μ = primary viscosity distribution
μ' = viscosity disturbance
$\tilde{\mu}$ = primary viscosity distribution ($\overline{\mu}/\mu_c$), dimensionless
ν = kinematic viscosity
ρ = density
$\bar{\rho}$ = primary density distribution
ρ' = density disturbance
σ = disturbance growth factor defined by Equation (12)
τ = amplitude of pressure disturbance divided by mean density
Ω = primary angular velocity distribution
$\tilde{\Omega}$ = primary angular velocity distribution (Ω/Ω_c), dimensionless
ξ = dummy radial position variable

Subscripts

c = centerline (points on circle of mean radius)
cr = critical
eff = effective
i = inner cylinder
min = minimum
o = outer cylinder

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The Influence of Diffusivity on Liquid Phase Mass Transfer to the Free Interface in a Stirred Vessel

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Liquid phase mass transfer coefficients were measured in a continuous flow, stirred vessel containing a gas and a liquid phase. Helium, hydrogen, oxygen, argon, and carbon dioxide were desorbed from distilled water into nitrogen at seven different levels of agitation. At low stirring speeds the system was stratified and mass transfer coefficients were proportional to diffusivity raised to a power between 0.5 and 0.6. At higher stirring speeds the interface was broken and corrections for desorption into the entrained bubbles indicated that the mass transfer coefficient at the main free interface was proportional to a higher power of diffusivity. The results are interpreted in the light of a general model considering eddy diffusion and surface renewal effects.

Many industrial processes involve mass transfer between a gas and a liquid. Often the interface between the two phases is relatively free to move about in space and is deformable; such is the case, for example, in plate distillation columns and for the main interface in agitated vessels. This characteristic has led to several different approaches to the description of liquid phase mass transfer near a free gas-liquid interface. Well-known theories include the film model of Whitman and Lewis (*30*), the penetration and surface renewal models of Higbie (*14*) and Danckwerts (*4*), and the postulate of turbulence-controlled mass transfer put forward by Kishinevsky (*20, 21*) and Kafarov (*18*). There are also "combination" theories, such as the film-penetration model (*7, 26*).

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Each approach predicts a different degree of dependence of the liquid phase mass transfer coefficient upon diffusivity. A general analysis of liquid phase mass transfer at a free surface in turbulent systems has been put forward by one of the present authors (*19*), and involves concepts of molecular diffusion, small-scale eddy diffusion, and large-scale surface renewals. From this analysis it follows that the exponent on diffusivity in a correlation for the liquid phase mass transfer coefficient depends upon the behavior of the eddy diffusivity near the interface and upon the surface age. If surface tension causes the eddy diffusivity in the liquid to damp out continuously to zero at the interface, the exponent m in

$$k_L \sim D^m \tag{1}$$

will be 0.5 for low ages of a surface element under consideration. It is convenient to denote this damping by postulating that the eddy diffusivity is proportional to y^n, where y is distance normal to the interface. If $n > 2$, increasing surface ages will cause m to rise continuously from 0.5 to an upper limiting value of $1 - 1/n$. If $n = 2$, m will be 0.5 for all ages, and if n lies between 0 and 2 the exponent upon D will continually decrease as surface age increases, reaching a nonzero limiting value only if $n > 1$.

If the small eddies causing the eddy diffusivity are somehow not damped out at the interface by surface tension, the exponent on diffusivity will be reduced. A limiting case of $m = 0$, corresponding to k_L being completely independent of molecular diffusivity, can be reached only for very high surface ages when $n \leq 1$, or for a situation where the eddy diffusivity is very large in comparison to the molecular diffusivity at all points including the interface.

The lack of a confirmed model has hampered the understanding of liquid phase mass transfer processes near a free surface. Knowledge of the effect of diffusivity on k_L is a key factor in the evaluation of various theoretical approaches, but there is little agreement within the available data. For the case of liquid phase resistance to gas absorption in a stirred vessel, Hutchinson and Sherwood (*17*), Dobbins (*8, 9*) and Davies, Kilner, and Ratcliff (*5*) have reported values of m lying between 0.25 and 0.9. Kishinevsky and Serebryansky (*21*) find that k_L is completely independent of diffusivity for a high level of agitation.

The conclusions of these four prior studies were based on a comparison of absorption rates for helium and/or hydrogen into water with absorption rates for gases such as carbon dioxide, oxygen, and/or nitrogen. There is a wide range of diffusivities previously reported for helium and hydrogen in water, and it is obvious that the reported exponent on diffusivity in a mass transfer study will depend upon the particular diffusivities chosen for the analysis. Vivian and King (*28*) have discussed this problem of diffusivities and conclude that the values shown for helium and hydrogen in Table 1 are probably the most reliable. Discrepancies do exist in the past data, however, and additional measurements by independent methods will certainly be welcome. The diffusivities for various gases dissolved in water shown in Table 1 are given at the temperature of original measurement and have also been corrected to the uniform temperature of 28°C. by holding the group $D\mu/T$ constant.

When the diffusivities of Table 1 are employed as a basis, the data of Hutchinson and Sherwood indicate an exponent of about 0.3 at 171 rev./min. and 0.4 to 0.6 at 1,025 rev./min. The results of Dobbins correspond to an exponent lying between 0.5 and 0.75; the results of Davies et al. give an exponent of 0.6 to 0.7; and the finding of Kishinevsky and Serebryansky that k_L is independent of D is, of course, unchanged.

