walls. In effect, the actual interface between the constituent layers is replaced by a rigid wall that separates the layers.

Values of $\dot{m}$ were evaluated from Equation (2) by using the data from the homogeneous bed experiments for the 1 and 3 mm spheres. The resulting mass flow predictions* for each of the layered beds are shown as solid lines in Figure 2. The experimental data for the layered beds are plotted as open circles and are connected by dashed lines for continuity. For each layered bed, the information represented by the solid and dashed lines thus involves the results of three separate sets of experiments.

Inspection of Figure 2 indicates that, in general, the measured mass flow for the two-layer bed is smaller than that predicted by adding the flows that would pass through the constituent layers if they were separate entities. The deviations are of the order of 10%. The finding that the measured mass flow is smaller can be made plausible by comparing the local permeability in the zone adjacent to the interface between the layers with that adjacent to a solid wall. In the interface zone, owing to the intermeshing of the larger and smaller spheres, the local permeability will be diminished and the mass flow correspondingly reduced. On the other hand, for a bed of spheres, the packing is less dense adjacent to a solid wall than in the interior of the bed. As a consequence, the permeability for streamwise flow is relatively high adjacent to a solid wall. Inasmuch as the predictive model, in effect, replaces the actual interface with a solid wall, the foregoing arguments are suggestive of an overprediction of the mass flow, although it is not likely that such arguments can fully account for the magnitudes of the deviations evidenced in Figure 2. Any intrusions of smaller spheres into the bed of larger spheres would lower the local permeability and reduce the mass flow.

ACKNOWLEDGMENT

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NOTATION

A = cross-sectional area
c = Forchheimer inertia coefficient
k = permeability
$\dot{m}$ = mass flow rate
p = pressure
V = mean filter velocity (superficial velocity)
x = axial coordinate
μ = viscosity
ν = kinematic viscosity
ρ = density

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* The area A in the ordinate variable is the total cross section of the layered bed.

Chemical Absorption Kinetics Over a Wide Range of Contact Time: Absorption of Carbon Dioxide into Aqueous Solutions of Monoethanolamine

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When a gas, after being absorbed in liquid, may react not only with a reactant dissolved in the liquid but also with a product of this first reaction, then the second (gas with product) reaction will only influence the rate of gas absorption after an exposure time long enough for the product of the first reaction to form. This situation would be expected in many processes involving chemical absorption. However, previous experimental investigations on chemical absorption have been restricted to those with short contact times. In the present work, experiments for the carbon dioxide—monoethanolamine system were performed by using a laminar liquid jet, a wetted wall column, and a quiescent liquid absorber in order to examine the gas absorption mechanism and the reaction kinetics over a wide range of contact times. It is suggested from measured values of the enhancement factor that the present absorption process should be discussed by gas absorption with an irreversible consecutive reaction of the second order and that the reaction rate constant ratio can be estimated.

CHEMICAL ABSORPTION MECHANISM

The overall reaction occurring in the liquid phase is expressed by (Astarita, 1967)

$$CO_2 + 2RNH_2 \rightarrow RNHCOORNH_3 \qquad (1)$$

$$CO_2 + RNHCOORNH_3 + 2H_2O \rightarrow 2HCO_3RNH_3 \qquad (2)$$

where R refers to $(HCOH_2CH_2)$.

The rate constant of the reaction (1) has been obtained by several investigators (Jensen et al., 1954; Emmert and Pigford, 1962; Clarke, 1964). However, the reported value of the reaction rate constant at 25°C ranges from 5 400 to 8 500 l/(g-mole) (s). In the present work, the reaction rate constant was measured with a laminar liquid jet absorber and applied to analyses of chemical absorption data.

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With short contact times in laboratory absorbers, such as the laminar liquid jet and the wetted wall column, the amount of the carbamate, namely, $RNHCOORNH_3$, can be neglected. Hence, the chemical absorption can be analyzed by considering only reaction (1). On the other hand, with long contact times as in a quiescent liquid absorber, the effect of the reaction between carbon dioxide and $RNHCOORNH_3$, that is, reaction (2), is important and influences the absorption rate. In this research, the absorption process is discussed in terms of irreversible consecutive reactions. This might be the explanation for the variation of the enhancement factor over a wide range of contact times.

EXPERIMENTAL APPARATUS AND PROCEDURE

A laminar liquid jet, a wetted wall column, and a quiescent liquid absorber were used as absorption apparatus to obtain data over a wide range of contact times. The contact times range from 0.002 to 12 000 *s*. In experiments with the wetted wall column, 0.02 vol.% of surface active agent, Phensol NP-100, was added to the solution to prevent rippling at the surface of the falling film and to suppress interfacial turbulence. In the experiment with the quiescent liquid absorber, 3 wt.% of agar-agar was added to eliminate natural convection. The gas was pure carbon dioxide saturated with water vapor at atmospheric pressure, and the absorbent was monoethanolamine aqueous solution. The amine concentration was controlled by titrimetric analysis. All the runs were carried out in an air or water thermostat bath kept at a constant temperature of 25°C.

