successfully correlated by the relationship developed for kinetic control.

3. The reaction between carbon dioxide and diethanolamine is third-order; first-order in carbon dioxide and second order in diethanolamine.

4. A speculative mechanism explaining the observed order was developed.

5. It seems improbable that the reaction

$$CO_2 + 2(HOCH_2CH_2)_2NH \rightleftharpoons \text{product} \qquad (38)$$

is the controlling step in the absorption of carbon dioxide in aqueous solutions.

## ACKNOWLEDGMENT

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## NOTATION

$A$ = gaseous reaction component
$a$ = reaction order with respect to component $P$
$C$ = concentration
$D$ = liquid reaction component
$G$ = moles of diethanolamine
$H$ = Henry's law constant defined by Equation (11)
$\Delta E$ = activation energy
$h$ = liquid head illustrated in Figure 3
$K$, $K'$, $K''$ = equilibrium constants defined by Equation (35)
$k$ = reaction rate constant
$k^{\circ}$ = mass transfer coefficient defined by Equation (10)
$L$ = temperature coefficient for $H$
$m$ = reaction order with respect to component $D$
$N$ = gas flux across gas-liquid interface
$n$ = reaction order with respect to component $A$
$P$ = component $P$
$p$ = gas pressure
$R$ = gas constant
$T$ = absolute temperature
$t$ = temperature
$V$ = volume
$x$ = mole fraction
$Z$ = compressibility
$\Lambda$ = defined by Equation (19)
$\mu$ = viscosity
$\xi$ = defined by Equation (20)
$\Pi_{11}$, $\Pi_{12}$ = defined by Equation (23)

### Subscripts

$A$ = component $A$
$a$ = reaction order of component $P$
$D$ = component $D$
$i$ = interfacial
$l$ = liquid phase
$n$ = moles
$P$ = component $P$
$q$ = pseudo-value
$r, s$ = gas phases of Figure 3
$0$ = initial value

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# Effects of Solute Purity, Temperature, and Surfactants on Solid-Liquid Mass Transfer

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Mass transfer in solid-liquid systems has been investigated widely in a variety of geometries and for a number of solute-solvent combinations. The literature in this area emphasizes the effects of agitation and the physical properties of diffusivity and kinematic viscosity. Data are generally correlated by the dimensionless grouping

$$N_{Sh} = aN^{\alpha}_{Re}\, N^{\beta}_{Sc} \qquad (1)$$

The variables that are used in defining the Sherwood and Reynolds numbers depend on the system geometry. In particular, for mixed vessels of various types, the Sherwood number includes a linear dimension characteristic of the container or impeller size, and the Reynolds number is based on the rotational speed of the mixing device. This method of correlation was motivated at least in part by the great interest in the analogy between momentum, heat, and mass transfer.

In the present work the effects on mass transfer of solute purity, temperature, and the concentration of surface-active agents were studied. No previous work on solute purity could be found in the literature; however, several earlier investigations did study the effect of temperature. The experiments of Johnson and Huang (*21*) included a series at 10°C., 25°C., and 40°C. for the

TABLE 1. SOLUTES USED

| Solute | Specifications from supplier | Lab. analysis for this study[*] |
|---|---|---|
| Certified synthetic grade (Fischer) | Minimum purity: 98%<br>Color: Yellow<br>Melting point: 133-135°C. | $C = 72.98$ wt. %<br>$H = 5.46$ wt. %<br>Basicity = 0.994 |
| Cinnamic acid pure (Givandan-Delawanna) | Minimum purity: 99%<br>Halogen free, very stable<br>Congealing point: minimum 133.0°C. | |
| Once recrystallized cinnamic acid pure (from benzene) | | $C = 73.18$ wt. %<br>$H = 5.44$ wt. %<br>Basicity = 0.996 |

[*] Computations based on the cinnamic acid formula give carbon = 72.95 wt. %, hydrogen = 5.44 wt. %, basicity = 1.0. Basicity is here used to denote g.-moles of potassium hydroxide needed to neutralize a gram formula weight of cinnamic acid.

benzoic acid-water system. Linton and Sherwood (*26*) ran solid dissolution experiments over a range from 5°C. to 25°C. for several solutes, including benzoic and cinnamic acids. In each case the temperature was treated as a source of Schmidt number variation. In a recent study of metal dissolution in liquid mercury, Bennet and Lewis (*2*) compared rates for tin, lead, and zinc at 30°C. and 40°C. (The same authors also studied benzoic acid-aqueous systems.) Their results, which treat temperature as an independent parameter, show a series of essentially parallel lines.

