The extension of the Petersen (1957) model by Calvelo and Cunningham (1970) accounts for product formation, but not for any product layer diffusional resistance or changes in pore surface area.

The influence of the motion of the pore and reaction surfaces on conversion behavior is analyzed and compared for the various structural models. The results are applied to the experimental data of Borgwardt (1970).

## CONCLUSIONS AND SIGNIFICANCE

A generalized approach is presented to predict fluid-solid reaction behavior for a variety of structural assumptions on the solid. An important basis in the model, that each point on the growing or shrinking reaction surface moves at the same rate, is exact for a uniform pore or grain-size solid reactant.

A comparison of the grain model, the Petersen model, and the model developed here shows that the representation of the pore surface effects the predicted conversion behavior less severely than that of the reaction surface, unless the reaction is accom-

panied by a substantial increase in the volume of the solid phase, or when product layer diffusion is slow compared to reaction. When this is not the case, conversion time measurements under conditions of kinetic control should alone suffice to distinguish between the models.

Application of the model developed here to the experimental data of Borgwardt (1970) on the SO<sub>2</sub>-lime reaction, yields an activation energy for product layer diffusion of 108 MJ/kmol, suggesting a solid-state process. Comparison of the estimated product layer diffusivities with those obtained using the previous thin layer model (Bhatia and Perlmutter, 1981b) shows that the latter calls for larger diffusivity because it predicts slower reaction rates. This difference is enhanced at elevated temperatures where higher levels of conversion are attained.

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