TABLE 1. DIFFUSIVITIES AND SOLUBILITIES EMPLOYED FOR VARIOUS GASES IN WATER SOLUTION

Solute	Temp., °C.	Original measurement $D \times 10^5$, sq. cm./sec.	Ref.	$D \times 10^5$ at 28°C., sq. cm./sec.	$10^{-6} \times H$, at 28°C., (atm.)(cc.)/g.-mole
Helium	25	6.3	*16, 28*	6.8	2.63*
Hydrogen	25	4.8	*16, 28*	5.2	1.29
Oxygen	25	2.41	*16, 28*	2.62	0.810
Argon	21.7	2.0	*16*	2.3	0.694
Nitrogen	23.5	1.9	*16*	2.0	1.541
Carbon dioxide	25	1.95	*25, 28*	2.16	0.0312

* Reference *15*.

All these past experiments were conducted on a batch basis, in which a certain volume of initially solute-free water was brought into contact with a pure gas phase of the solute under consideration. The rate of solute uptake with respect to time was then monitored, either by measuring the flow rate of solute gas necessary to preserve a given pressure or by continually balancing a gas burette. Only for the low agitation runs of Davies et al. were liquid compositions monitored. The batch absorption technique presents three main drawbacks: Under conditions of high agitation the liquid tends to approach saturation very quickly, within 10 sec. in one case (*5*) and within 1 min. in another (*21*), thus reducing the time available for measurements. Also, helium and hydrogen are highly insoluble gases; consequently the total volume of gas absorbed is quite small, typically on the order of 1 to 5% of the total gas volume in the absorption system (*17, 21*). There is thus a possibility of significant error due to small temperature changes or to leaks. Finally, the analysis of the data in a batch system is based on the assumption that the bulk liquid within the vessel is completely mixed at all times.

The objective of the present study was to obtain measurements of rates of desorption of several different slightly soluble gases from water into a nitrogen carrier gas in a stirred and baffled vessel. From these results the influence of molecular diffusivity on the liquid phase mass transfer coefficient at the main, free gas-liquid interface could then be determined with a high degree of reliability. A desorption system was chosen so that the gas phase could retain the hydrodynamic properties of nitrogen for all solutes, rather than changing from case to case. The measurements were obtained by analyzing inlet and exit streams of nitrogen and water, both in continuous flow through the stirred vessel. In this way the problems of short run times and low total absorption present in the batch studies were circumvented and an overall mass balance was available as an experimental check. Uncertainties associated with the assumption of complete mixing could also be overcome if the degrees of depletion of solute in the liquid and of accumulation of the solute in the gas phase were kept low.

EXPERIMENTAL APPARATUS

A schematic of the apparatus is shown in Figure 1. The desorption vessel was a Pyrex No. 6947, 4-liter resin reaction kettle equipped with stirrers and four vertical baffles. Separate stirrers for the gas and liquid phases were mounted on a single shaft which passed through a bronze and glass casing at the top of the vessel and was driven by a 1/18 hp. variable speed motor. A rubber O-ring surrounded the shaft at the

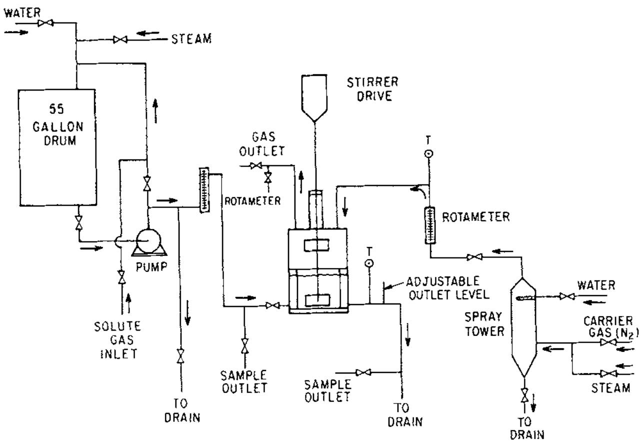

Fig. 1. Equipment flow diagram.

lower end of the casing to provide a leak-tight seal. Above the seal were nylon and Teflon bearings which enclosed an ice coolant. The inside cross-sectional area of the vessel was 140 sq. cm. The overall length of the vessel was 15 in. with the adjustable outlet level being positioned so as to make the liquid depth in the vessel 8 in. when there was flow without agitation. Four vertical baffles placed at 90 deg. intervals were employed. The baffles were ⅛ in. thick stainless steel and extended ¾ in. radially inward from the wall, ranging for a height of 7½ in. upward from a point 1¾ in. above the bottom of the vessel. The baffles were held in place by top and bottom rings and by protuberances on the vessel wall. The bronze liquid paddle consisted of four blades and was 2½ in. in diameter and 1 in. high; it was positioned so that the bottom was 1¾ in. above the vessel bottom. The gas paddle had two Bakelite blades, was 3½ in. in diameter and 1¼ in. high, and was placed approximately in the middle of the gas phase. The stirrer speed was monitored with a Stroboscope during operation.

Nitrogen from cylinders was contacted with steam and/or water in an 18 in. high spray tower. This procedure insured that the inlet gas would be saturated with respect to water vapor at the intended temperature of operation, as confirmed by wet and dry bulb thermometers. The nitrogen was then metered and passed into the vessel through a joint in the top. The exit gas came from another joint in the top and passed into an exhaust line which was equipped with a side arm for sampling.

