

was regulated by the injection of air into the absorption chamber in order to make the carbon dioxide concentration in the gas phase similar to the carbon dioxide concentration which would be expected for longtime absorption.

## RESULTS AND DISCUSSION

The desorption of air from water and the condensation of water vapor occurring in a bubble in the bubble column and in the absorption chamber of vertical jet or of horizontal water flow were investigated.

1. Bubble column. It was found experimentally that the concentration of air in a bubble increases continuously, and the volume of the bubble progressively decreases with the rise of bubble in falling water in a column. Accordingly, there occurs, in general, a maximum content of air, the transition point in Figure 1, in the course of absorption of a bubble into flowing water. At such a point, neither desorption nor absorption of air but the condensation of water vapor in gas phase is thought to occur in spite of the progressive contraction of the bubble with the absorption of carbon dioxide into water. The maximum content of air varies widely in the range of about 20 to 85% and seems to be correlated with the height of column, the rate of falling water, and the total interfacial area of bubbles in the bubble column. The excessive increase of the percentage of air in the bubble beyond the maximum content of air results in a transition of the direction of diffusion of air from the bubble to the water to keep equilibrium of air between the bubble and the water. Namely,  $N_A > 0$  and  $N_B > 0$ ; therefore  $\alpha > 0$  (see Figures 1 and 2).

When  $\alpha$  becomes small, the absorption of a bubble of carbon dioxide is regarded as unidirectional diffusion, but the partial pressure of air in the bubble cannot be neglected in the final period of absorption because of its high concentration. The rise in temperature of the water by the heat of dissolution of carbon dioxide into water and by that of condensation of water vapor is negligible in this experiment but will not be necessarily the same for the absorption of a great many bubbles into a liquid. The variations of the condensation of water vapor in bubbles with time and with  $X_{AO}$  are shown in Figures 1 and 2.

2. Vertical jet and horizontal flow. In water jet and horizontal water flow systems, the volume of the gas phase is constant. Accordingly, no maximum volume of air appears in the gas phase, and the change of humidity in the gas phase may be neglected. As the concentration of air increases with time, namely, as  $X_{AO}$  decreases in

the absorption chamber,  $\alpha$  is found to tend somewhat toward  $-1$ , the equimolar counterdiffusion, as shown in Figure 2, which can also be understood theoretically from Equation (9).

## NOTATION

- $A$  = interfacial area between gas and water,  $\text{cm}^2$   
 $n$  =  $n_A + n_B + n_C$ , gmole  
 $n_A, n_B, n_C$  = mole concentrations of carbon dioxide, air, and water vapor, respectively, gmole  
 $N_A$  = absorption rate of carbon dioxide,  $\text{gmole}/\text{cm}^2 \text{ s}$   
 $N_B$  = desorption rate of air,  $\text{gmole}/\text{cm}^2 \text{ s}$   
 $N_C$  = condensation rate of water vapor,  $\text{gmole}/\text{cm}^2 \text{ s}$   
 $P$  = total pressure =  $[\rho_L(Z - Z_c)/1.030] + P_0$ , atm  
 $P_0$  = atmospheric pressure, atm  
 $p_0$  = vapor pressure of water at 1 [atm], atm  
 $R$  = gas constant =  $82.05 \text{ cm}^3 \text{ atm}/\text{gmole } ^\circ\text{K}$   
 $T$  = absolute temperature,  $^\circ\text{K}$   
 $u_L$  = velocity of water,  $\text{cm}/\text{s}$   
 $V$  =  $V_A$  (volume of carbon dioxide) +  $V_B$  (volume of air) +  $V_C$  (volume of water vapor),  $\text{cm}^3$   
 $v^*$  = rate of gas indicated at soap-film flowmeter,  $\text{cm}^3/\text{s}$   
 $X_{AO}, X_{BO}, X_{CO}$  = mole fractions of carbon dioxide, air, vapor, respectively  
 $Z$  = height of bubble in column, cm  
 $Z_c$  = effective height of column, cm  
 $\alpha$  =  $N_B/N_A$   
 $\alpha'$  =  $N_C/N_A$   
 $\theta$  = time, s  
 $\rho_L$  = density of water,  $\text{g}/\text{cm}^3$

## LITERATURE CITED

- Bourne, J. R., and G. C. Coggan, "A Note on Heat Effects in Gas Absorption," *Chem. Eng. Sci.*, **24**, 196 (1969).  
Dwyer, O. E., and B. F. Dodge, "Rate of Absorption of Ammonia by Water in a Packed Tower," *Ind. Eng. Chem.*, **33**, 485 (1941).  
Grenier, P., "Solvent Counterdiffusion on Gas Absorption," *Can. J. Chem. Eng.*, **44**, 213 (1966).  
Mitsutake, H., "Decrease of Liquid Film Coefficient of Mass Transfer in Process of Absorption of Series of Single Bubble," *J. Chem. Eng. Japan*, **6**, 420 (1973).  
———, and M. Sakai, "Gas-Side Mass Transfer Coefficient in Absorption of Carbon Dioxide into Water Jet," *ibid.*, **9**, 501 (1976).  
Tanaka, K., et al., "Effect of Evaporation of Water on Gas Absorption in Water Jet," Preprints of the 41th Annual Meeting of the Soc. of Chem. Engrs., Japan, D204, 262 (1976).

Manuscript received December 16, 1976; revision received and accepted March 4, 1977.