Absorption rates in both the liquid jet and the wetted wall column were measured volumetrically with the help of a soap film meter. In the quiescent liquid absorber, absorption rates were measured by observing the displacement of a small amount of concentrated aqueous sodium chloride solution in the capillary tube connected with the absorber.

RESULTS AND DISCUSSION

In order to analyze experimental results, the physical solubility of carbon dioxide and the diffusivities of carbon dioxide and RNH_2 in aqueous RNH_2 solution are required as a function of RNH_2 concentration. The values of the physical solubility of carbon dioxide were estimated by a correlation given by Sada and Kito (1972). The diffusivities of carbon dioxide and RNH_2 in the liquid phases D_A and D_B were given by Clarke (1964) and Thomas and Furzer (1962), respectively. The value of the reaction rate constant was taken as 8 400 l/(g-mole)(*s*), which was derived from the liquid jet data under presumably pseudo first-order reaction. Figure 1 shows experimental results of the relationship between the enhancement factor Φ and the modulus $\sqrt{M}$. The solid lines in this figure represent the penetration predictions for gas absorption with the second-order irreversible reaction of the form of $A + 2B \rightarrow$ products. A series of experimental points in the liquid jet and the wetted wall column absorbers coincide with the solid lines. However, experimental data from the quiescent liquid absorber with much longer exposure times deviate from the solid line and approach the broken line. This shows that the reaction rate of the second step becomes important relative to diffusion rates. Thus, in order to analyze the present absorption process over a wide range of contact times, it is satisfactory to consider the process as gas absorption with the consecutive reactions of the form of $A + 2B \rightarrow R$ and $A + R \rightarrow$ products.

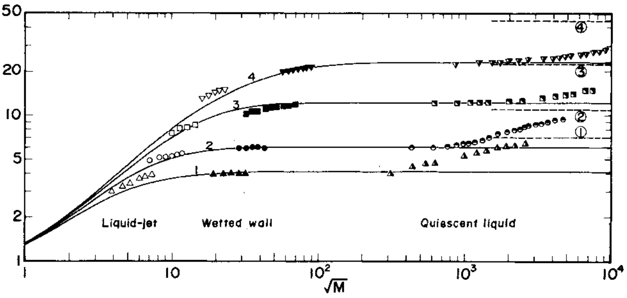

Fig. 1. Variation of enhancement factor Φ with $\sqrt{M}$. Aqueous monoethanolamine concentration C_{Bo}, mole/liter: △, ▲, ▲ 0.245; ○, ●, ◓ 0.435; □, ■, ◪ 0.950; ▽, ▽, ▽ 1.905.

Curve ($\nu = 2$)	Broken line ($\nu = 1$)	r_B	q
1	①	0.588	7.32
2	②	0.600	13.10
3	③	0.604	29.40
4	④	0.529	62.00

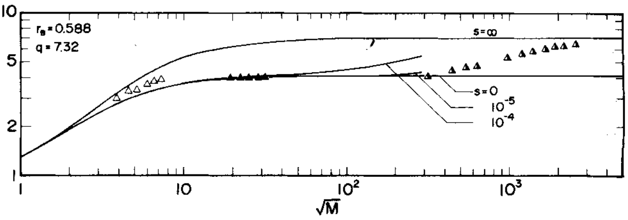

Fig. 2. Comparison of experimental data with theoretical curves for RNH_2 equal to 0.245 mole/l. Keys as in Figure 1.

The approximate solutions for gas absorption with the consecutive reaction on the basis of the film theory were derived and compared by Onda et al. (1970). However, it is desirable that experimental results obtained by present research be compared with penetration theory solutions. Then the enhancement factor will be derived numerically.

For the present problem, the basic differential equations on the penetration theory can be expressed in the following dimensionless form:

$$\frac{\partial^2 Y_A}{\partial x^2} - \frac{\partial Y_A}{\partial \theta} = Y_A Y_B + s Y_A Y_R \tag{3}$$

$$r_B \cdot \frac{\partial^2 Y_B}{\partial x^2} - \frac{\partial Y_B}{\partial \theta} = \left(\frac{2}{q}\right) Y_A Y_B \tag{4}$$

$$r_R \cdot \frac{\partial^2 Y_R}{\partial x^2} - \frac{\partial Y_R}{\partial \theta} = -\left(\frac{1}{q}\right) Y_A Y_B + \left(\frac{s}{q}\right) Y_A Y_R \tag{5}$$

