An Eddy Cell Model of Mass Transfer into the Surface of a Turbulent Liquid

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Experimental gas absorption studies for bubbles transported in turbulent pipe flow of water strongly indicate that liquid phase controlled mass transfer is due to surface renewal by turbulent eddies. Predictions of transport behavior from the conditions of turbulent flow cannot be made in support of this mechanism because no satisfactory theory of turbulent transport near a gas-liquid interface is available. This work considers a model of the hydrodynamic behavior near the surface which provides a link between the observed mass transfer behavior and the state of the turbulent field.

In this model, the very small scales of turbulent motion are considered to be controlling. These motions are idealized, and their flow and mass transfer behavior are solved analytically. The overall result for eddies of various sizes is related to the turbulent energy spectrum by using only the easily accessible parameter ϵ, the energy dissipation rate. This model gives quantitative agreement to within a factor of 2 for three widely different experimental situations including gas-liquid and liquid-solid interfaces. However, the predicted Reynolds number dependence is somewhat higher than the experimental result.

The model attempts to clearly define the basic physical process at the interface. Therefore, it indicates the direction for further experimentation needed to clarify the basic relationship between the mass transfer rates in the liquid phase and the hydrodynamic behavior of the turbulent liquid.

In a recent study (*1*) of mass transfer from bubbles flowing concurrently in a turbulent liquid, it was suggested that the mechanism of mass transport in the liquid phase was by renewal of the liquid at the bubble surface. This renewal was assumed to be due to the small scale eddies of the turbulent field rather than to any gross mean flow of fluid relative to the bubble. In attempting to establish theoretical support for this mechanism, it was found that no adequate theory existed in this particular case to relate interfacial mass transfer to the state of turbulence in the fluid. A simple model based on the turbulent mixing length concept was proposed, therefore, and was described in our earlier publication (*1*).

In the present paper a second model, which is felt to be physically more realistic, is presented to describe the turbulent renewal near a liquid surface. In this model, the mass transfer into a single idealized eddy located near the interface is calculated. The overall effect of the turbulence on the macroscopic mass transfer rate is determined from a consideration of eddies of all sizes and energies according to a proposed structure of the turbulent field. This model should apply not only to bubbles in concurrent turbulent flow, but equally also to any phase contacting situation in which fluctuating turbulent velocities make up the dominating velocity field.

The concept of surface renewal originally proposed by Higbie (*2*) and by Danckwerts (*3*) has been incorporated into more elaborate models by a number of more recent workers (*4* to *6*). The results of these models are similar to Danckwerts' result

$$k_L = \sqrt{\mathcal{D}s} \tag{1}$$

The well-tested dependence of k_L on the diffusivity to the one-half power in many gas/liquid systems is predicted by (1). However, no means of relating s to the state of liquid turbulence is provided. King (*7*) has described turbulent surface renewal in terms of eddy diffusivity, but the eddy diffusivity can only be empirically related to the turbulence from mass transfer behavior.

Calderbank and Moo Young (*8*) semiempirically related mass transfer from solids in a number of turbulent flow situations to the rate of energy dissipation by the turbulence

$$k_L \alpha\ (\epsilon\nu)^{1/4} \tag{2}$$

The pressure drop equation for turbulent pipe flow can be used to relate ϵ to N_{Re}:

$$\epsilon = 0.16\ N_{Re}^{2.75}\ \nu^3/D^4 \tag{3}$$

A physical interpretation of the model was not presented to describe the fluid motions and to permit extension to the gas/liquid case. Levich (*9*) considered that the mass transfer from a particle or bubble suspended in a turbulent stream is controlled by its velocity relative to the fluid as a result of the density difference between bubble and fluid, where the fluid is accelerating owing to turbulent motions. This theory predicts that the mass transfer coefficient should be proportional to the 0.75 power of the Reynolds number of the overall liquid flow. The above models are reviewed in more detail in reference *17*.

