

# MASS TRANSFER STUDIES

## II. MEASUREMENT OF INTERFACIAL AREAS IN PACKED TOWERS BY GAS ABSORPTION WITH CHEMICAL REACTION

by

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### INTRODUCTION

In connection with a study of the distribution of surface areas of the liquid in a packed column and which was previously reported (6), it was necessary to determine the interfacial area under the various conditions employed. As is well known, accurate knowledge of the interfacial area for mass transfer in packed towers has long been lacking. This difficulty in estimating the area of contact between gas and liquid flowing in a packed column necessitates the use, in practice, of the product,  $k_L a$ , of the transfer coefficient  $k_L$  and  $a$ , the effective area per unit volume of packing.

Three kinds of area have been distinguished in a packed tower: the geometric total area of the packing, the 'wetted' area (described as the fraction of the packing surface wetted by liquid), and the 'effective area.' The latter is usually less than the wetted area and is probably equivalent to those regions of moving liquid which are most effective for mass transfer.

## STANDARD METHODS

Separation of volumetric mass-transfer coefficients, such as  $k_g a$  and  $k_L a$ , into their components  $k_g$  or  $k_L$  and  $a$ , has been attempted by several workers (8,11,12 and 13). The methods employed by Shulman and de Gouff (8) and Weisman and Bonilla (11) were equivalent to using  $k_g$ , obtained by vapourisation of naphthalene or water from special Raschig rings of known transfer area, and various sources of  $k_g a$  data to evaluate  $a$ , the effective interfacial area. As no liquid was used to irrigate the packing in the vapourisation experiments, no attempt was made to take into account the effect on  $k_g$  of liquid in the packing under practical operating conditions.

It may be expected that some discrepancy will arise from the difference in mechanism between evaporation and absorption. If a packed column is used for vapourisation, the effective interfacial area consists of the surface area of the moving liquid as well as of liquid in the semi-stagnant pockets. If the column is used for absorption the semi-stagnant pockets tend to become saturated in a short time, their surface areas become ineffective, and so the effective interfacial area is substantially that of the moving liquid alone.

The fluid mechanics of the gas phase may be radically altered in the transition from dry to irrigated packing. It was implicitly assumed that the nature of the gas flow through dry packing is the same as through wet packing. This may not be a reasonable assumption since an appreciable portion of the void space may be occupied by liquid, leaving a much smaller free space for gas flow. Thus, for example, the liquid hold-up in 1/2-inch Raschig rings is approximately equivalent to 9.5 percent of the free volume available for gas flow when the packing is irrigated by liquid at 1100 lb/hr. ft<sup>2</sup>. Much of this liquid exists in the packing as pockets of almost stagnant liquid. It might be even greater at the higher liquid flow-rates employed in industrial practice.

Weisman and Bonilla (loc. cit.) divided height-of-transfer-unit values for the evaporation of water into air on the usual non-porous packings by those from porous, totally wetted, packing of the same dimensions and under the same conditions. Yoshida and Koyanagi (12) determined the effective interfacial area for liquid phase mass transfer by comparing rates of absorption in a packed column with similar data on a bead column.



Such analyses appear to be dependent on the assumption that the average values of  $k_g$  or  $k_L$  in the reference apparatus are the same as on the effective surface in irrigated packings. Areas obtained by these means, although widely scattered, appear to be in approximate agreement (13).

They would lead one to expect a figure of about 10 percent or less for gas absorption on 1/2-inch Raschig rings with an irrigation rate of 1100 lb/hr. ft.<sup>2</sup>, one of the flow-rates employed in the present work.

## PRESENT METHOD

The method used to separate  $k_L$  from a overcomes the limitations of the methods described hitherto. For an irreversible first-order or pseudo first-order chemical reaction, the rate of absorption,  $F(t)$ , per unit area of surface after exposure of time  $t$  is given by (2):

$$F(t) = C^* \sqrt{Dk} \left[ \operatorname{erf} \sqrt{kt} + \frac{e^{-kt}}{\sqrt{\pi kt}} \right] \quad (1)$$

where  $C^*$  is the saturated concentration of the solute at the surface,

$k$  is the velocity constant of the reaction between solute and medium and

$D$  is the diffusion coefficient of the solute in the medium.