# Wall Region Mass Transfer for Large Schmidt Numbers in Turbulent Pipe Flow

G. A. HUGHMARK

Ethyl Corporation  
Baton Rouge, Louisiana 70821

Shaw and Hanratty (1976) have presented experimental mass transfer data for the Schmidt number range of 693 to 37 200 with turbulent flow in a circular pipe. The authors suggest that a greater precision was attained than in previous investigations because of the care given to the execution of these experiments. The fully developed mass transfer coefficients were correlated by

$$k = 0.0889 u^* N_{Sc}^{-0.704} \quad (1)$$

Excellent agreement is shown between Equation (1) and the experimental data.

Hughmark (1975) proposed the equation for fully developed mass transfer in a circular pipe:

$$\frac{1}{k^+} = \frac{1}{\frac{1}{1.6 N_{Sc}} + \alpha N_{Sc}^{-2/3}} + \frac{1}{\frac{1}{33 N_{Sc}} + 0.0615 N_{Sc}^{-1/2}}$$

$$+ \frac{1}{\frac{3.58\mathcal{D}}{Ru^*} + 2\sqrt{f/2}} \quad (2)$$

This equation is consistent with the experimental observation of Popovich and Hummel (1967) that  $y^+ = 1.6$  is the limit of the laminar sublayer, and  $y^+ = 34.6$  is the limit of the transition region. Hughmark (1973) has shown that the eddy term for the transition region is consistent with the penetration model and the mean period of fluctuation near the wall. The eddy term for the transition region was also shown to be consistent with experimental data for the eddy diffusivities of heat and mass. Hughmark (1971) has also shown that the two-thirds exponent for the laminar region is consistent with developing laminar boundary-layer model. The core term and the molecular diffusion term for the transition region represent a negligible contribution with high Schmidt numbers. Thus, for this case, Equation (2) reduces to

$$\frac{1}{k^+} = \frac{1}{\frac{1}{1.6 N_{Sc}} + \alpha N_{Sc}^{-2/3}} + \frac{1}{0.0615 N_{Sc}^{-1/2}} \quad (3)$$

Equation (3) with the Shaw and Hanratty data provides an average value of  $\alpha = 0.047$ . Comparison of Equation (3) with this value and the data shows an average absolute deviation of about 2%, and comparison of Equation (1) with the data shows an average absolute deviation of about 3.6%. Thus, both equations represent excellent correlations of these experimental data.

Equation (3) provides an estimate of the relative contributions of the laminar and transition regions. At a Schmidt number of 100 000, about 12% of the total

resistance would appear to be in the transition region, and molecular diffusion represents about 20% of the laminar layer resistance. These estimated values are consistent with Shaw and Hanratty's conclusion that the commonly proposed relations  $N_{Sc}^{-2/3}$  or  $N_{Sc}^{-3/4}$  are incorrect for the Equation (1) model with high Schmidt numbers.

#### NOTATION

$\mathcal{D}$	= molecular diffusivity
$f$	= friction factor
$k$	= mass transfer coefficient
$k^+$	= dimensionless transfer coefficient, $k/u^*$
$N_{Sc}$	= Schmidt number
$R$	= core radius for circular pipe
$u^*$	= shear velocity
$y^+$	= $yu^*/\nu$
$y$	= radial distance from pipe wall
$\nu$	= kinematic viscosity

#### LITERATURE CITED

- Hughmark, G. A., "Heat and Mass Transfer for Turbulent Pipe Flow," *AIChE J.*, **17**, 902 (1971).  
 —, "Additional Notes on Transfer in Turbulent Pipe Flow," *ibid.*, **19**, 1054 (1973).  
 —, "Heat, Mass, and Momentum Transport with Turbulent Flow in Smooth and Rough Pipe," *ibid.*, **21**, 1033 (1975).  
 Popovich, A. T., and R. L. Hummel, "Experimental Study of the Viscous Sublayer in Turbulent Pipe Flow," *ibid.*, **13**, 854 (1967).  
 Shaw, D. A., and T. J. Hanratty, "Turbulent Mass Transfer Rates to a Wall for Large Schmidt Numbers," *ibid.*, **23**, 28 (1977).

Manuscript received February 10, and accepted April 12, 1977.

## Simple Criteria for Mixing Effects in Complex Reactions

J. R. BOURNE

Eidgenössische Technische Hochschule Zurich  
8006 Zurich

and

H. L. TOOR

Carnegie-Mellon University  
Pittsburgh, Pennsylvania 15213

Detailed modeling of an incompletely mixed reactor is complex and usually calls for data and parameter values which are inaccurately known or possibly inaccessible. These difficulties are particularly marked when we consider complex (that is, multistep) reactions. In this case, only knowledge of the reaction mechanism and a few kinetic data are usually available, and the effort required to obtain all the kinetic and hydrodynamic parameters required by a full modeling can probably be justified for only a few frequently occurring reactions. Furthermore, no model has been sufficiently well tested to allow its general application.

With knowledge of the reaction mechanism, but with-

out the kinetics, a simple method can be applied which does not determine quantitatively the extent of a mixing effect but rather indicates qualitatively how partial segregation and feed configuration influence the rates of formation of the desired and undesired products and hence the selectivity. This method was previously applied in the detailed development for a second-order reaction (Toor, 1962; Vassilatos and Toor, 1965; Toor, 1975). It will be illustrated here for some complex reactions, where the objective is to produce an intermediate. (It is also applicable in other situations, for example, when producing the final product of a sequence of reactions.) In this note we consider both incompletely mixed con-