The turbulent transfer at gas-liquid free (clean) surfaces, at liquid-liquid and partially contaminated gas-liquid interfaces, and at fluid-solid surfaces can be satisfactorily compared and understood only when a physically realistic (but

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undoubtedly idealized) model of the velocity field near the various interfaces is available. Several aspects of this problem are considered in recent papers (*7, 11* to *15*), but no satisfactory quantitative link between mass transfer rates and the turbulent motions has emerged. This area of fluid mechanics needs a much improved understanding, because the computation of mass transfer rate is simple in principle once the fluid velocity field is known in detail.

The current model, therefore, provides this link by making use of the turbulent energy spectrum to superimpose the mass transfer behavior of idealized small eddy motions near the interface. Fluctuating turbulent velocities are supposed to be the dominating velocity field near the surface. The idea that the small scales of motion should be more efficient than the large ones for mass transfer across an interface is presented and examined in terms of the eddy cell model.

In a recent paper, Fortescue and Pearson (*16*) have presented a theory based on turbulent eddy cells that is very similar in approach to the present model. In Pearson's experimental situation (gas absorption into the surface of channel flow with artifically generated turbulence behind a grid), the large energy containing eddies are assumed to control the mass transfer. A comparison between the approach of Fortescue and the present theory is made. The present theory provides an extension of Fortescue's model to allow for the wide range of eddy sizes actually present in a well-developed turbulent field.

EXPERIMENTAL EVIDENCE FOR TURBULENT RENEWAL

In an earlier publication (*1*), data were given for an experimental investigation in which mass transfer from carbon dioxide bubbles of controlled size and frequency in a turbulent liquid field was measured in horizontal tubes of 5/16- and ⅝-in. I.D. Additional data for vertical tubes of the same sizes with upward concurrent flow of water and gas bubbles have been obtained also, and these results are reported in this work together with the previous data. Bubbles had diameters in the range 0.3 to 0.7 tube diam., and were separated by at least 5 tube diam. as they traveled along the tube. Superficial liquid Reynolds numbers were between 1,810 and 22,400.

Results are summarized in Figure 1. For well-developed turbulence the results are all represented (independent of bubble size) by

$$k_L = 0.019\ (\text{Tube Diameter})^{-0.85}\ N_{Re}^{0.52} \qquad (4)$$

where the tube diameter is in centimeters. The coincidence of both horizontal and vertical results for a given tube size at high N_{Re} provides good support for the proposal that the turbulent velocity fluctuations are the dominant mass transfer mechanism. Consider a bubble in horizontal flow. A very thin film of liquid with a high velocity gradient exists at the top of the bubble. In the absence of turbulent motions, this film would provide most of the mass transfer, because the remainder of the bubble surface is in contact with liquid moving at about the same velocity as the bubble. In vertical flow, this film between bubble and tube wall is very much thicker, although not absent because the bubbles travel eccentrically in the tube. If the film mechanism were controlling mass transfer, different results should be obtained for the horizontal and vertical cases because of the different geometries and velocity gradients. For turbulent renewal controlling, however, there should be little difference between the two cases. The bubbles occupy a large enough portion of the tube that the surface is exposed to the same range of radial positions in either case, in spite of the small difference in mean radial position.

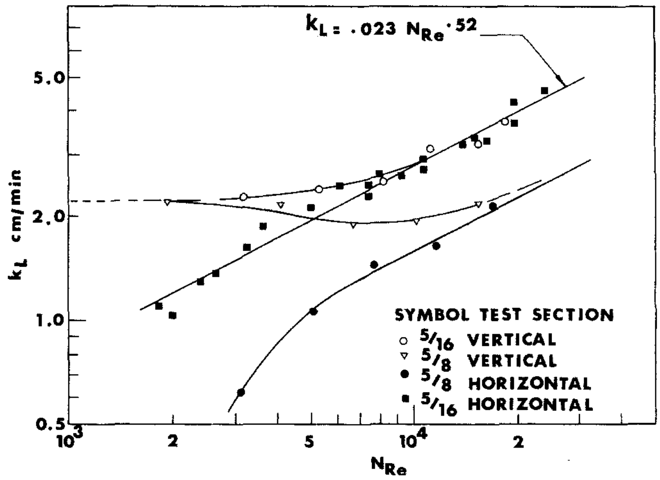


Fig. 1. Comparison of mass transfer coefficients for all test sections.