When  $kt$  is sufficiently large,  $\operatorname{erf} \sqrt{kt} \approx 1$ ,  $e^{-kt} \approx 0$ , and equation (1) can be approximated by:

$$F(t) \approx C^* \sqrt{Dk} \quad (2)$$

i.e.  $F(t)$  is independent of  $t$ . Danckwerts (2) has shown that the error in equation (2) is less than 2 percent if  $kt > 4$ . For a very fast irreversible first-order reaction, therefore, all parts of the wetted surface absorb at the same rate and this provides a means of obtaining the interfacial area.

If  $C_0$  is the concentration of unreacted dissolved gas in the bulk of the liquid and

$\Theta(t)$  is the surface-age distribution function,  
 $k_L(C^* - C_0) = \int_0^\infty F(t) \Theta(t) dt$   
 at high  $kt$ ,  $k_L C^* \approx C^* \sqrt{Dk} \int_0^\infty \Theta(t) dt$  if  $C_0$  is assumed  
 equal to zero.

$$\text{i.e. } k_L \approx \sqrt{Dk} \quad (3)$$

Multiplying both sides of equation (3) by  $a$ , which is defined as the effective interfacial area per unit volume of packing, we have

$$k_L a \approx a \sqrt{Dk}$$

i.e.  $a \rightarrow \left( \frac{k_L a}{\sqrt{Dk}} \right)$  at high values of  $kt$ .

The effective wetted area per unit volume,  $a$ , can therefore be deduced from the slope of the plot of the experimental values of the volumetric mass-transfer coefficient,  $k_L a$ , against  $\sqrt{Dk}$  as  $k \rightarrow \infty$ .

## DESCRIPTION OF APPARATUS AND EXPERIMENTAL PROCEDURE

The column consisted of a 4-inch i.d. Pyrex tube, 12 inches long, randomly packed with 1/2-inch ceramic Raschig rings to a depth of just over 10 inches. The liquid was distributed evenly over the top of the packing through 35 nozzles. In so far as was possible, the conditions of operation of the packed column were standardised. All resistance in the gas phase was eliminated by absorbing from pure gas saturated with water vapour at 25.0°C while hydrodynamic factors were held constant by using a constant liquid flow-rate and a fixed packing arrangement (with a density of 10,500 rings per cubic foot). The viscosities of all solutions were kept constant and the range of densities confined to narrow limits. The arrangement of the apparatus is shown diagrammatically in Figure 1.