Inlet water was stored in a 55 gal. stainless steel drum, equipped with a direct steam inlet for heating. The drum was closed except for a small Tygon vent line attached to the top. A ½ hp. centrifugal pump was provided for water recirculation. The water to the vessel was drawn off from the recirculation line, was metered and entered the desorption vessel at a point about 3 in. above the bottom. The exit water was withdrawn from a point directly opposite the inlet and was discarded. Sample ports were provided for both the inlet and outlet water streams. A thermometer was positioned in the outlet water stream.

PROCEDURE

Experimental

Before a run the 55-gal. drum was filled with distilled water, which was recirculated while solute gas was injected for a period of 3 to 5 min. This provided a solute concentration on the order of 30% of saturation. After the solute gas flow was stopped, the water in the tank was circulated for another 10 min. to insure a uniform concentration. This single tank load of water served as feed for an entire run.

The flow rates of water and nitrogen were held constant for all runs, in order to make the stirrer speed the only variable affecting the hydrodynamics. The water flow was kept at 11.4 liters/min. and the nitrogen flow was maintained at 6.37 liters/min. (24°C., 1 atm.). The apparatus was run for about 10 min., after which samples of exit gas, inlet liquid, and exit liquid were taken as nearly simultaneously as possible. A second set of samples was taken 3 to 4 min. later; these never differed by more than 6% in concentration from the first set, in a random direction. Samples were taken into two-arm bulbs of calibrated volume, ranging around 13 cc. A large number of bulb volumes of fluid were passed through before the entrance and exit stopcocks were closed, capturing the sample.

Five solute gases were employed: helium, hydrogen, oxygen, argon and carbon dioxide. As shown in Table 1 these afford a 3.2-fold variation in diffusivity. For all solutes, except oxygen, concentrations were measured with an Aerograph A-90-P2 gas chromatograph. For helium and hydrogen a 5-ft. molecular sieve column and a nitrogen carrier were employed. For argon a 5-ft. silica gel column was used along with an oxygen carrier. For carbon dioxide the molecular sieve column and a helium carrier were employed. Gas phase samples were placed directly in the carrier entrance line; thus the entire sample of known volume was injected. Since the water samples could not be put directly into the chromatograph, the dissolved solute gas was first flashed out of the water and collected into another bulb. A modified Van Slyke blood gas apparatus was used for this purpose; the principle was quite similar to the gas separation apparatus described by Vivian and King (29). A given water sample was flashed repeatedly into a vacuum chamber to insure complete solute removal. The gas collected from the known water volume was then placed directly in the chromatograph carrier inlet line.

Duplicate samples of oxygen in water were taken in 250-cc. stoppered Erlenmeyer flasks after several sweepouts. The Winkler titration was then used to determine the dissolved oxygen level. No gas analyses were made in oxygen runs.

Most runs were made with a solute saturation level of about 30% in the inlet water. Several carbon dioxide and helium runs were made at higher levels of initial water saturation and indicated that the observed k_LA was not a function of solute concentration.

Since a mass balance was available for all solutes except oxygen, it was possible to reject any run in which the nonclosure of the balance was greater than 15%. Usually the closure was considerably better than 15%. The poorest material balances were obtained at low rates of agitation where very small changes in concentration occurred in the liquid. The total number of acceptable runs was one hundred and fourteen. These covered seven different stirrer speeds (0, 350, 400, 580, 700, 850, and 1,000 rev./min.). At least two runs were made for a solute at a given stirrer speed. Most runs were made at temperatures of 25° to 30°C.

Calculational

Mass transfer coefficients were computed from both gas and liquid phase concentration changes on the assumption of complete mixing within either phase.

$$k_LA = L\frac{(C_1 - C_2)}{\left(C_2 - \dfrac{Py_2}{H}\right)} \tag{2}$$

$$k_LA = G_M\frac{(y_2 - y_1)}{\left(C_2 - \dfrac{Py_2}{H}\right)} \tag{3}$$

The reported mass transfer coefficients include those obtained from both Equations (2) and (3) for each run. Gas phase resistance to mass transfer was considered to be negligible.

In most cases the assumption of complete mixing of the bulk phases in the evaluation of the driving force for mass transfer was not especially critical. For solutes other than carbon dioxide the term Py_2 was never more than 5% of HC_2, and was usually much less. For carbon dioxide runs Py_2 was up to 20% of HC_2. At 580 rev./min. and less, C_2 was between 93 and 99% of C_1; thus the driving force was essentially independent of assumptions concerning mixing. At higher speeds incomplete mixing in the liquid could cause an increasingly significant error in the driving force of Equations (2) and (3). The ratios C_2/C_1 at 700, 850, and 1,000 rev./min., respectively, were 0.80, 0.57, and 0.36 for helium; 0.86, 0.70, and 0.50 for hydrogen; 0.92, 0.79, and 0.64 for oxygen; 0.92,

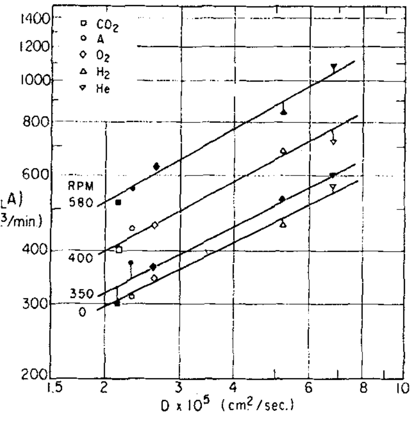

Fig. 2. k_LA vs. solute diffusivity, unbroken interface.

