cause of the paucity of low temperature data.

We do not intend to imply that using fewer parameters than indicated by Figure 1 will produce unsatisfactory correlations. We do imply that using the indicated number of parameters will produce correlations more nearly approximating the data and that the polynomial parameters will be more nearly identifiable with virial coefficients.

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Mass Transfer Coefficients and Interfacial Areas in Agitated Dispersions

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The recent article by Robinson and Wilke (1974) reports some interesting results and conclusions on liquid-phase mass transfer coefficients in an agitated vessel involving gas-liquid dispersion. The authors claim a new technique for the simultaneous evaluation of the liquid mass transfer coefficients and gas-liquid interfacial areas for gas-liquid dispersions in an agitated vessel. The success claimed by the authors and the results reported may lead many workers interested in this topic to conclude that therein lies the answer to a long search in trying to understand gas-liquid mass transfer in an agitated vessel. It is therefore pertinent at this point to examine the results obtained by these workers.

Robinson and Wilke reached the unexpected conclusion that the mass transfer coefficient k_L in an agitated dispersion decreases with increasing energy dissipation (power input) in the agitated vessel. They state that the mass transfer coefficient in physical absorption decreases in value as the bubbles decrease in size and the bubbles decrease in size as the power input in the system increases and as the ionic concentration increases. The result of the decrease in bubble size is presumably to change the character of the gas-liquid interface from a somewhat free interface to a somewhat rigid (fixed) interface as the bubble decreases in size. This definitely alters the boundary conditions at the interface, but to claim that the mass transfer coefficient in the liquid phase decreases with increasing energy dissipation goes counter to any known theory in mass transfer. Lamont (1970), solving the problem of transfer in a turbulent field in terms of the eddies in the equilibrium range for the case of both the fixed interface (solid-liquid) and the free (gas-liquid) interface, obtained similar expressions for the mass transfer coefficient in the form

$$k_L = \alpha N_{Sc}^{-m} (\epsilon\nu)^{1/4} \tag{1}$$

where m is 2/3 for the rigid interface and 1/2 for the case of the free interface. Calderbank (1961) confirmed the variation of k_L with energy dissipation in case of transfer from submerged solid surfaces to liquid in agitated vessels for a limited range of energy dissipation [$k_L = 0.13 N_{Sc}^{-2/3} (\epsilon\nu)^{1/4}$]. In the case of solid-liquid transfer, the increase in k_L with energy input in agitated vessels has been established by a number of workers (Harriott, 1961; Keey, 1966; Sykes and Gomezplata, 1967; Nienow, 1969; Miller, 1971; Levins, 1972; and others), although some of them found that some geometrical parameter is also needed to correlate k_L. In view of this, it is desirable to examine critically the technique that has been used to evaluate the results in the study by Robinson and Wilke and others.

Robinson and Wilke calculated their results by simultaneously conducting the absorption of CO_2 from a CO_2-N_2 mixture into an $[OH^-]$ solution and the desorption of O_2 from the solution into a CO_2-N_2 mixture. From the theory of diffusion with reaction, for a fast reaction the rate of absorption with reaction is given by (Danckwerts, 1951)

$$R^r = a_r C_I^* \, (k_{L3}^2 + D_{L3} k_2 C_B)^{0.5} \tag{2}$$

where $k_{L3}^2 << D_{L3} k_2 C_B$ and hence the rate in Equation (2) is independent of hydrodynamics. For the case of physical absorption or desorption of species 4 R is given by

$$R = a_p \Delta C \, k_{L3} \left(\frac{D_{L4}}{D_{L3}}\right)^{0.5} \tag{3}$$

Equation (2) has been used by Wilke and Robinson to describe the rate of CO_2 uptake by the $[OH^-]$ solution and Equation (3) for the desorption of O_2 into the gas bubbles. They further assumed that the effective interfacial area in the case of the reacting system is equal to the effective interfacial area a_p in the case of physical desorption. A little reflection about the dynamics of the agitated vessel will intuitively indicate that this assumption is open to serious doubt. In the case of the absorption system with a fast chemical reaction, the mass transfer coefficient is independent of the hydrodynamics. Hence all the interfacial area distributed in all parts of the agitated vessel contribute equally to the mass transfer since the mass transfer coefficient is equal at every point in the vessel.

On the other hand, in the case of physical absorption or desorption in an agitated vessel, the mass transfer coefficient cannot be assumed to be equal at all points in the vessel. Cutter (1960) has shown that the distribution of energy dissipation in the agitated vessel is grossly uneven. In the case of turbine impellers, Cutter has shown that $(\epsilon/\bar{\epsilon}) = 0.26$ for flow in the bulk of the vessel, whereas in the impeller stream which occupies about 10% of the tank volume $(\epsilon/\bar{\epsilon}) = 7.7$. If the mass transfer coefficient is assumed to vary as $\epsilon^{1/4}$, which is consistent theoretically, then the mass transfer coefficient around the impeller would be larger than the mass transfer coefficient far away from the impeller by a factor of 2.5. This variation would be even larger if the region towards the top surface of the agitated vessel is considered. Because of this the interfacial region in different parts of the vessel do not contribute equally to the mass transfer.