A sizable literature exists on the effects of surfactants in gas-liquid and liquid-liquid systems. Harvey and Smith (*16*) measured resistance due to surface-active agents in the carbon dioxide-water system. For the same components Cullen and Davidson (*6*) found no resistance in the presence of pure agents, but noted resistance when commercial grade surfactants were used. For liquid-liquid systems both positive and negative effects have been reported. Holm and Terjesen (*19*) found a decrease in mass transfer when small concentrations of surfactants were used, but observed the opposite effect at higher concentrations of the same additives. Gordon and Sherwood (*15*) found no appreciable resistance. The work of Boye-Christensen and Terjesen (*3*) as well as that of Garner and Hale (*11*) indicated that increased resistances were caused by surfactant addition.

Although no published results were found on the effects of surfactants on solid dissolution rates, such work has been reported on crystal growth rates. Buckley (*4*) found a number of systems in which growth was seriously modified by additives which did not affect dissolution at concentrations 100 to 1,000 times as large. Yamamoto (*7*) observed that the same impurities which when present in small concentrations improved growth qualities of alkali halides, reversed their effect and destroyed growth when present in large concentrations.

The mass transfer measurements of this investigation were made in a well-mixed flow system under steady state conditions. A disk which carried the solid solute (cinnamic acid) was rotated at constant speed in an enclosing cylindrical housing. This choice of apparatus was intended to provide a constant and predetermined interfacial area. It was not necessary to average concentrations with distance (as in packed beds) or with time (as in batch contactors), nor was surface-area averaging needed (as for suspended solute slurries).

The hydrodynamic character of this geometry has been studied theoretically and experimentally by a number of investigators (*13, 23, 25, 30, 33*). According to references *30* and *33* transition from viscous flow to turbulence occurs in this equipment at about $N_{Re} = 10^5$. The range of Reynolds numbers covered in this investigation was from $10^4$ to $10^6$. In a number of runs at the lower Reynolds numbers a vortex pattern was etched on the surface of the solute during a run. This observation suggests that the boundary layer can be considered turbulent over most of the range tested, since according to Kreith (*23*) and Gregory et al. (*13*), the vortex pattern is generated in the transition region and may be present in the turbulent region (but less prominently). The vortex observation indicates also that a somewhat increased surface area was present at the lower stirring speeds. This effect did not appear to be large and was not included in the results reported.

## EXPERIMENTAL

The mass transfer cell was a transparent plastic cylinder in which a close-fitting aluminum disk was rotated. The details of the cell assembly are shown in Figure 1.

Demineralized water from a constant head tank passed through a rotameter and a copper coil immersed in a temperature control bath and entered the mass transfer cell through the central port of the bottom plate. Effluent from the cell passed through a sampling point and a rotameter before it was discarded. The solute was cast into an annular groove (6 1/16 in. I.D. × 11 1/8 in. O.D.) machined into the underside of the rotating disk. In several runs (where indicated)

TABLE 2. SOLUBILITY DATA OF CINNAMIC ACID IN WATER
Solubility in units of normality

| Temperature, °C. | 99% Cinnamic acid | 99% Cinnamic acid | 98% Recrystallized once | 98% Recrystallized 5 times | 98% Recrystallized 8 times | 99% Recrystallized once |
|---|---|---|---|---|---|---|
| 0.4 | 0.00154 | — | — | — | — | — |
| 15 | 0.00253 | — | — | — | — | 0.002230 |
| 25 | 0.00345 | — | — | — | — | 0.00318 |
| 30 | 0.00421 | — | — | — | — | — |
| 35 | 0.00510 | 0.00474 | 0.00479 | 0.00468 | 0.00470 | 0.00470 |
| 40 | 0.00618 | — | — | — | — | — |
| 45 | 0.00749 | — | — | — | — | 0.00691 |

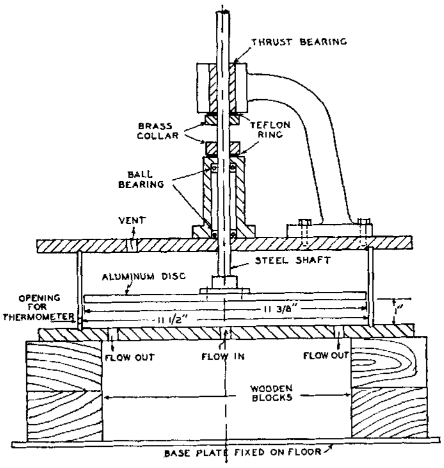

Fig. 1. Scale drawing of mass transfer cell.