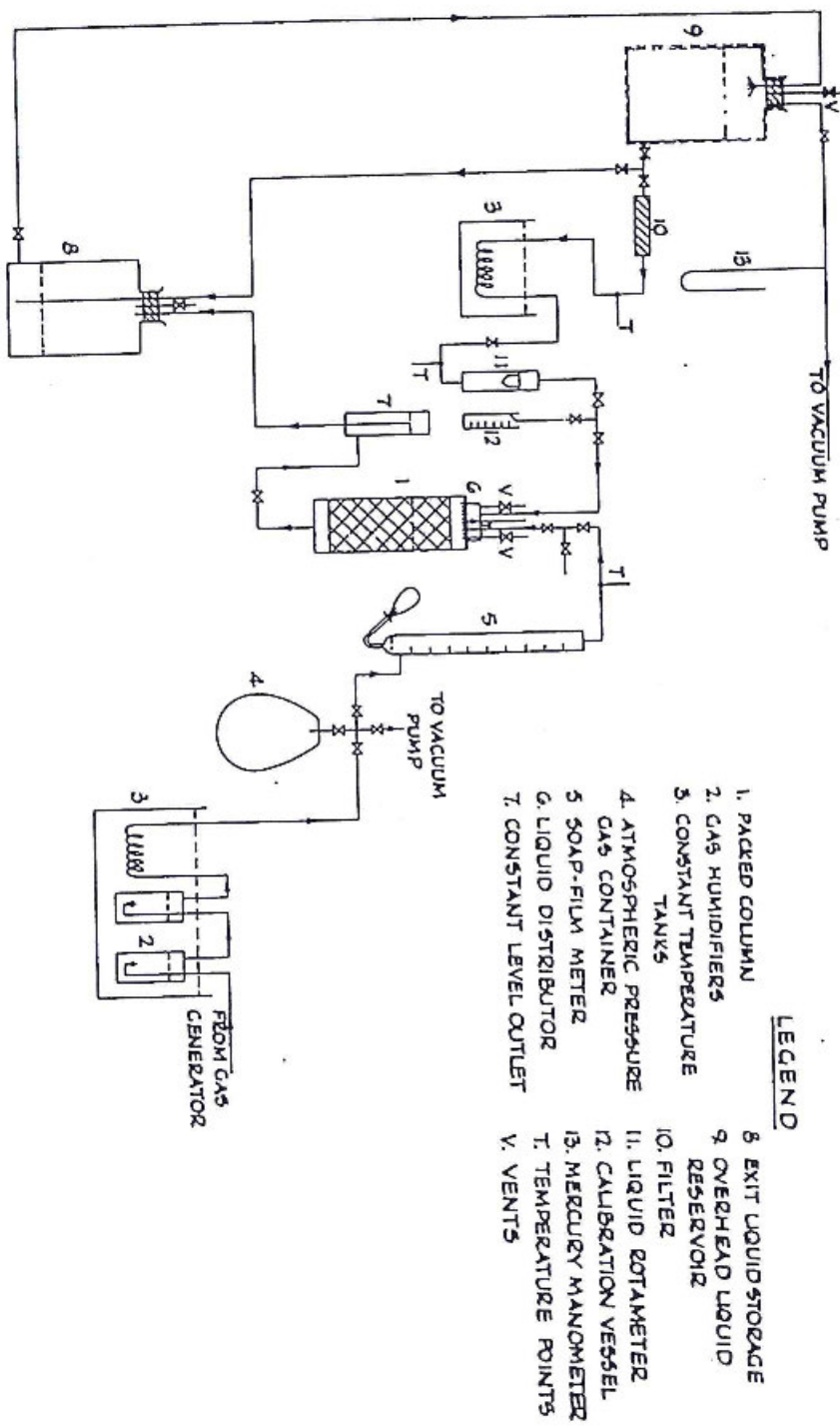


FIG. 1 FLOW DIAGRAM OF APPARATUS FOR ABSORPTION OF CARBON DIOXIDE



The column was operated by the 'differential method' i.e. the lower part was filled with liquid and the effective height of the packing could be varied by adjusting the position of a constant-level outlet. At any given position of the free liquid surface, therefore, the rate measured will be that due to mass transfer in the spray zone above the packing, in the packing actually exposed, and in the liquid surface itself. A measurement at some other position will give the rate due to the spray zone, the new volume of exposed packing and the liquid surface in its new position. The difference between the two measurements should give directly the absorption rate due to the section of packing between the two levels assuming that absorption into the free liquid surface may be neglected or that the surface is always equivalent to a constant depth of packing. If the process is repeated in a sufficient number of steps a smooth curve of total absorption-rate,  $M$ , against exposed depth of packing,  $h$ , can be derived.

If the average rate of absorption per unit wetted area at a given height in the column is  $R$ , then

$$\frac{dM}{dh} = AaR$$

where  $A$  is the cross-sectional area of the column and  $a$  is the wetted surface-area per unit volume.  $(aR)$  can therefore be found for a specific level in the column from the slope of the curve of  $M$  against  $h$ . It was found that the concentration of unreacted absorbed solute in the bulk of the liquid was negligible even in the slowest-reacting solutions and  $(aR)$  was constant over the whole range of column heights employed.

