LIQUID PHASE MASS TRANSFER IN PACKED BED REACTOR WITH COCURRENT GAS-LIQUID DOWNFLOW^{*}

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Volumetric absorption coefficient $(ka)_{lg}$, specific interfacial area a_{lg} and mass transfer coefficient k_{lg} were measured for two-phase cocurrent flow of O₂—water and CO₂—NaOH systems in a column packed with glass spheres of 3 different sizes (2.59–12.2 mm). Values of $(ka)_{lg}$ observed were so high as to be that can be hardly attainable in conventional gas-liquid contactors. This is due to large a_{lg} of small bubbles dispersed in liquid where a_{lg} very often exceeds the geometrical surface area of packing. Values of k_{lg} range from 2 to 8×10^{-4} m/sec, which are comparable to that of circulating bubbles in the usual systems. The effect of superficial gas velocity on $(ka)_{lg}$ and a_{lg} is much greater than that in a countercurrent packed column, while the effect of liquid velocity is approximately same. A liquid-phase energy loss E_l per unit volume of liquid contained in a bed was newly defined as a measure of microscopic flow intensity and was used for discussion and correlation of mass transfer properties. It was found that the bubble diameter is proportional to $E_l^{-2/5}$.

1. Introduction

Advantages of packed column reactors with cocurrent gas-liquid flow have been pointed out by many investigators^{4,5,7,10,14,16}. This type of reactor may be employed in a) gas-liquid reaction with inert packing, b) gas-liquid reaction catalyzed by packing solid⁷, and c) solid-catalized gas reaction in inert liquid phase introduced for temperature control¹⁴. In any case, the reactant gas must first be dissolved in liquid for the reaction to proceed. Thus, gas-liquid mass transfer is one of the most fundamental steps in determining the overall reaction rate as well as the intrinsic chemical kinetics and liquid-particle (catalyst) mass transfer, if any.

Volumetric absorption coefficient $(ka)_{lg}$, specific gas-liquid interfacial area a_{lg} and mass transfer coefficient k_{lg} have been used for characterizing the mass transfer performance of various gas-liquid contactors. However, surprisingly little is known about these factors for coccurrently contacting packed columns. No prediction correlations are available except those of Reiss¹⁰ for $(ka)_{lg}$ and of Gianetto, Baldi and Specchiá⁵ for a_{lg} . As for k_{lg} , not even the order of magnitude has been reported yet. Thus, much more investigation is desired to understand the mass transfer behaviour.

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From this point of view, the purpose of the present article is to present new data and correlations of gas-liquid mass transfer properties and to discuss the results in the light of the fluid flow behaviour reported previously^{12,13)}.

2. Experiments

A schematic diagram of the experimental apparatus is shown in **Fig. 1**. Since no appreciable effect of column diameter was found in the fluid flow characteristics^{12,13}, one column of 65.8 mm^{ϕ} I.D. and 0.25 m long was used. The column height was made rather short to prevent the attainment of equilibrium between phases in the exit stream. The range of variables investigated is summarized in **Table 1**. The details of the distributor head and void fraction of bed were reported previously¹².



Fig. 1 Schematic diagram of apparatus for mass transfer measurements

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Table 1 Range of variables investigated										
			Column		Packing		Superficial velocity			
Measurement	Solute	Liquid	Dia. $D \times 10^3$ [m]	Height h [m]	Dia. $d \times 10^3$ [m]	Void ε []	$Gas U_g [m/sec]$	Liquid U_l [m/sec]	Temp. <i>t</i> [°C]	
Volumetric absorption coefficient	O_2	H ₂ O	65.8	0.25	2.59 5.61 8.01 12.2	0.370 0.391 0.408 0.438	0.05-1.0	0.01-0.2	~15	
Specific interfacial area	$\rm CO_2$	0.1∼1 N NaOH	65.8	0.25	2.59 5.61 12.2	0.370 0.391 0.438	0.01-1.0	0.01-0.1	30	