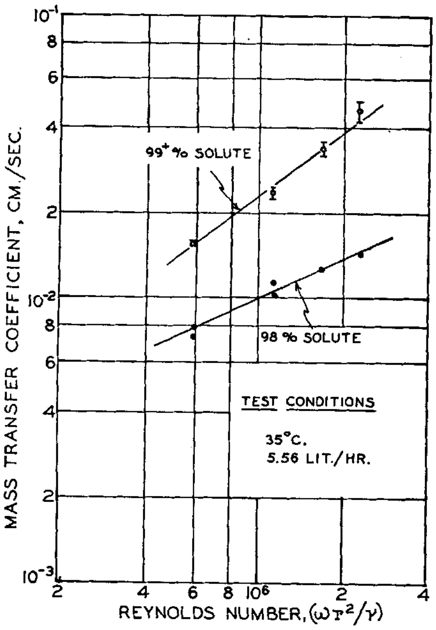

Fig. 2. Effect of solute purity on mass transfer coefficient.

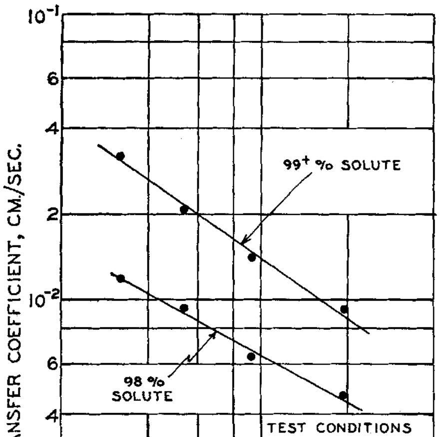

Fig. 3. Effect of solute purity on mass transfer coefficient.

a full 11 1/8-in. diam. disk was used instead of the annulus. Several casting procedures were tried before a smooth fissure-free surface was produced by cooling the melt with a water spray on the opposite side of the aluminum disk. The surface was finished by sandpapering. The disks were rotated by an adjustable constant-speed motor through a belt and pulley. The motor was equipped with a tachometer generator, whose output was fed back to a transformer-rectifier speed control system.

The mass transfer computations of this investigation are based on the well-mixed character of the cell volume. This expectation was confirmed experimentally by following the system response to a step change in inflow composition. As predicted by a material balance, the decay in concentration was exponential with time at flow rates from 6.0 to 50.4 liters/hr. (at 420 rev./min.). Visual observation of an injected dye stream and the lack of an effect due to a baffle above the inlet point indicated also that there was no appreciable short circuiting between inlet and outlet. To insure that all measurements represented steady state conditions, each run was extended until the time-concentration curve leveled off. In some cases this required several hours of running time.

Three grades of cinnamic acid were used in the mass transfer experiments: Fischer synthetic grade, nominally pure cinnamic acid, and the pure cinnamic acid once recrystallized from benzene. These will be referred to as 98%, 99%, and 99+% acids, respectively. Specifications for these materials are listed in Table 1. All solutions used were made with demineralized water. Concentrations were determined by titration with standard alkali using a phenolphthalein indicator.

In a well-mixed transfer cell at steady state the coefficient $K$ can be found from the experimental data by the material balance

$$F(C_B - C_i) = KA(C_S - C_B) \tag{2}$$

When $C_i = 0$

$$K = \frac{F}{A}\frac{C_B}{(C_S - C_B)} \tag{3}$$

The standard deviations for the computed values of $K$ were found by the method given by Scarborough (29). They are shown on the various figures as the lines for the spread at a data point. As expected, the major contribution to the error in $K$ was found to be in the concentration determination.

## PHYSICAL PROPERTIES

Because of the inconsistencies in previously reported data (*8, 14, 20, 22, 27, 28, 32*) the solubilities of cinnamic acid in water and in several aqueous solutions were determined experimentally from both undersaturated and supersaturated solutions. The results for water are shown in Table 2. It may be noted that a single recrystallization of the 99% material produced samples comparable in solubility to those requiring five to eight stages when starting with the less pure 98% acid. This observation led to the use of the once recrystallized pure cinnamic acid for subsequent comparisons.