0.80, and 0.66 for argon; and 0.94, 0.91, and 0.88 for carbon dioxide.

More details concerning the apparatus and procedure are available (*22*).

RESULTS

The results of the main body of runs made at 25° to 30°C. were corrected to a uniform temperature of 28°C. on the basis of results obtained at different temperatures (see below), and are presented in Figures 2 and 3 as plots of k_LA vs. solute diffusivity. The points for each solute represent the median k_LA for the particular conditions. The average of the range estimates of the standard deviation (*6*) for the various solutes at the various stirring speeds was 7%.

Slopes of log k_LA vs. log D were obtained for stirring speeds of 580 rev./min. and below by means of least squares regression techniques. These slopes are shown in Table 2, along with standard errors of estimate for the slopes.

At stirring speeds above 580 rev./min. the main gas-liquid interface was broken by vortexing action at the baffles, and bubbles of gas were entrained into the bulk liquid. As shown in Figure 3 there was a tendency for the points on the logarithmic plots of k_LA vs. D not to be colinear under conditions where bubbles were entrained.

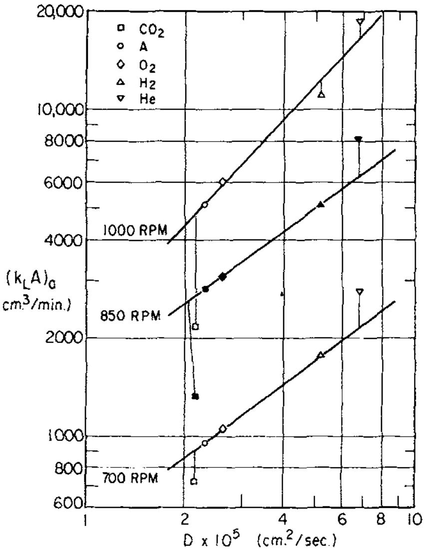

Fig. 3. Apparent k_LA vs. solute diffusivity, broken interface.

The straight lines in Figure 3 are explained below; they are not intended to be a representation of all the points. The helium mass transfer coefficients were comparatively high and the carbon dioxide coefficients were comparatively low. Directionally, this is the kind of effect which would be expected if a significant gas phase resistance to mass transfer had occurred; however, if the gas phase resistance were sufficient to account for the discrepancies between helium, hydrogen, oxygen, and argon, the observed coefficient for carbon dioxide would necessarily be an order of magnitude lower than actually encountered. This would be dictated by the fact that carbon dioxide is twenty times more soluble than the other gases.

A more likely explanation is afforded by consideration of the mass transfer to the entrained bubbles. The bubbles contribute a small volume but a large area for mass transfer; hence the concentration change within the bubbles was much larger than within the bulk gas phase. The total measured desorption rate may be divided into the contributions of the main free interface and of the bubble interface:

$$N_T = (k_LA)_a\,(C_2 - y_2P/H) \tag{4}$$

$$N_T = (k_LA)_m\,(C_2 - y_2P/H) + \frac{PV_B}{RT\theta_B}\left(\frac{C_2H}{P} - y_2\right)\left(1 - e^{-N_{OGB}}\right) \tag{5}$$

where

$$N_{OGB} = \frac{(k_LA)_B\,RT\theta_B}{HV_B} \tag{6}$$

Equation (5) postulates that bubbles have the bulk gas phase composition when formed and are continuously enriched in solute during their residence time in the bulk liquid by desorption from the well-mixed liquid. Since nitrogen continuously absorbs while solute desorbs, it may be shown (*22*) that the change in bubble volume is negligible. Upon leaving the liquid the bubbles reenter the bulk gas phase and blend with it. If the effective diameter of the entrained bubbles is d_B, Equation (6) becomes

$$N_{OGB} = \frac{6(k_L)_B\,RT\theta_B}{H\,d_B} \tag{7}$$

Equations (4), (5), and (7) combined give

$$(k_LA)_a = (k_LA)_m + \frac{HV_B}{RT\theta_B}\left[1 - \exp\left\{-\frac{6(k_L)_B\,RT\theta_B}{H\,d_B}\right\}\right] \tag{8}$$

The problem is to determine the influence of diffusivity on $(k_LA)_m$ from the measured values of $(k_LA)_a$. If both $(k_LA)_m$ and $(k_L)_B$ are proportional to D^m and if D^m/H is constant for any pair of solutes, it is apparent from Equation (8) that $(k_LA)_a$ will bear a fixed ratio to $(k_LA)_m$ for those solutes. Table 3 gives relative values of D^m/H for the five solutes studied. For $m = 0.75$, the values of D^m/H for hydrogen, oxygen, and argon fortuitously lie close together. Figure 3 shows that the slope of $(k_LA)_a$

TABLE 2. SLOPES OF LOG k_LA VS. LOG D UNBROKEN INTERFACE

N, rev./min.	Slope	Standard error/slope, %
0	0.51	9
350	0.52	14
400	0.56	12
580	0.58	14

TABLE 3. RELATIVE VALUES OF D^m/H

Solute	$m = 0.75$	$m = 1.00$
Helium	0.63	0.80
Hydrogen	1.05	1.24
Oxygen	1.00	1.00
Argon	1.06	1.03
Carbon dioxide	22.4	21.4

vs. D for hydrogen, oxygen, and argon is 0.78 at 700 rev./min. and 0.74 at 850 rev./min. Thus these slopes should apply to $(k_LA)_m$ if $(k_LA)_m$ and $(k_L)_B$ vary with the same power of D. At 1,000 rev./min. a greater dependence of k_LA upon diffusivity is indicated. Values of D^m/H for oxygen and argon lie between the values for hydrogen and helium. The 1,000 rev./min. line in Figure 3 is located with this fact in mind, giving a slope of 1.12, which again would apply if $(k_LA)_m$ and $(k_L)_B$ vary with the same power of D.