The initial and the boundary conditions to be imposed are

$$\theta = 0, \quad x > 0; \quad Y_A = Y_R = 0, \quad Y_B = 1 \tag{6}$$

$$x = 0, \quad \theta > 0; \quad Y_A = 1, \quad \frac{\partial Y_B}{\partial x} = \frac{\partial Y_R}{\partial x} = 0 \tag{7}$$

$$x = \infty, \quad \theta > 0; \quad Y_A = Y_R = 0, \quad Y_B = 1 \tag{8}$$

The enhancement factor is given by

$$\Phi = \sqrt{\pi/4\theta} \int_0^{\theta} \left(-\frac{\partial Y_A}{\partial \theta}\right)_{x=0} d\theta' \tag{9}$$

First, the transformation of independent variable

$$y = \frac{x}{K\sqrt{\theta + \epsilon}} \qquad (10)$$

was used to transform Equations (3), (4), and (5). A set of transformed equations was approximated by the time centered, implicit finite-difference equations by the same procedure as adopted by Brian and Beaverstock (1965). These implicit equations were simplified by linearizing the reaction terms. A set of simultaneous linear equations was solved by the method of tridiagonal equations.

Figure 2 presents the computational results of the relationship between enhancement factor and modulus $\sqrt{M}$ as a parameter of s when q equals 7.32 and r_B equals 0.588, which corresponds to RNH_2 concentration equal to $2.45 \cdot 10^{-4}$ mole/cm^3. In order to obtain the solution to $\sqrt{M}$ equal to 300 shown in Figure 2, approximately 10 min. of FACOM 230-60 computer time was required. Computed enhancement factors gradually increase from those for gas absorption with the second-order irreversible reaction with an increase of $\sqrt{M}$, as would be expected. By comparing the experimental data at the value of C_{BO} equal to $2.45 \cdot 10^{-4}$ mole/cm^3 with theoretical curve, the ratio of reaction rate constants s amounts to 10^{-5}. Experimental results suggest that only the first chemical reaction needs to be considered in all practical situations because the very maximum contact time likely to occur in such equipment is no more than half a minute with the exception of the process where liquid is recirculated.

NOTATION

C = concentration in liquid phase, mole/cm^3
D = diffusivity in liquid phase, cm^2/s
k = reaction rate constant, liters/(g-mole)(s)
K = arbitrary constant in Equation (10)
M = $\pi\theta/4$
N = time average mass transfer rate, mole/(cm^2)(s)
q = C_{B0}/C_{Ai}
r_B = D_B/D_A
r_R = D_R/D_A
s = k_{II}/k_I
t = gas-liquid contact time, s
x = $z\sqrt{k_I C_{B0}/D_A}$
y = transformed distance variable defined by Equation (10)
Y_A = C_A/C_{Ai}
Y_B = C_B/C_{B0}
Y_R = C_R/C_{B0}
z = distance from the interface into liquid, cm
ϵ = arbitrary constant in Equation (10)
θ = $k_I C_{B0} t$
ν = stoichiometric coefficient in the reaction of the form, $A + \nu B \rightarrow$ products
Φ = enhancement factor

Subscripts

A = dissolved gas A (carbon dioxide)
B = liquid reactant B (RNH_2)
i = gas-liquid interface
R = intermediate product R ($RNHCOORNH_3$)
0 = initial value
I = first reaction step, Equation (1)
II = second reaction step, Equation (2)

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Heat Transfer in a Packed Bed

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Bhattacharyya and Pei (1975) have developed a model which separates particle-to-particle and fluid-to-particle contributions to heat transfer in a packed bed. The model is then applied to data for the turbulent flow region. Experimental data are reported for a microwave heated system which was used to obtain steady state data with air as the fluid. Additional data are presented by Balakrishnan and Pei (1974) with the conclusion that heat transfer for spherical particles in the fluid-particle mode is represented by

$$j_h = 0.018\,(Ar/Re^2_{pm})^{1/4} \qquad (1)$$

Equation (1) is shown to apply to data in the particle Reynolds number range of 100 to 800. This Reynolds number range is in the turbulent flow region for packed beds, so one would expect that particle-to-particle heat transfer would represent a minor contribution to total heat transfer. Mass transfer in packed beds without heat transfer provides fluid-to-particle data without a particle-to-particle contribution. Thus, Equation (1) should apply as the mass transfer analogue to experimental data for packed bed mass transfer in the turbulent region. McCune and Wilhelm (1949) report isothermal data for 2-napthol in water and Gaffney and Drew (1950) for succinic acid in n-butanol and aqueous acetone. Table 1 compares these data with values calculated from Equation (1).

It is apparent that Equation (1) does not represent these particle-to-fluid data.