The absence of any dependence of the mass transfer coefficient on the bubble diameter for the large bubbles studied lends further support to this mechanism. Hayduk's (*18*) diffusivity exponent of about 0.5 for gas absorption in concurrent bubble flow is also consistent with the surface renewal viewpoint.

EDDY CELL MODEL FOR TURBULENT SURFACE RENEWAL

In the following development, the way in which an idealized eddy motion close to the interface operates to transport solute (or heat) from the surface into the bulk of the fluid will be considered in detail. The need for a better understanding of the fluid mechanics of turbulence near an interface has been stressed earlier. This need provides the incentive to develop the present model.

Surface renewals in the Danckwerts' sense (*3*) are approximations of turbulent upwellings in which fluid flows toward the interface and is then deflected parallel to the interface. The idea of instant renewal of fluid right to the very surface layer is not completely realistic hydrodynamically. The eddy diffusivity concept of King (*7*) is explainable in terms of upwellings, since the velocity components normal to the surface are responsible for the normal eddy diffusivity. These normal velocities decrease to zero at the surface for an upwelling motion, just as King's eddy diffusivity does. It is therefore felt that a model of these turbulent upwellings should fit in well with existing models and perhaps define them more exactly. In addition, the model should help to provide basic knowledge about the velocity field close to a turbulent surface, provide a link with the turbulent velocity spectrum through the size and energy of the upwelling motions, and provide an insight into the similarities and differences between transfer at different types of surface.

The approach proposed here will give some useful information about the liquid motions near the interface, even with an oversimplification of the behavior of the real turbulent fluid, provided the most essential features are retained. The model assumes that turbulent velocity fluctuations predominate over any mean relative velocity. Motions of size scales considerably smaller than the dimensions of the bubble or particle are assumed to exist, and for such scales the surface appears nearly flat. It is also supposed that all scales of motion smaller than the bubble are in the equilibrium (*19*) range of turbulence. The applicability of these conditions to bubble flow will be discussed after development of the model. Complete details and calculations are given in (*17*).

BASIS FOR EDDY CELL MODEL

The upwellings or eddies (Figure 2) which are effective for mass transfer across an interface flow toward the surface owing to turbulence forces (inertial, pressure, or viscous coupling). These elements are deflected by the surface, flow along the surface, and subsequently plunge back into the body of the fluid. This motion brings fresh fluid very close to the surface so that heat or mass is transferred to it by molecular diffusion. The fundamental difference in behavior between the two extreme surface types, solid and free fluid (clean gas-liquid), is the flow pattern within the upwelling, particularly close to the surface, due to the different boundary conditions, $v = 0$ and $\partial v/\partial y = 0$, respectively, at the surface. Therefore, it may be possible to predict differences in mass transfer behavior for the two surfaces from a simplified flow model. The liquid-liquid case has a behavior between these extremes, depending on the relative viscosities of the two liquid phases.

A second difference in flow pattern between solid and free fluid surfaces results because the restraint to velocity component u at the gas-liquid interface can only be provided by surface tension forces after the surface has yielded to provide sufficient curvature. This latter effect should be small for a high surface tension liquid, such as clean water, and for small scales of motion, because the curvature is very large even for a small amplitude, if the scale of the deformation is small. In the theory of Davies (*15*) for turbulent mass transfer, surface tension and surface deformation play an important role, as they do in Levich's theory (*20*), which forms part of the basis for Davies' theory. However, Davies' theory is concerned with eddies at the surface of a stirred vessel, where scales of motion are of the order of several millimetres. For the very much smaller scales of the equilibrium range of turbulence, the surface would appear to be very nearly flat relative to these eddy sizes. Furthermore, a clean surface should provide no restraining force against the separation or approach of surface elements of fluid. Hence, it is postulated that surface tension is not an important parameter in the transfer process under consideration.