It also appears that the composition of the bubbles approached equilibrium during their stay in the liquid, as indicated by the following analysis for 850 rev./min. Visual inspection revealed that any large bubbles formed at the vortices were invariably swept downward into the stirrer blade area and were broken up. The largest bubbles reentering the gas phase had diameters on the order of 0.3 to 0.5 cm. The residence time of the largest bubbles returned to the gas phase appeared to be on the order of 0.5 to 1 min. If $(k_L)_B$ is taken as approximately equal to k_{Lm} (shown in Figures 4*a* and 4*b*), it is possible to obtain an estimate of N_{OGB} for the various solutes from Equation (7). The resultant values of N_{OGB}, allowing for uncertainties in $(k_L)_B$, θ_B and d_B, are 40 to 100 for carbon dioxide, 2.0 to 5.0 for argon, oxygen, and hydrogen, and 1.2 to 3.0 for helium. Since the term in brackets on the right-hand side of Equation (8) lies between 0.9 and 1.0 for $N_{OGB} \gtreqless 2.5$, it may be concluded that the escaping bubbles had become almost completely equilibrated for all solutes, with the possible exception of helium. Similar results are obtained at 700 and 1,000 rev./min.

The observed mass transfer rates may be corrected for bubble transfer. Assuming that the bubbles equilibrate entirely, one may use Equation (8) to derive $V_B/RT\theta_B$ at a given stirring speed from the $(k_LA)_a$ values for carbon dioxide and oxygen:

$$\frac{V_B}{RT\theta_B} = \frac{(k_LA)_{a,\mathrm{O}_2} - \delta(k_LA)_{a,\mathrm{CO}_2}}{H_{\mathrm{O}_2} - \delta H_{\mathrm{CO}_2}} \tag{9}$$

where $\delta = (D_{\mathrm{O}_2}/D_{\mathrm{CO}_2})^m$ and m is an assumed exponent in the expression $k_L \sim D^m$. Carbon dioxide and oxygen were chosen for several reasons: Data for these two solutes showed the least scatter; the difference in solubilities is great, lending accuracy to computations via Equation 9; and the diffusivities of these solutes are close enough together so that $V_B/RT\theta_B$ is insensitive to the value chosen for m. The plots of $(k_LA)_m$ vs. D shown in Figure 4*a* were obtained by subtracting from $(k_LA)_a$ the values of $H\ V_B/RT\theta_B$ determined in this manner. The points fit a linear logarithmic relationship well and give slopes of 0.81 at 700 rev./min., 0.72 at 850 rev./min. and 1.13 at 1,000 rev./min. Indicated values of V_B/θ_B from the corrections are 7 cc./min. at 700 rev./min., 50 cc./min. at 850 rev./min., and 100 cc/min. at 1,000 rev./min. These are in agreement with estimates of gas holdup and bubble residence time, and lend credence to the postulate of near complete bubble equilibration.

There remains the question of the effect of incomplete liquid mixing on the calculated values of k_LA and slopes of log k_LA vs. D. The original calculations of $(k_LA)_a$ were made on the assumption that the average bulk liquid concentration in the vicinity of the free surface was the measured C_2. Figures 2, 3, and 4*a* are prepared on this basis. Visual observations of ink injections suggested that mixing in the liquid was quite rapid. On the other hand, the flow pattern in the vessel could bring an appreciable portion of the inlet liquid directly up to the main surface, thereby making the average driving force larger than was assumed in Equations (2) and (3). Figure 4*b* is included to give an idea of the possible effect of incomplete liquid mixing. The values of $(k_LA)_m$ shown in Figure 4*b* have been obtained by recomputing $(k_LA)_a$ on the presumption that the average bulk concentration near the free interface lies only 70% of the way between the inlet and outlet liquid concentration, that is

$$k_LA = L\frac{(C_1 - C_2)}{\left(0.7\,C_2 + 0.3\,C_1 - \dfrac{Py_2}{H}\right)} \tag{10}$$

or

$$k_LA = G_M\frac{(y_2 - y_1)}{\left(0.7\,C_2 + 0.3\,C_1 - \dfrac{Py_2}{H}\right)} \tag{11}$$

The correction for equilibrated bubble transfer was then computed and applied as before. The indicated values of V/θ_B were not greatly changed. The largest reductions in $(k_LA)_m$ occur for helium at 850 and 1,000 rev./min. and for hydrogen at 1,000 rev./min. At 850 and 1,000 rev./min., the values of $(k_LA)_m$ for helium lie substantially below the line through the points for the other solutes; however, the amount by which helium is low is only 15 to 20% of the amount of the bubble correction for helium. This is in line with the above statement that N_{OGB} could be as low as 1.2 for helium, while being no lower than 2.0 for the other solutes, and thus must be accepted as a logical possibility. Slopes of log $(k_LA)_m$ vs. log D based upon the solutes other than helium are 0.76 at 700 rev./min., 0.69 at 850 ref./min., and 0.78 at 1,000 rev./min. It should be noted that the indicated exponent on diffusivity at 1,000 rev./min. is greatly reduced by a lack of complete mixing, while the indicated exponent at lower speeds is much less affected.