For the above reasons it can be seen why the assumption of $a_p = a_r$ by Robinson and Wilke can lead to quite unexpected conclusions with respect to the variation of the physical mass transfer coefficient versus the energy input to the system. The effective interfacial area in the case of the fast reaction system is probably much larger than the effective interfacial area for physical desorption.

Another point is that with increasing agitation intensities the distribution of actual interfacial areas in an agitated vessel changes in character. Figures 1 and 2 represent hold-up data and interfacial areas obtained by light-transmission methods by Calderbank (1958, 1959). Close examination of these figures will indicate that at low agitation intensities the gas hold-up and interfacial areas are of comparable magnitudes near the impeller and close to the liquid surface in the tank. But as the agitation intensities increase, the hold-up and interfacial areas begin to assume larger and larger values at the top near the liquid surface as compared to values near the impeller. These are, of course, observations concerning dispersions in nonelectrolyte solutions. In the case of electrolyte solutions, the actual values would most likely be different, although the trends could be expected to be the same. The variations represented by this phenomenon are possibly other factors contributing to the unexpected conclusions concerning the mass transfer coefficient in the study by Robinson and Wilke.

Calderbank and Moo-Young (1961) also reported that liquid phase mass transfer coefficients in gas-liquid dispersions remain constant with agitation intensities although they identified two bubble regimes. Both in the small and large bubble regimes, k_L was shown to vary according to $(\rho_L - \rho_G)^{1/3}$. It is difficult to conceive how the buoyancy forces, which are negligible as compared to the agitation intensities, can affect mass transfer coefficients as against energy input. Calderbank and Moo-Young obtained the values of k_L by evaluating k_La experimentally and also using a_d obtained by optical measurements. Again here the assumption has been made that $a_d = a_{\text{eff}}$. In view of the highly uneven distribution of energy dissipation in the vessel and also the variation in the distribution of actual interfacial areas with agitation intensities, the conclusion that k_L does not vary with energy input is probably inaccurate.

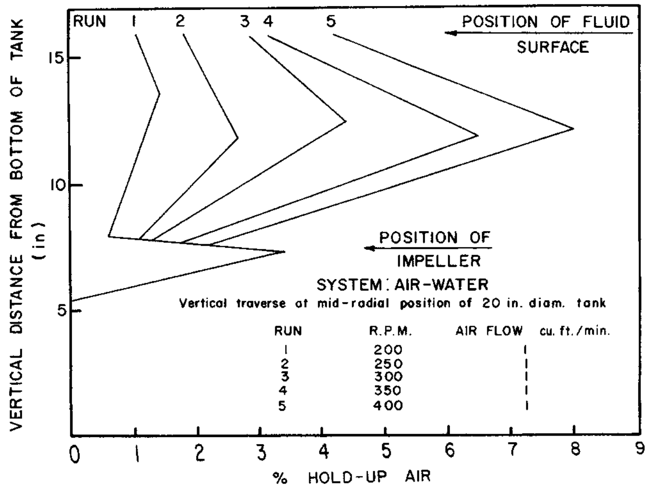

Fig. 1. Typical vertical distribution of gas hold-up in 100 l. tank. [Reproduced from Calderbank (1958)].

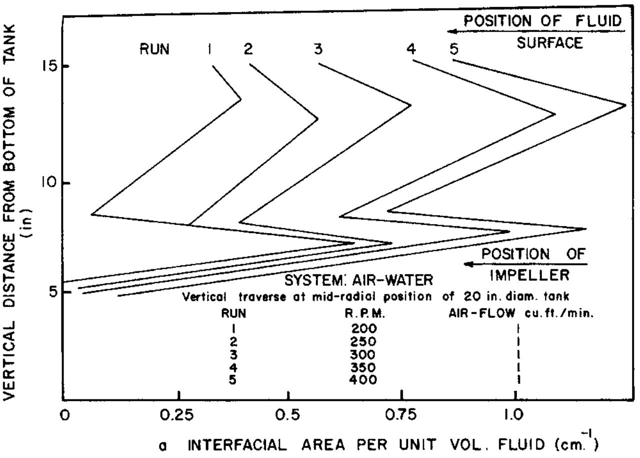

Fig. 2. Typical vertical distribution of interfacial area in 100 l. tank [Reproduced from Calderbank (1958)].