The results may be expressed in terms of the liquid-film mass-transfer coefficient,  $k_L a$ , defined by the equation:

$$Ra = k_L a C^*$$

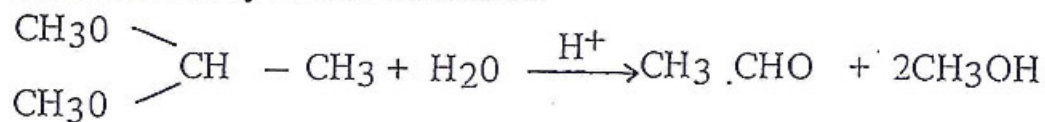
This can be re-written for the packed column as

$$dM = K_L a C^* A dh$$

i.e.  $k_L a = \frac{1}{AC^*} \frac{dM}{dh}$

The mass transfer coefficients were therefore obtained directly from the slope of the straight lines of  $M$  against  $h$ , using the method of least squares.

Two irreversible first-order reacting systems were employed in the experimental work. The first of these was the hydrolysis of dimethyl acetal (1,1-dimethoxyethane) by water into acetaldehyde and methanol:

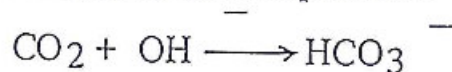


This reaction has been studied by Holdcroft (3), who presented data for  $C\sqrt{D}$  and the velocity constant  $k$ . Some independent measurements of the rate constant were also available (1,5). In a large excess of water the reaction is essentially first-order and the rate is given by:

$$-\frac{d}{dt} [\text{C}_4\text{H}_{10}\text{O}_2] = k_2 [\text{H}^+] [\text{C}_4\text{H}_{10}\text{O}_2] = k_1 [\text{C}_4\text{H}_{10}\text{O}_2]$$

where  $k_2$  is the second and  $k_1$  the first order velocity constant. The rate of reaction is proportional to the hydrogen ion concentration and is also increased by the addition of inorganic salts such as sodium chloride. It is therefore possible to obtain some variation in the velocity of the reaction by altering the concentrations of, say, hydrochloric acid and sodium chloride in an aqueous solution.

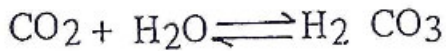
The second system used was the absorption of carbon dioxide into sodium carbonate-sodium bicarbonate buffer solutions with added arsenious oxide. In the absence of a catalyst the predominating reaction is an effectively irreversible second-order one of moderate speed between carbon dioxide and the hydroxyl ions present:



Because of the buffering effect the hydroxyl ion concentration remains approximately constant as absorption proceeds so that this reaction may be regarded as being pseudo-first order.



The slower alternative reaction between carbon dioxide and water molecules:



is, however, catalysed by the arsenite ions formed in an alkaline solution of arsenious oxide. The reaction of carbon dioxide and hence the overall absorption rate is therefore accelerated. Roberts (7) has determined the rate constants of this reaction for various concentrations of arsenious oxide. Figures 2 and 3 are plots of the absorption rate against column height for typical dimethyl acetal and  $\text{CO}_2$  - catalysed buffer solution runs.