Fig. 2 Typical examples of results for volumetric absorption coefficient

Volumetric absorption coefficient $(ka)_{lg}$ was determined through desorption mass transfer of dissolved oxygen from the presaturated water into the nitrogen stream. An oxygen analyzer (Toshiba-Beckman Co., Model 777) was immersed in the entrance stream to detect the inlet concentration C_l° . Gas-liquid dispersion issuing from the column was separated in the bottom and part of the liquid was led to a liquid line, where another oxygen analyzer was set to detect the outlet concentration C_{l1} . Since unfortunately no information is available on the longitudinal dispersion, the present data were analyzed tentatively in terms of plug flow and volumetric absorption coefficient $(ka)_{lg}$ was calculated from the equation

$$(ka)_{lg} = (U_l/h) \ln (C_l^{\circ}/C_{l1})$$
(1)

Oxygen partial pressure in the bulk gas phase was practically zero due to the low solubility. The gasphase resistance to mass transfer was neglected. Desorption was preferred to absorption since the latter case was complicated by the longitudinal variation in gas-phase concentration of oxygen due to pressure drop through the bed.

Specific interfacial area a_{lg} was measured using a diffusion-limited chemical absorption of carbon dioxide into aqueous sodium hydroxide. Carbon dioxide was diluted with nitrogen so that the total flow rate



Fig. 3 Correlation of volumetric absorption coefficient in terms of operating parameters

of CO₂ and N₂ did not change more than 30 % between entrance and exit. Feed gas and liquid were sampled from the entrance streams. Outlet liquid was sampled from the outlet liquid line while outlet gas sample was taken after the removal of entrainment drops. Gas (CO₂) and liquid (NaOH), respectively, were analyzed by gas chromatography and by Warder's titration. The rate of gas absorption N was determined from the difference of the concentrations of both NaOH in solution and CO₂ in bulk gas between the entrance and exit streams, the material balance being satisfactorily checked.

Under the condition of a fast pseudo first-order reaction the absorption rate per unit volume of bed N is given by

$$N = a_{lg} \lambda \bar{C}_g \sqrt{\mathscr{D} k_r \bar{C}_b} \tag{2}$$

To evaluate a_{lg} , arithmetic and logarithmic mean concentrations, respectively, between entrance and exit were used for \bar{C}_b and \bar{C}_g . The intrinsic reaction rate constant k_r , the diffusion coefficient \mathscr{D} and solubility λ , respectively, were estimated for the above determined mean concentration according to Yoshida and Miura²²⁾, Wilke¹⁹⁾, and van Krevelen and Hofftijzer¹⁷⁾.

The mass transfer coefficient k_{lg} for oxygen was determined by dividing $(ka)_{lg}$ by a_{lg} obtained above.



The requirements for a diffusion-limited first-order reaction were examined using the resultant k_{lg} .

3. Volumetric Absorption Coefficient

Some experimental results of the volumetric absorption coefficient $(ka)_{lg}$ are shown in **Fig. 2** together with available data obtained for the corresponding systems in countercurrent flow^{15,20)}. The values of $(ka)_{lg}$ at low gas flow rate fall on a line extrapolated from countercurrent data. Increase in gas flow rate increases these values up to ten times their values at low gas flow rate.

This strong dependence on gas flow rate is quite a different behaviour from that in countercurrent flow, where $(ka)_{lg}$ is known to be independent of gas flow rate lower than the loading point. At high flow rate of gas and liquid, some values of $(ka)_{lg}$ exceed 1 sec⁻¹, which can hardly be attained in other types of gas-liquid contactors such as an agitated vessel or a bubble column.

Most of the data were taken under the pulse or dispersed bubble flow regime. At liquid velocity lower than 1 cm/sec the flow approached gas continuous flow, in which it has been reported that $(ka)_{ig}$ decreases rapidly, probably due to the poor distribution of liquid⁵. Thus pulse and dispersed bubble flow, containing gas-liquid dispersion, seem preferable from a mass-transfer point of view.

The volumetric absorption coefficient $(ka)_{lg}$ is proportional to $U_l^{0.8}$, as shown in Fig. 2, and is observed to decrease with increasing packing diameter d as shown in **Fig. 3**. Thus the present data are correlated by

$$(ka)_{lg} = 1.0 \, d^{-0.5} U_l^{0.8} U_g^{0.8} \tag{3}$$

in terms of flow rates and packing size.