For purposes of data correlation, values were also needed for solution viscosities and densities and solute diffusivities. Several check comparisons of literature data (*8, 20*) showed that saturated cinnamic acid solutions have viscosities and densities in close agreement with the corresponding values for pure water, and these were subsequently used. Diffusivity data was taken from Shao-Yuen Chang's thesis (*5*). It was assumed that these binary system properties are not altered by low concentrations of surfactants.

## RESULTS

The extensive literature that is available on solid dissolution rates offers a number of comparisons of the correlating constants in Equation (1). The various analogy

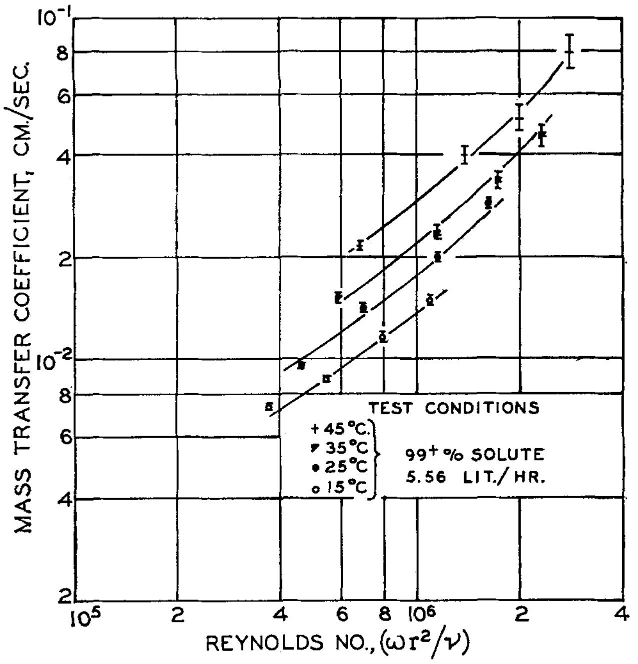

Fig. 4. Effect of temperature on mass transfer coefficient.

viewpoints call especially for similarity in the exponents. Different investigators have worked with solutes cast in the form of spheres (*10, 12, 18*), cylinders (*2, 9, 31*), disks (*23, 24*), rings (*21*), and suspended solid particles (*1, 17, 19*). The correlations of several of these are compared in Table 3, where considerable variation is evident. This result is certainly not wholly unexpected. A similar situation was pointed out for gas-liquid systems by Gordon and Sherwood (*15*), who tabulated exponents from 0.15 to 0.67 for the effect of diffusivity. Evidently, the many different geometries involved in these studies cause various degrees of turbulent and molecular mechanisms to operate.

Comparable results of this investigation indicate that these exponents are also notably dependent on solute purity, even over the narrow contaminant range of only several percent. In Figure 2, for example, where mass transfer coefficient is plotted against Reynolds number, the two lines represent measurements on systems differing only in the solute purity. On the logarithmic coordinates used, the slopes of the lines represent correlating exponents: they are 0.55 for the 98% acid and 0.75 for the $99^+$% acid. A similar effect can be found in Figure 3, where Schmidt number is plotted on the abscissa; the slopes are 0.54 and 0.71 for the two lines.

The explanation for this effect is to be found in the solubility value, $C_S$, that enters the mass transfer coefficient computation in Equation (3). The solubility was found to vary sharply with solute purity (Table 2), and this variation is reflected in $K$, particularly in the range where $(C_S - C_B)$ is a relatively small difference. Indeed, the purity effect could have been predicted from the solubility information and Equation (3). Since it is usual to make a tacit assumption that solubility is fixed by specification of a particular temperature, this discrepancy does not ordinarily show up in mass transfer studies. These results show the importance of solute purity and solubility information. As confirming evidence, it is interesting to find that the variation with solute purity virtually disappears if the results are plotted in terms of bulk concentration, $C_B$, instead of the computed $K$. The purity effect enters primarily through the change in solubility, and it seems likely that the disagreement among the literature references (as in Table 3) is at least in part due to purity variation.

A series of experiments were run to study temperature as an isolated variable. Similar results were obtained regardless of solute purity or disk geometry used. Typical behavior is shown in Figure 4 where temperature is the parameter. The $99^+$% solute was tested at four temperature levels from 15°C. to 45°C. The control was good to ± 0.1°C. The characteristically nearly parallel lines agree with the findings of Bennet and Lewis (*2*). If the procedure used by Johnson and Huang (*21*) and Linton and Sherwood (*26*) is followed, and the observed changes are attributed to concomitant diffusivity, density, and viscosity changes, a Schmidt number correlation is suggested. A graphical test generates straight, parallel lines indicating that the results are consistent with the dimensionless group approach.