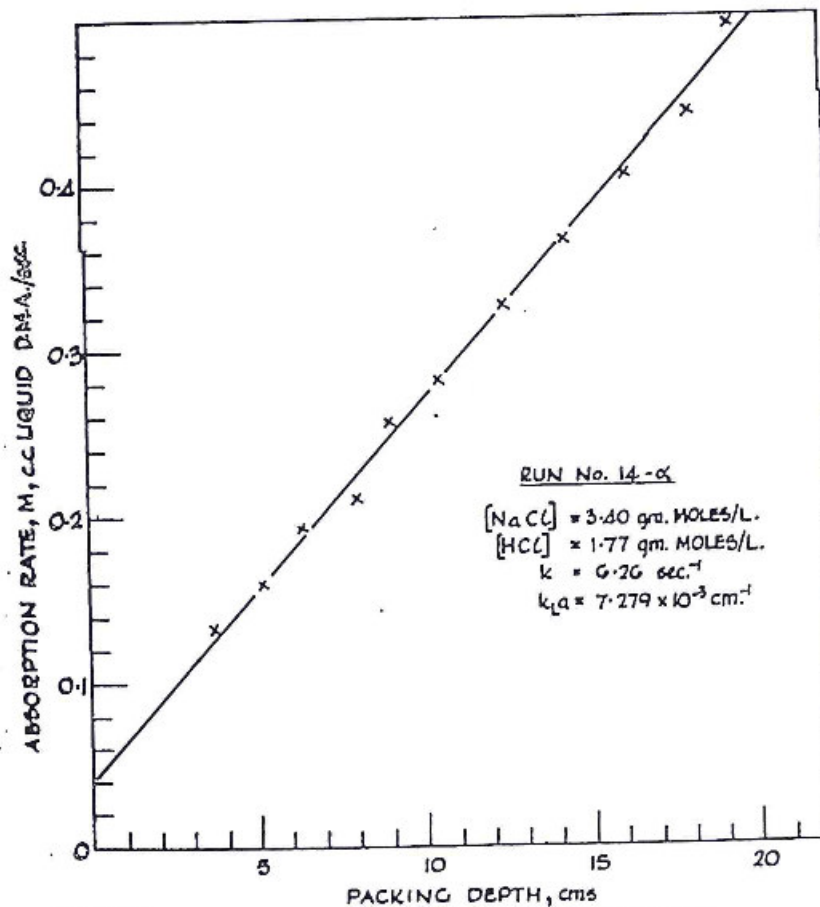


FIG. 2 TYPICAL PACKED COLUMN RESULTS FOR THE ABSORPTION OF 1,1-DIMETHOXYETHANE INTO ACID SOLUTION



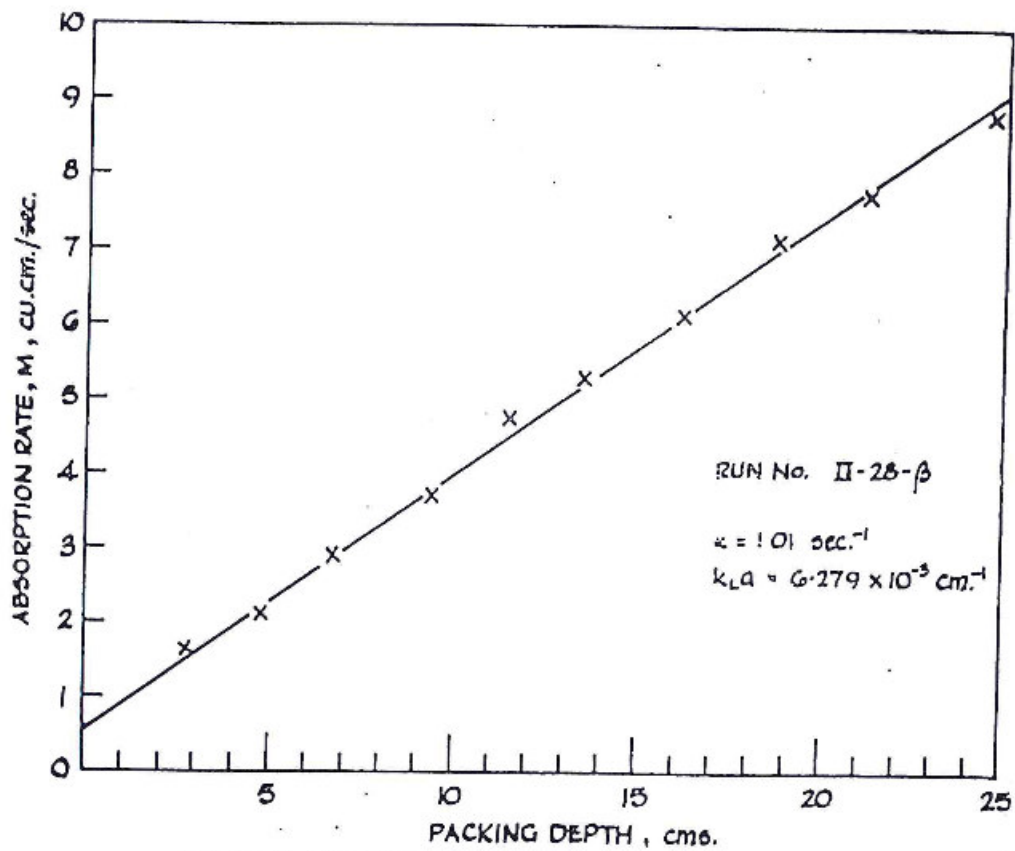


FIG. 3 TYPICAL PACKED COLUMN RESULTS FOR THE ABSORPTION  
OF CARBON DIOXIDE INTO SPIKED BUFFER SOLUTION AT  
25.0°C

Determinations of the mass-transfer coefficient were made at a flow-rate of 11.8 cu. cm./sec. for the dimethyl acetal system over the entire practical range of reaction velocities, viz. 0 to 7 sec. <sup>-1</sup>. They were also carried out, in turn, for five different flow-rates, viz. 5.9, 11.8, 17.7, 23.6 and 29.5 cu. cm. per sec. for the catalysed buffer system. In these runs the reaction velocity constant was varied from 0.55 to 30 sec. <sup>-1</sup>. The data obtained by Kennedy (4) on the absorption of carbon dioxide by uncatalysed sodium carbonate – sodium bicarbonate buffer solutions were also used.

## RESULTS

An example of a plot of  $k_L a$  against  $\sqrt{Dk}$  (for the absorption of carbon dioxide by sodium carbonate – sodium bicarbonate buffer solutions catalysed by arsenious oxide and at a flow rate of 11.8 cu. cm./sec.) is shown in Figure 4. The asymptote of this curve passes through the origin and the slope yields a value of 1.00 cm. <sup>-1</sup> for the effective wetted area per unit volume. Similar plots were also made for four other flow