In summary, it may be concluded that the exponent on diffusivity as it affects the free surface mass transfer coefficient is near 0.5 at low stirring speeds, and that it rises as stirring speed increases. By 850 rev./min. the exponent has risen to a level of 0.7 to 0.8. At 1,000 rev./min. questions concerning the degree of liquid mixing preclude assigning a reliable value to the exponent.

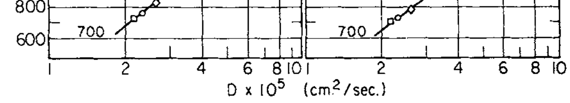

Fig. 4. k_LA, corrected for bubble equilibration, vs. solute diffusivity, broken interface.

DISCUSSION

Mass Transfer Mechanism

The results for the influence of diffusivity upon the free liquid surface mass transfer coefficient may be examined in the light of the model put forward by King (*19*), interpreting free surface mass transfer in terms of surface renewals and a damped profile of eddy diffusivity near the interface. Differences in the exponent m between agitation levels and between the various past studies may be considered to be well established, but the absolute magnitude of the exponents is dependent upon the reliability of the diffusivity data employed, as discussed earlier.

The exponent of 0.5 obtained at low stirring speeds is characteristic of surface renewal control. The increase in exponent as the stirring speed increases is in accord with a continuous transition toward a mass transfer regime controlled by steady state transport into the damped eddy diffusivity profile. If the eddy diffusivity near the interface is proportional to the fourth power of distance away from the interface, one would expect the exponent on diffusivity to level out at 0.75 at high levels of agitation. One cannot fix the upper limit on the exponent from the present data in view of the uncertainty provided by the mixing question at 1,000 rev./min. The ensuing discussion will be conducted on the assumption that the upper limit on the exponent is 0.75, based largely on the results of Dobbins (see below) and to some extent on the present work; however this value should not be considered to be well established.

Additional insight may be gained from a reexamination of the results of other studies. Davies et al. (*5*) measured absorption rates at a uniform stirring speed of 437 rev./min. under conditions where the interface was mobile and also under conditions where tangential motion of the interface was suppressed by counterrotating stirrers in the liquid. If the diffusivities of Table 1 are used for analysis, their results for the mobile interface indicate that the mass transfer coefficient was proportional to diffusivity to a power of 0.59 to 0.63. This corresponds to expected behavior in the transition region between surface renewal control and eddy diffusion control. At the same stirring speed, but under the conditions of suppressed tangential interfacial motion, the mass transfer coefficient fell by a factor of about three and the diffusivity exponent based on Table 1 rose to 0.65 to 0.71. The lower rate and higher exponent are both in accord with a transition toward the extreme of eddy diffusion control. When tangential interfacial motion is suppressed, surface renewals should occur less frequently. When a protein monolayer was added at the same stirring speed with tangential interfacial motion suppressed, the mass transfer coefficient decreased a factor of 1.8 further and the exponent on diffusivity based on Table 1 rose to 0.80 to 0.82. As suggested by Davies et al. it is likely that the rigidity of the monolayer or surface elasticity due to the surfactant made surface renewals altogther unimportant in this case. The exponent indicated by the results of Davies et al. with the protein monolayer is somewhat higher than the value of 0.75 predicted for the complete suppression of surface renewal if the eddy diffusivity is taken to vary as the fourth power of distance from the interface, but the difference is within experimental error.

Davies et al. also measured the effect of diffusivity at a very high rate of agitation, 1,500 rev./min., which gave a single large vortex in an unbaffled vessel. Their results, based on short time runs, indicate an exponent on diffusivity of 0.62 to 0.65, corresponding to a point in the transition region where surface renewal effects and eddy diffusion are both important.

In the work of Dobbins (*8*) agitation was provided by means of a vertically oscillating metal lattice within the liquid. Batch absorption rates of helium and nitrogen into water were measured. Variables included the frequency of oscillation, the amplitude of oscillation, and the depth of the top of the lattice under the gas-liquid interface at the top of the stroke (called "cover"). The results obtained by Dobbins were replotted and analyzed in terms of the diffusivities given in Table 1. The results of this analysis are given in Table 4. Exponents in parentheses are less well known because of scatter. Dobbins' results are in accord with the hypothesis that the exponent on diffusivity lies between the extremes of 0.50 and 0.75. As shown in Table 4, decreasing "cover" and increasing amplitude both decrease the exponent and thus appear to increase the importance of surface renewals relative to eddy diffusion. This is in accord with the physical picture that surface renewals are favored by large eddies in the vicinity of the interface.

Energy Dissipation

The free surface model based on surface renewals and damped eddy diffusion has been used for the interpretation of data for liquid phase controlled gas absorption in wetted-wall columns (*19*). Near quantitative agreement is obtained if the mass transfer coefficient for the extreme of eddy diffusion control is obtained from a semi-empirical correlation of data for rates of turbulent mass transfer to fixed interfaces in terms of energy dissipation

$$k_L = 0.25 \left(\frac{\epsilon \mu}{\rho^2} \right)^{1/4} \left(\frac{\mu}{\rho D} \right)^{-3/4} \qquad (12)$$

The general free surface model predicts a mass transfer coefficient greater than given by Equation (12) if surface ages are low enough to give transient mass transfer at a significant portion of the interface.