Mass transfer properties in two-phase dispersion have sometimes been related to energy dissipation, in which various geometrical factors may be excluded from the resulting correlations. For example, such treatment was applied to agitated gas-liquid Fig. 4 Correlation of volumetric absorption coefficient in terms of liquid-phase energy loss

contactors by Cooper, Fernstrom and Miller³) and Yoshida, Ikeda, Imagawa and Miura²¹), to two-phase tubular contactors by Gregory and Scott⁶) and to twophase flow in packed beds by Reiss¹⁰).

When gas flows with a high velocity, as in twophase flow in a packed bed, a considerable amount of energy dissipation occurs in the gas phase as well as in the liquid phase. However, the energy dissipation in the liquid phase is of primary importance for the present system, the liquid-phase resistance to mass transfer being controlling. Thus, the liquidphase energy loss per unit volume of liquid contained in the bed is defined in this work as

$$E_l = (\Delta P_{lg} / \Delta h) U_l / \varepsilon R_l \tag{4}$$

Strictly speaking, the above-defined E_t is the power given to liquid by an external machine (i.e. pump) and is not always equal to the energy dissipated in liquid phase when energy is exchanged between gas and liquid phases. However, it may be a good measure to characterize the latter quantity.

When the energy loss E_l and the interstitial gas velocity U_g/ε are chosen as two correlating parameters, the correlation shown in **Fig. 4** is obtained. It is explicitly independent of packing size although the packing diameter affects $(ka)_{lg}$ by changing the energy loss E_l . The best-fit line to the present data is given by

$$(ka)_{lg}/\varepsilon = 0.163 (U_g/\varepsilon)^{0.6} E_l^{0.31}$$
(5)

for the dispersed bubble flow regime and

$$(ka)_{lg}/\varepsilon = 0.135(U_g/\varepsilon)^{0.6}E_l^{0.31}$$
 (6)

for the pulse flow regime. ΔP_{lg} and R_l necessary for calculation of E_l are evaluated by previously reported correlations¹².

$$\phi_{l} = \sqrt{\Delta P_{lg} / \Delta P_{l}} = 1.30 + 1.85 \chi^{-0.85}$$
(7)

$$R_l = 0.04 \, a_s^{1/3} \chi^{0.22} \tag{8}$$

The value of $(ka)_{lg}$ in pulse flow is a little lower than that in dispersed bubble flow since the bubble dispersion does not occupy the whole bed, unlike the case in the latter regime.



Fig. 5 Correlation of specific interfacial area in terms of operating parameters



Fig. 6 Bubble diameter calculated from gas holdup and specific interfacial area

Reiss¹⁰⁾ has proposed a correlation

$$(ka)_{lg} = 0.0542 (U_l \varDelta P_{lg} / \varDelta h)$$
(9)

for spheres and rings, which is independent of gas flow rate as well as of packing size. The present data included in his reported range of gas velocity $(U_l > 0.5 \text{ m/sec})$ are consistent with the Reiss¹⁰ equation. However, to cover the data at lower gas velocity, the gas velocity must be included in the correlation.

4. Specific Interfacial Area

The specific interfacial area a_{lg} was found to be proportional to the square root of liquid flow rate U_l . Its dependence on packing size and gas flow rate are shown in **Fig. 5**. The values of a_{lg} decrease with packing diameter to 0.8 power and increase with gas flow rate to 0.6 power till they tend to flatten at high gas flow rate as shown in Fig. 5. An empirical equation is sought as

$$a_{lg} = 175 \ d^{-0.8} U_l^{0.5} U_g^{0.6}, \quad U_g < 0.6 \ \text{m/sec}$$
(10)

The gas-liquid interfacial area very often exceeds the geometrical surface area of packings, indicating a large contribution of small bubbles in pulse flow and dispersed bubble flow regimes.