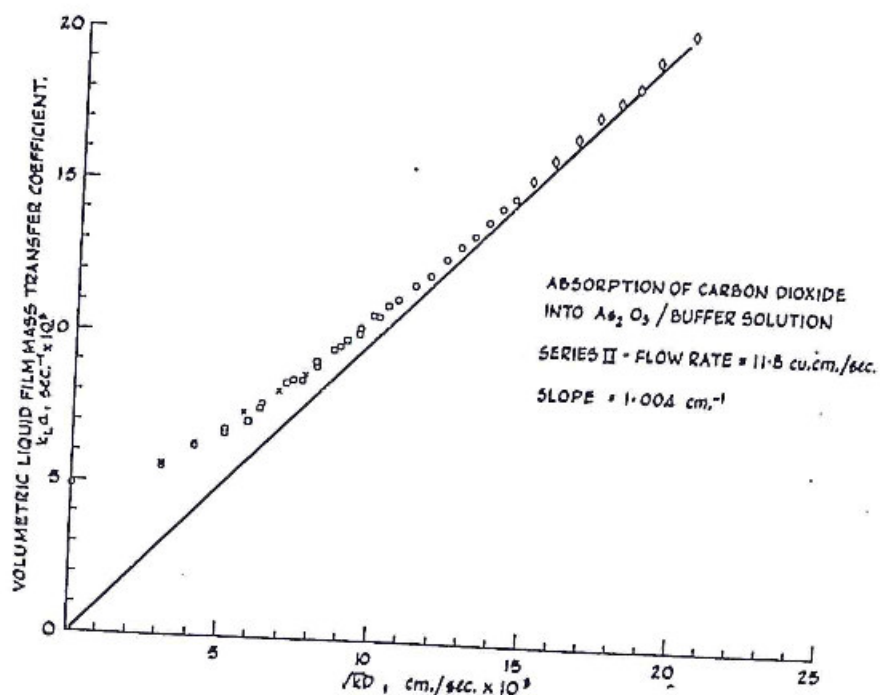


FIGURE 4. DETERMINATION OF INTERFACIAL AREA BY LIMITING SLOPE - VARIATION OF VOLUMETRIC LIQUID FILM MASS TRANSFER COEFFICIENT WITH  $\sqrt{Dk}$



rates viz. 5.9, 17.7, 23.6 and 29.5 cu. cm./sec. as well as for the two other reacting systems — the absorption of carbon dioxide by uncatalysed sodium carbonate – sodium bicarbonate buffer solutions (using the data of Kennedy (4)) and the hydrolysis of 1,1-dimethoxyethane in aqueous solutions. The values of  $a$  obtained are shown in the following table:-

Absorption System	Flow-rate, cu. cm./sec.	Effective wetted area per unit packed volume, $a$ , cm. <sup>-1</sup>	Percentage of packing surface effective
1,1-Dimethoxyethane into aqueous solutions	11.8	1.06	28.1
Carbon dioxide into uncatalysed buffer solutions (Data of Kennedy)	11.8	1.12	29.8
Carbon dioxide into buffer solutions	5.9 11.8	0.81 1.00	21.6 26.6
catalysed by arsenious oxide	17.7 23.6 29.5	1.23 1.34 1.52	32.6 35.5 40.2

These values are considerably higher than those reported by the previous investigators and it would appear that their methods measure something quite different. More recently Vassilatos et al (10) have calculated interfacial areas from data on the absorption of carbon dioxide into ammonia solutions with the aid of the penetration theory. Their value (interpolated) for a liquid flow-rate of 1100 lb/hr. ft.<sup>2</sup> (11.8 cu. cm./sec.) was equivalent to 28 percent of the total packing surface. While this is comparable with the results of the present work, their interfacial areas showed little tendency to increase as the flow-rates were increased. Examination of their data shows that  $K_g$ , the overall gas-phase mass-transfer coefficient, was not independent of liquid flow-rate at high reaction velocities, as might be expected.

No great weight was attached to the values derived from the data on the 1,1-dimethoxyethane and carbon dioxide – uncatalsed buffer systems since the range of reaction velocities obtainable was severely limited and the absorption results show a certain amount of scatter. The approximate agreement with the value obtained at the same flow-rate for the arsenious oxide-buffer system is, however, significant.

Interfacial areas obtained for the arsenious oxide catalysed buffer system at different flow-rates are plotted in Figure 5. The effective interfacial area increases quite rapidly with increasing flow-rate as a greater portion of the packing surface becomes covered by moving liquid. It probably tends to the value of the 'wetted' area at the highest flow-rates.