Table 5 summarizes the results of eleven past studies of liquid-phase controlled mass transfer across a contiguous gas-liquid interface in a stirred vessel. In cases where stirring speed was varied the power on stirring speed ($d \ln k_L / d \ln N$) is given. The ratio of the measured k_L to that predicted by Equation (12) is shown for those studies in which sufficient vessel and stirrer dimensions are given to allow estimation of the overall energy dissipation rate from existing power number correlations (*2*, *24*). The best basis for comparing the results of different studies is probably k_L itself; that is, similar values of k_L should correspond to similar regimes of mass transfer mechanism.

An examination of Figure 2 reveals that $(k_L A)_m$ in the present work increased slowly with increasing revolutions per minute at the lower stirring speeds and then increased much more rapidly with increasing revolutions per minute at higher stirring speeds. There was a substantial amount of visible surface disturbance even in the absence of stirring, and the mass transfer coefficient did not double over the 0 rev./min. value until a stirring speed greater than

TABLE 4. EXPONENTS ON DIFFUSIVITY ($k_L \sim D^m$) DERIVED FROM MEASUREMENT OF DOBBINS (*8*)

	Amplitude = 2.5 cm.		Amplitude = 1.2 cm.	
Frequency	Cover = 0 cm.	Cover = 0.5 cm.	Cover = 0.5 cm.	Cover = 1.0 cm.
	←	m		→
50 cycles/min.	0.67	(0.73)	(0.73)	0.67
100	0.67	0.60	0.69	0.72
150	0.58	0.54	(0.63)	0.70
200	0.51	(0.70)	(0.60)	0.71
250	—	(0.65)	0.52	0.73

TABLE 5. SUMMARY OF MEASUREMENTS OF LIQUID PHASE RESISTANCE TO GAS ABSORPTION AT THE MAIN FREE INTERFACE IN A STIRRED VESSEL

	Investigator	Ref.	k_L, cm./min.*	Power on N	Ratio to k_L predicted by Equation (12)	Baffles?
1.	Becker	*1*	0 to 0.0017	0.9 to 0.6	—	No
2.	Goodgame and Sherwood	*11*	0.06	—	(0.2)†	Yes
3.	Vassilatos et al.	*27*	0.07	—	0.5	Yes
4.	Linton and Sutherland	*23*	0.02 to 0.10	0.9	0.4 to 0.6	Yes
5.	Whitman and Davis	*31*	0.06 to 0.10	0.72	—	No
6.	Hutchinson and Sherwood	*17*	0.05 to 0.13	0.6	—	
7.	Davies et al.	*5*	0.06 to 0.12	0.62		No
	(137 to 437 rev./min.)				0.4 to 0.5	Yes
8.	Downing and Truesdale	*10*	0.04 to 0.17	1.0	—	Yes
9.	Goodridge and Bricknell	*12*	0.03 to 0.08	0.75	0.8 to 0.9	Yes
			0.3 to 0.8	1.1	1.7 to 2.1	
10.	Goodridge and Robb	*13*	0.08 to 2.2	1.2	1.1 to 3.6	Yes
11.	Yoshida et al.	*32*	0.1 to 0.3	1.1	1.4 to 2.0	Yes
12.	Present work (0 to 580 rev./min.)		1.8 to 3.7	—	>1‡	Yes

* For carbon dioxide or oxygen in water.

† Stirrer dimensions estimated.

‡ Assuming energy dissipations from flow and stirring are additive.

580 rev./min. was attained. These facts indicate that substantial agitation was afforded by the flow process itself; thus the dependence upon N in this study cannot be compared in a meaningful way with the dependence in the other studies in Table 5. The values of k_L encountered in the past studies of Table 5 are almost invariably lower than those found in the present work (line 12); a logical conclusion is that the agitation levels throughout the present work are higher than those in the other studies in the table.

Over a wide range of conditions below the limit of interfacial breakup the energy dissipation rate in a stirred vessel without through flow is proportional to the cube of the stirring speed (*2, 24*). If k_L is proportional to $\epsilon^{1/4}$ in the extreme of eddy diffusion control as indicated by Equation (12), one would expect k_L to be proportional to $N^{3/4}$. Although the powers on N shown in Table 5 vary from case to case, they are reasonably close to 0.75 at the lower values of k_L.

Data for absorption in channels and for stream aeration indicate that k_L varies as ϵ to a power greater than 0.25 and that k_L is substantially greater than predicted by Equation (12). This suggests that surface renewals control. Exponents of 0.33 to 0.41 on energy dissipation have been indicated by an experimental study of a channel and by dimensional analysis based upon the assumption that one is in a regime where surface tension is unimportant (*19*). These results suggest that k_L should be proportional to N raised to a power of 1.0 to 1.2 in the extreme of surface renewal control in a stirred vessel. Such behavior is shown by the results of Downing and Truesdale (*10*), Goodridge and Bricknell (*12*), Goodridge and Robb (*13*), and Yoshida et al. (*32*), which correspond to the higher values of k_L in Table 5.

The values of k_L found for conditions of lesser agitation in Table 5 are substantially below those predicted by Equation (12). A logical explanation is that the rate of energy dissipation is not uniform throughout the liquid bulk; it is greater in the vicinity of the stirrer and less in the vicinity of the free surface. The four past studies in the higher k_L range provide values of k_L which are higher in relation to the predictions of Equation 12. This is to be expected if surface renewals are more important than at the lower stirrer speeds.