Six commercial surfactants were studied individually for their possible effects. These included three nonionic, two anionic, and one cationic agent. The effects were quite distinct.

The nonionic agents had a pronounced concentration-dependent effect which persisted when disk geometry was varied. Typical behavior is shown in Figure 5. With 98% acid, low concentration of nonionic agents caused a decrease in mass transfer but higher concentrations produced an increase. The sharp minimum on the curve cannot be blamed on experimental scatter since the standard deviations in this region of measurement are smaller than the diameter of the circles on the graph. In this figure as in Figure 6, the standard deviation markers were omitted when this was the case. The observation of a minimum is very much like that reported by Holm and Terjesen (*19*) who used an anionic agent in a liquid-liquid transfer process. The minimum in $K$ did not occur in tests with the same surfactant when 99% and $99^+$% acids were used; however, as before the transfer rate did increase at higher surfactant concentrations.

The cationic agent caused an increase in transfer rate for both solute purities tested (Figure 6). The $C_B$ ordinate is shown instead of K because of some uncertainty in the solubility value. Supplementary measurements showed this surfactant to have an appreciable effect on the solubility of cinnamic acid, possibly owing to chemical reaction. Thus the observed effect was at least in part caused by increased solubility. Neither of the two anionic agents tested had any clear effect except to cause the results to scatter somewhat more than in their absence. The results of one set of measurements are shown in Figure 7.

Table 3. Variation of Schmidt Number and Reynolds Number Exponents

| Group with $K$ | Geometry used | Exponent on $N_{Sc}$ | Exponent on $N_{Re}$ | Reference |
|---|---|---|---|---|
| $\frac{Kl}{D}$ | Stirred vessel | 0.500 | 0.710 | *21* |
| $\frac{Kd^*}{D}$ | Rotating cylinder | 0.356 | 0.70 | 9 |
| $\frac{Kd}{D}$ | Slurry suspension | 0.5 | 0.833 | *1* |
| $\frac{Kd}{D}$ | Flow past a single sphere | 0.33 | 0.5 | *12* |

* The equation of Eisenberg, et al. (*9*) has been rearranged to fit this table.

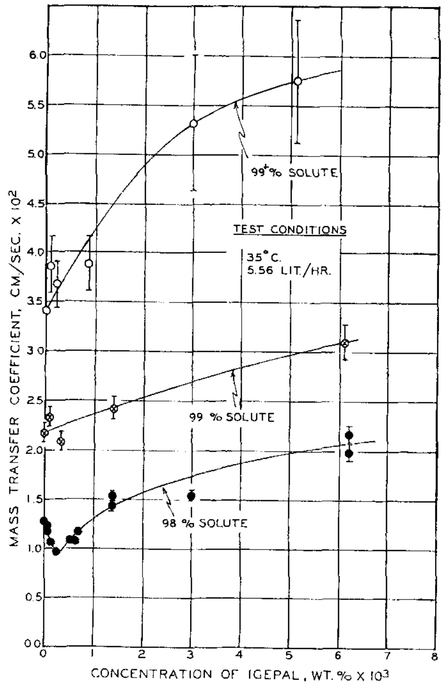

Fig. 5. Effect of nonionic agent on mass transfer.

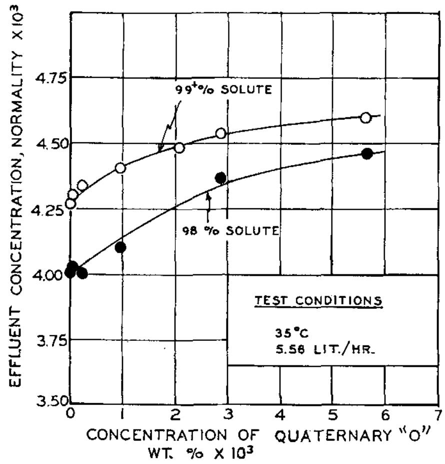

Fig. 6. Effect of cationic agent on mass transfer.