Joosten and Danckwerts (1973) come to the same conclusion as the thesis put forth here in the case of absorption in a packed column that the value a_r/a_p deviates appreciably from unity. Yet one would suspect that the hydrodynamics betwen the packings does not probably vary so widely as the case is with an agitated dispersion.

CONCLUSIONS

In the case of absorption with fast chemical reaction since the mass transfer coefficient is independent of hydrodynamics

$$\overline{k_L'} = k_L'(r, z) \tag{4}$$

where $k_L'(r, z)$ is the mass transfer coefficient for the reacting case at any position (r, z) in the vessel. Also for absorption with fast and pseudo first order reactions because the mass transfer coefficient is independent of hydrodynamics

$$a_{\text{eff}} = a_d \tag{5}$$

where a_d is the interfacial area obtained by direct measurement (for example, photographic, light transmission, etc.).

For the case of physical absorption $\overline{k_L'} \neq k_L(r, z)$ since the distribution of energy dissipation in the vessel is grossly nonhomogeneous. Also, $a_{\text{eff}} \neq a_d$ since the interfacial areas at different locations in the vessel contribute very differently to the mass transfer due to the wide variations in mass transfer coefficients.

Robinson and Wilke, Calderbank, and others reported unexpected results concerning the variation of liquid phase mass transfer because they assumed very little difference between a_p, a_r, and a_d. Also as discussed earlier, as agitation intensities increase the interfacial areas in the region of low energy dissipation seem to increase relatively as compared to interfacial areas in the region of high dissipation (around the impeller stream). This has the apparent effect of making it appear as though $\overline{k}_L$ decreases in value as power input increases.

Also, it must be recognized that k_L varies as $\epsilon^{1/4}$ theoretically, the 1/4 exponent being small. So any error in computing the effective interfacial areas would be reflected significantly on k_L since k_La varies as $\epsilon^{0.75-0.9}$ in general. The assumption of $a_r = a_p$ may introduce a considerable degree of error in a_{eff} which would easily make it appear that k_L decreases or remains constant with ϵ.

The technique of conducting simultaneous absorption with reaction and physical desorption (or absorption) concurrently used by Wilke and Robinson is certainly a novel feature in attempts to understand the whole complex problem of transfer in a dispersion. But the analytical technique is open to serious questions.

The results could have been better obtained if the absorption with reaction used in this study was also conducted in a regime where both hydrodynamics and reaction would have comparable effects. To minimize the error, conditions could be adjusted in such a way that the enhancement factor $\beta = k_L'/k_L$ would be such that it would not exceed 1.5 or 1.7. Of course, for a second-order reaction between CO_2 and $[OH^-]$ involved the numerical solution of the following partial differential equations to find k_L', since pseudo first order reaction cannot be assumed because of depletion of OH^- at the interface.

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} - k_2 C_A C_B \tag{6}$$

$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2} - 2k_2 C_A C_B \tag{7}$$

The penetration model could be used with the appropriate boundary conditions. Then β could be obtained from the solutions of Equations (6) and (7) for k_L' with the appropriate boundary conditions and the expression for physical mass transfer k_L. Thus

$$\beta = f(C_A^*, C_B, t, D_A, D_B, k_2) \tag{8}$$

Then if it is assumed that $a_p = a_r$ (and this would be closer since the absorption with reaction is not very strongly dependent on reaction), then k_L and a can be evaluated simultaneously by conducting the two types of transfers concurrently. Such a numerical procedure was adopted by Prasher and Wills (1970, 1973), Bieber (1971), and Smith and Wills (1966) although the concurrent experimental technique by Wilke and Robinson, which is a definite improvement in the sense that conditions for both absorption with reaction and desorption are strictly equal, was regrettably not conceived before this time.

NOTATION

a = interfacial area
a_p = interfacial area in physical desorption
a_r = interfacial area in chemical absorption
a_d = interfacial area by direct measurement
C_A = concentration of solute gas
C_B = concentration of reactant
C_I^* = interfacial concentrations for reacting species
ΔC = concentration driving force in desorption
D_{Li} = diffusivity coefficient for species i
k_L = liquid phase mass transfer coefficient
k_{Li} = liquid phase mass transfer coefficient for diffusing species i
$\overline{k}_L$ = average liquid phase mass transfer coefficient
k_L' = liquid phase coefficient for mass transfer with reaction
$\overline{k}_2$ = second order reaction rate constant
m = constant in Equation (2)
N_{Sc} = Schmidt number
R_r = absorption rate with reaction
R = physical absorption rate
r = radial distance from impeller axis
z = vertical distance from tank bottom

Greek Letters

α = constant in Equation (1)
β = enhancement factor due to reaction
ϵ = dissipation energy in tank
$\overline{\epsilon}$ = average dissipation energy in tank
ν = kinematic viscosity

Subscripts

3 = quantity involved with respect to species being absorbed
4 = quantity involved with respect to species being desorbed

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