These inferences imply that the liquid phase resistance to gas absorption at the lower agitation levels of Table 5 is controlled by steady state diffusion into a region of increasing eddy diffusivity. There are few large eddies with sufficient kinetic energy to overcome surface tension and cause surface renewals. At the higher levels of agitation of Table 5 the mass transfer passes through a transition to become surface renewal controlled as large eddies obtain sufficient kinetic energy to overcome the resistance to renewals afforded by surface tension. The magnitude of k_L and the exponent on D imply that the present operation was in this regime of surface renewal control even in the absence of stirrer motion. The increasing dependence on D at the higher levels of agitation of the present work indicates that the mass transfer undergoes a transition back toward eddy diffusion control at very high levels of agitation. This last transition could be the result of the rate of energy dissipation becoming more uniform throughout the liquid, or might possibly be due to a reduction in the maximum scale of turbulent eddies. This picture of transitions between surface renewal control and eddy diffusion control must be considered to be speculative, however, in the absence of confirming data taken over the entire agitation range.

Some further support for this point of view comes from studies of the effect of surfactants on absorption rate. Since the consensus of measurements of the influence of diffusivity upon mass transfer rates is that the eddy diffusivity damps to zero at the gas-liquid interface, it is unlikely that the presence of a surfactant in an aqueous system would have much effect upon the eddy diffusivity profile. On the other hand, as pointed out above, elasticity and/or rigidity of the surface imparted by the surfactant should markedly reduce the rate of surface renewal. Davies et al. (*5*) examined the effect of a protein monolayer on the rate of gas absorption at 137 rev./min. and found a reduction in rate of about 10%, much less of a reduction than they had found at 437 rev./min. Goodridge and Bricknell (*12*) found a reduction in k_L of only 10 to 20% caused by C_{10}-C_{20} surface films at low k_L (0.03 to 0.08 cm./min.), but found a reduction of 60 to 70% in their range of higher k_L values. Goodridge and Robb (*13*) confirmed the range of reductions reported by Goodridge and Bricknell and found that the exponent on

N was reduced to 0.7 in the presence of a surfactant. Linton and Sutherland (*23*) also found a greater reduction in k_L due to a hexadecanol monolayer at their higher stirring speeds than they found under less agitation. These results are all in agreement with the views that surfactants suppress surface renewals and that in the absence of surfactants surface renewals are less important at lower stirring rates than in the intermediate range of agitation.

Temperature Effect

Power number correlations indicate that ϵ is insensitive to temperature in a stirred vessel; as a consequence Equation (12) indicates that k_L should incerase by 2.8% per degree Centigrade for aqueous systems over the temperature range 28° to 38°C.

The effect of temperature on k_LA was evaluated in the present work by conducting two or three runs for each solute gas at 1,000 rev./min. and a temperature of about 38°C. The results of these runs were compared with the results of runs in the vicinity of 28°C. It was found that

$$k_LA \sim \exp\,(+\,0.039\,T)$$

where T is in degrees Centigrade. Past studies of absorption in stirred vessels generally have found that an exponential expression of this sort affords a satisfactory correlation (*3, 10*). The standard deviation of the factor 0.039 was ± 0.006. Test runs at 400 rev./min. indicated that the increase with respect to temperature decreased somewhat, but no firm conclusions could be drawn concerning the amount of the reduction.

It is possible that there was a substantial effect of temperature on the area of the main interface at 1,000 rev./min. Imperfect liquid mixing at 1,000 rev./min. would also cause the true temperature coefficient for k_{L_m} to be less than observed. Downing and Truesdale (*10*) and the Committee on Sanitary Engineering Research (3) report temperature effects on k_L of 2.2 and 2.4% per degree Centigrade from their stirred vessel absorption studies. As is shown elsewhere (*19*), a temperature effect of 2.4% per degree Centigrade is predicted for the extreme of surface renewal control if the mass transfer coefficient depends upon D, ϵ, ρ, μ and a characteristic length.

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NOTATION

A = interfacial area between gas and liquid, sq. cm.
C = solute concentration in liquid, g.-mole/cc.
d = effective diameter, cm.
D = diffusivity of solute in liquid, sq. cm./min.
E = eddy diffusivity, sq. cm./min.
G_M = nitrogen flow rate, g.-mole/min.
H = Henry's law constant, (atm.) (cc.)/g.-mole
k_L = liquid phase mass transfer coefficient, cm./min.
L = water flow rate, cc./min.
m = $d \ln (k_L)/d \ln (D)$
N = stirring speed, rev./min.
N_T = total rate of mass transfer, g.-mole/min.
N_{OGB} = number of transfer units experienced by bubbles entrained into liquid
n = exponent, defined in $E \sim y^n$
P = pressure, atm.
R = gas constant = (82.05 atm.) (cc.)/(g.-mole) (°K.)
T = temperature, °C. or °K.
V_B = volume of bubbles, cc.
y = mole fraction of solute in gas phase

Greek Letters

δ = $(D_{O_2}/D_{CO_2})^m$
ϵ = rate of energy dissipation per unit volume, g./(cm.) (min.^{3})
θ_B = residence time of bubbles, min.
μ = liquid viscosity, g./(cm.) (min.)
ρ = liquid density, g./cc.

Subscripts

a = apparent, based on Equations (2) and (3)
B = bubble
m = main free interface
1 = inlet
2 = outlet

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