Some available results are also reproduced in the figure for comparison. Data of Voyer and Miller¹⁸⁾

and Gianetto, Baldi and Specchia⁵⁾ were read directly from their figures. Those of Dodds, Stutzman, Sollami and McCarter⁴⁾ were evaluated from the tabulated absorption rates of CO₂ into 2N–NaOH solution according to Eq. (2) by the present authors. The density of gas, if necesssary, was taken as that of air under atmospheric pressure. The agreement between the present data and these results seems reasonable in spite of the different geometries and sizes of packing. Results of Dodds *et al.*⁴⁾ and Gianetto *et al.*⁵⁾ show the same dependence on gas flow rate as do the present data, but lower dependence on liquid flow rate, i.e. 0.3–0.4 power instead of 0.5.

The mechanism of the dispersion of bubbles and drops has been interpreted in the light of turbulence theory⁹⁾. It is assumed that the diameter of a bubble or drop is controlled by a balance of the kinetic energy of turbulence and the surface energy, i.e. there exists a critical Weber number

$$We_{\rm erit} = \rho_c \bar{v}^2 d_b / \sigma \tag{11}$$

In Eq. (11), \bar{v}^2 is the average value of the squares of velocity differences over a distance equal to the bubble diameter d_b and is given by

$$\bar{v}^2 \propto (E_l g_c d_b / \rho_c)^{2/3}$$
 (12)

for an isotropic homogeneous turbulence where the Kolmogoroff energy distribution law applies. Substituting Eq. (12) into Eq. (11) gives

$$d_b = a \rho_c^{-1/5} \sigma^{3/5} E_L^{-2/5} g_c^{-1/5} \tag{13}$$

Hinze⁹⁾ determined $\alpha = 0.725$ for the maximum drop diameter in two coaxial cylinders, and Rodriguez, Groze and Engle¹¹⁾ gave $\alpha = 0.286$ for the average drop size in agitated vessels.

For the present system ($\rho_{\sigma}=10^{3}$ kg/m³, $\sigma=7\times10^{-3}$ Kg/m) Eq. (13) reduces to

$$d_b = 1.46 \times 10^{-2} E_l^{-2/5} \text{ (a=0.725, Hinze}^{9}\text{)}$$
(14)
$$d_b = 0.58 \times 10^{-2} E_l^{-2/5}$$

 $(a=0.286, \text{Rodriguez et al.}^{11})$ (15)

Assuming that all the gas holdup is in the form of spherical bubbles, the bubble diameter was calculated from the equation

$$d_b = 6(1 - R_l)\varepsilon/a_{lg} \tag{16}$$

where liquid holdup R_i was evaluated by Eq. (8). The results are shown in **Fig. 6** and compared with Eqs. (14) and (15) for the drop dispersion in the different apparatuses. Data for $\chi > 10$ are not included in Fig. 6 because the values of R_i are close to unity for large χ and a large error is produced in evaluating the term $(1-R_i)$ in Eq. (16). As shown in Fig. 6, the bubble diameter in the dispersion in packed beds under two-phase flow again follows the -2/5 power law of the energy loss in liquid phase. In particular, the numerical agreement with Hinze's equation, Eq. (14), is interesting. It is somewhat unreasonable that the calculated bubble diameter is sometimes large than the interstitial void or the packing diameter. This is interpreted by the fact that two-phase flow is in or close to gas continuous flow at the lowest liquid flow rate $(U_l=0.122 \text{ cm/sec})$, for which the equivalent bubble diameter becomes very large. When data in this region are excluded, it reduces to the more reasonable result that d_b/d is smaller than 1/2.

When d_b is proportional to $E_l^{-2/5}$, Eq. (16) is rewritten as follows, and finally the interfacial area a_{lg} is related to a two-phase parameter χ .

$$a_{lg}E_l^{-2/5} \propto \varepsilon(1-R_l) = \psi(\chi) \tag{17}$$

The present results are plotted in this manner in Fig. 7. Data of Gianetto, Baldi and Specchia⁵⁾ and Dodds, Stutzman, Sollami and McCarter⁴⁾ fall within a dotted circle. In spite of the wide scatter the data for different geometries and sizes of packings follow a relation of the type of Eq. (17). A sharp decrease of $a_{lg}/E_l^{2/5}$ for $\chi > 5$ is due to the corresponding decrease of gas holdup, $1-R_l$.