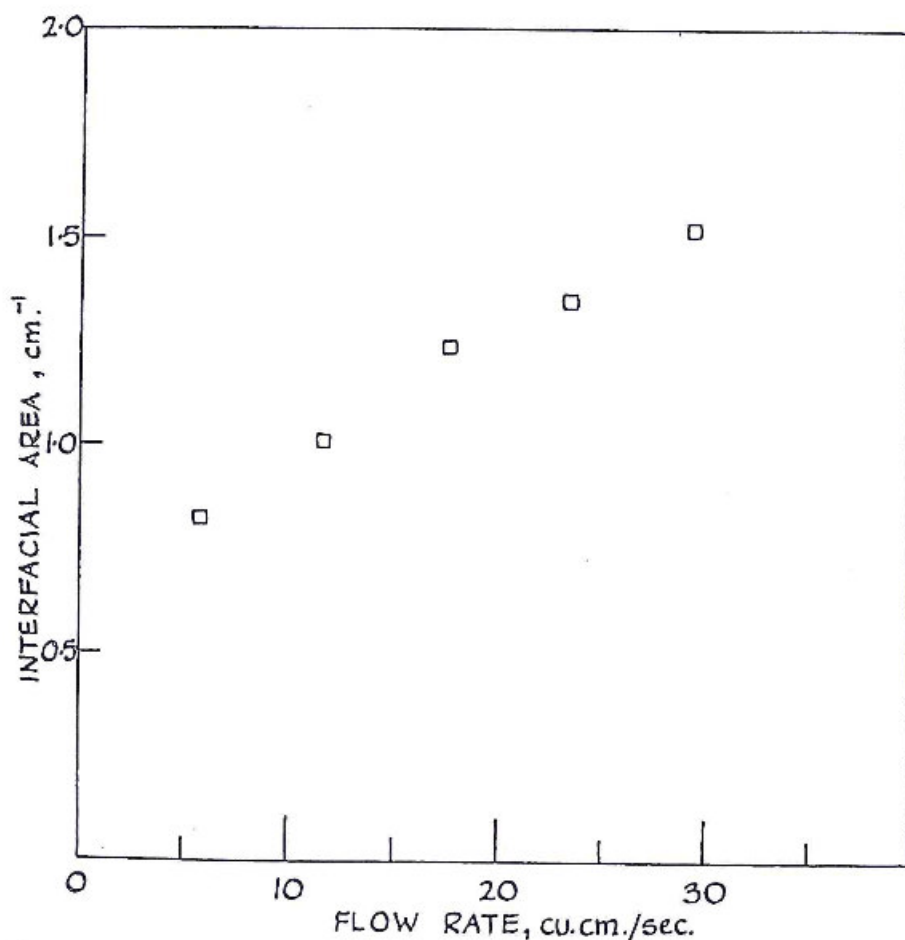


FIGURE 5 VARIATION OF INTERFACIAL AREAS WITH LIQUID FLOW RATE



## SYMBOLS USED

a	Effective interfacial area per unit packed volume.	$\text{cm}^{-1}$
A	Cross-sectional area of packed column	$\text{cm}^2$
C*	Equilibrium concentration of solute in liquid phase	$\text{gm.mole/cm}^3$
C <sub>0</sub>	Concentration of unreacted dissolved gas in bulk of liquid	$\text{gm.mole/cm}^3$
D	Diffusivity of solute gas in the liquid phase	$\text{cm}^2/\text{sec.}$
F(t)	Rate of absorption per unit area after exposure for time t	$\text{gm.mole/cm}^3\text{sec.}$
h	Height of exposed packing in column	cm.
k, k <sub>1</sub>	First-order reaction velocity constant	$\text{sec.}^{-1}$
k <sub>2</sub>	Second-order reaction velocity constant	$1/\text{gm.mole/sec.}$
k <sub>g</sub>	Gas-phase mass-transfer coefficient	$\text{cm/sec.}$
k <sub>g</sub> <sup>a</sup>	Volumetric gas-phase mass-transfer coefficient	$\text{sec.}^{-1}$
k <sub>L</sub>	Liquid-film mass-transfer coefficient	$\text{cm./sec.}$
k <sub>L</sub> <sup>a</sup>	Volumetric liquid-film mass-transfer coefficient	$\text{sec.}^{-1}$
K <sub>g</sub>	Overall gas-phase mass-transfer coefficient	$\text{cm./sec.}$
M	Total rate of absorption in height h of packed column	$\text{cm}^3/\text{sec.}$
R	Average rate of absorption per unit area of wetted surface in packing	$\text{cm}^3/\text{sec.}$
t	Time	sec.
Θ(t)	Surface-age distribution function	$\text{sec.}^{-1}$

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