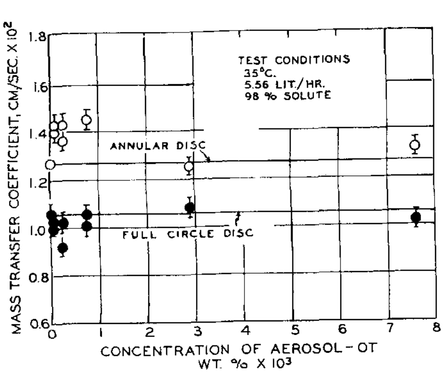

Fig. 7. Effect of anionic agent on mass transfer.

It appears from the experimental minimum referred to above that there are at least two opposing effects of the surfactants. Even in the absence of mass transfer, surfactants are known to exhibit complex behavior on solid surfaces. A more detailed interpretation of the observed behavior is beyond the scope of this investigation. It is interesting to note, however, that the surface phenomena involve at least some effects not included in discussions of the earlier work on fluid-fluid systems. In these reports, it is commonly argued that the surfactant effects detected are hydrodynamic in origin. They are usually explained as owing to increase of interfacial area, damping of internal circulation and surface ripples, or formation of rigid films. Because a solid was used in this study these explanations are not applicable. Evidently, important surface effects can exist over and above those of hydrodynamic origin.

## CONCLUSIONS

The solubility of cinnamic acid in water and the mass transfer coefficients for the process of dissolution are dependent on solute purity. The degree of dependence of $K$ on the dimensionless groups $N_{Sc}$ and $N_{Re}$ changes with solute purity even over the narrow contaminant range of only several percent.

The effects of surfactants on solid-liquid mass transfer depend on the purity of the solute as well as the chemical nature of the surfactant. Nonionic agents at higher concentrations cause increases in transfer rate regardless of solute purity, but at low concentrations the effect is dependent on solute purity (with 98% acid there is a minimum in $K$). Anionic agents have no effect on the mass transfer rate. The cationic agent tested causes an increase in rate, probably owing in large part to chemical reaction with the solute.

## ACKNOWLEDGMENT

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## NOTATION

$A$ = interfacial area
$a$ = constant in Equation (1)
$C$ = concentration
$D$ = molecular diffusivity
$F$ = flow rate
$K$ = mass transfer coefficient
$l$ = characteristic length
$r$ = outside radius
$N_{Re}$ = Reynolds number = $\left(\frac{\omega r^2}{\nu}\right)$
$N_{Sc}$ = Schmidt number = $(\nu/D)$
$N_{Sh}$ = Sherwood number = $\left(\frac{Kl}{D}\right)$
$\alpha$ = constant exponent in Equation (1)
$\beta$ = constant exponent in Equation (1)
$\nu$ = kinematic viscosity
$\omega$ = angular velocity

### Subscripts

$i$ = inlet
$B$ = bulk
$S$ = saturation

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# Performance of Packed Columns VII. The Effect of Holdup on Gas-Phase Mass Transfer Rates

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**To account for the differences in the gas-phase mass transfer coefficients obtained by the use of vaporization and absorption techniques, data were obtained for ring and saddle packings in a 12-in. diam. column employing water vaporization and methanol absorption. The ratio of the vaporization to absorption coefficient, corrected for differences in diffusivity, is found to be directly proportional to the ratio of the total holdup to the operating holdup in confirmation of the proposed model in which the effective interfacial area for each type of operation is proportional to the holdup of the liquid active for that operation.**

Numerous investigations of mass transfer rates in packed columns have resulted in the accumulation of a large amount of data which is of value in estimating the effects of changes in flow rates and physical properties on the performance of packed columns. The methods proposed for the determination of the absolute values of the mass transfer coefficients, however, are of doubtful value because there are large discrepancies between the data published by different investigators. The discrepancies are particularly apparent when gas-phase coefficients are measured by two different methods for the same packing. Comprehensive reviews of the literature presented by Pigford and Colburn in Perry's "Handbook" (2) and by Sherwood and Pigford (5) reveal discrepancies of several hundred percent between gas-phase coefficients obtained by water vaporization and ammonia absorption methods. Explanations in terms of end effects and the possibility of a slow chemical reaction accompanying the solution of ammonia are inadequate to account for such large differences.

In the first paper of this series (*6*) a tentative explanation of these differences was offered in terms of static, $h_s$, and operating, $h_o$, holdups. It was observed that the total liquid holdup, $h_t$, in a packed column was made up of relatively stagnant pockets corresponding to the static holdup and liquid which flows rapidly over the packing surface corresponding to the operating holdup, that is, $h_t = h_o + h_s$. It was proposed that for vaporization work