5. Mass Transfer Coefficient

The mass transfer coefficient k_{lg} for oxygen-water system was separated from the volumetric absorption coefficient $(ka)_{lg}$ by dividing by interfacial area a_{lg} , based on an assumption that a_{lg} for water is equal to that for NaOH solution at the same flow rates of gas and liquid despite some difference in liquid properties. The k_{lg} thus determined for about $15^{\circ}C$ (experimental temperature) ranges from 2×10^{-4} to 8×10^{-4} m/sec. This range of k_{ig} is consistent in order of magnitude with that for circulating bubbles in free rise²⁾, in bubble columns¹⁾ and agitated gasliquid contactors¹⁾. Thus, it is concluded that the high values of $(ka)_{ig}$ encountered in cocurrent packed columns is attributable to large interfacial area a_{lg} of small dispersed bubbles, but not to the mass transfer coefficient k_{lg} .

Eqs. (3) and (10) for $(ka)_{lg}$ and a_{lg} , respectively, imply k_{lg} to be proportional to $U_l^{0.3}$. $k_{lg}/U_l^{0.3}$ is plotted against the gas velocity U_g in Fig. 8, where it is seen that the effect of U_g is small. k_{lg} decreases slightly with increasing packing diameter. The calculated bubble diameter is smaller for smaller packing at the same flow rates. Thus, according to the mass transfer theories, k_{lg} is expected to be higher for smaller packing, to which the present experimental trend is opposite. This disagreement may be explained tentatively by the fact that the relative motion between a bubble and liquid may be restricted due to narrow channels surrounded by small packings.

Substituting the root mean square fluctuation velocity $\sqrt{\overline{v^2}}$ given by Eq. (12) and the bubble diameter



Fig. 7 Alternate correlation of interfacial area in terms of liquid-phase energy loss



phase energy loss

given by Eq. (13) into an equation of the penetration theory of gas absorption, one gets

$$k_{lg} \propto (\sqrt{\bar{v^2}/d_b})^{1/2} \propto E_l^{11/30}$$
 (18)

In Fig. 9, k_{lg} is plotted against E_l . Although a single correlation is obtained for each packing diameter, it gives lower values of k_{lg} for smaller packing, probably due to the restriction of relative motion between phases mentioned in the preceding paragraph.

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Nomenclature

a_{lg}	=	specific interfacial area per unit vo	olume of bed
			[m²/m³]
a_s	==	geometrical surface area of packin	ig per
		unit volume of bed	[m²/m³]
C_l°, C_{l1}		liquid-phase concentration of O2	at
		entrance and exit	[kg-mol/m ³]
\overline{C}_{g}		average concentration of CO2	[kg-mol/m ³]
\overline{C}_b	=	average concentration of NaOH	[kg-mol/m ³]
D	=	diffusion coefficient of CO ₂	[m ² /sec]
d, d_b	_	diameter of packing and bubble	[m]
E_l		liquid-phase energy loss, Eq. (4)	[Kg·m/sec·m ³]
h	=	height of packed bed	[m]
k_{lg}	=	mass transfer coefficient	[m/sec]
kr	=	reaction rate constant []	m³/sec · kg-mol]
$(ka)_{lg}$		volumetric absorption coefficient	[1/sec]
Ν	_	absorption rate per unit volume	
		of bed []	kg-mol/sec⋅m³]
$\Delta P_g, \Delta P_l$		single-phase pressure loss for gas a	nd
		liquid	$[Kg/m^2]$
ΔP_{lg}	—	two-phase pressure loss	$[Kg/m^2]$
R_l	=	liquid holdup per unit void volum	e [—]
U_g, U_l	=	superficial gas and liquid velocity	[m/sec]
α		constant for Eq. (13)	
8	-	void fraction of bed	[-]
λ	=	Ostwald absorption coefficient	[]
ρ_c	—	density of continuous phase	[kg/m ³]
σ	_	interfacial tension	[Kg/m]
ϕ_l	=	two-phase parameter, $=\sqrt{\Delta}P_{lg}/\Delta P_{l}$	[-]
χ	_	two-phase parameter, $=\sqrt{\Delta P_1}/\Delta P_a$	[-]
			* *

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