If we suppose that an eddy as described above has superimposed on it a similar motion on a much smaller scale (Figure 3), then in the vicinity of this smaller eddy the mass transfer should be mainly controlled by the small scale motion if its energy is sufficiently large. This same argument should apply down to the smallest scales that exist. Hence it appears that the smallest scales in the field may control the overall transfer rate. If this is the case, then a greatly simplified analysis of the process may be possible, for these smallest motions are predominantly viscous, and no smaller eddies can be superimposed to complicate their flow pattern. Fortescue and Pearson (*16*) take the opposite view in their channel flow, that is, that the large scale energy containing eddies control the process. The view in our work is that the small scale motions may be more efficient for interphase transfer in spite of their low energy because they cause mixing within the very surface of a large eddy. The consequences of these two views will be compared with the experimental results in a later section.

In order to fully exploit our view of the mass transfer process, the following steps have been carried out:

1. First, the above small eddies were represented by greatly idealized viscous eddy cells for which the flow patterns and mass transfer could be evaluated.
2. The effect of cell size, energy of the motion, and molecular diffusivity (that is, N_{Pe} = velocity · length/diffusivity) on the local transfer rate of solute across the interface for the solid and free fluid surfaces were then determined.
3. From the theory of the energy of small scale turbulence, and the mass transfer energy dependence of the eddy cells, the relative contributions of different sized motions to the overall mass transfer were evaluated also.
4. The contributions to mass transfer for each size of eddy were superimposed to determine how the overall transfer depended on the parameters governing the size and energy of motion of the eddies, that is, on ϵ and ν.

IDEALIZED VISCOUS EDDY CELLS

An idealized eddy motion is required to make the fluid flow and convective diffusion equations tractable. The main features of the upwelling flow described earlier might be well represented by the two-dimensional motion shown in Figure 4, where a sinusoidal shearing motion of amplitude A exists at an arbitrary distance a beneath the surface. Because of symmetry, it is only necessary to consider the region between adjacent upflow and downflow stagnation points. This distance is arbitrarily supposed to be a also, giving a square flow cell, since it seems unlikely that very wide, shallow cells or very narrow, deep cells would occur. No consideration is given to the mechanism of driving such a motion from the body of the fluid. The motion in one eddy cell might closely represent a rotating element of fluid near the surface, as in Figure 5*a*. Alternately, it might represent a jet of fluid directed toward the interface and forced to flow back into the body of the fluid because of continuity considerations, as in Figure 5*b*. Furthermore, it is not supposed that all of the energy of the turbulence is in the form of these motions that are useful for mass transfer, but only some significant portion of the total energy.

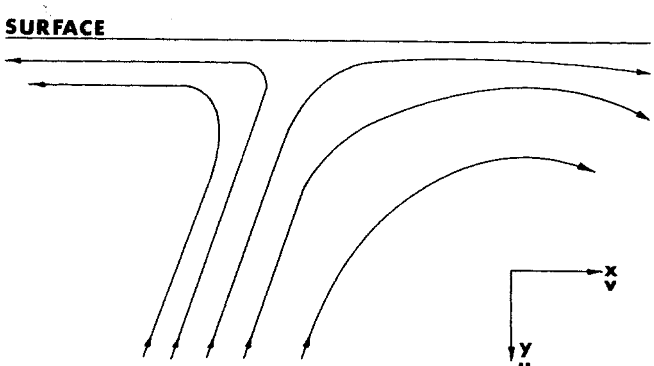


Fig. 2. Fluid eddy deflected by an interface.

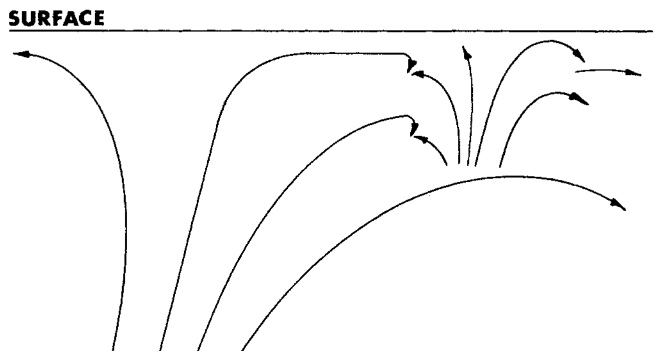


Fig. 3. A small eddy superimposed on a large body.

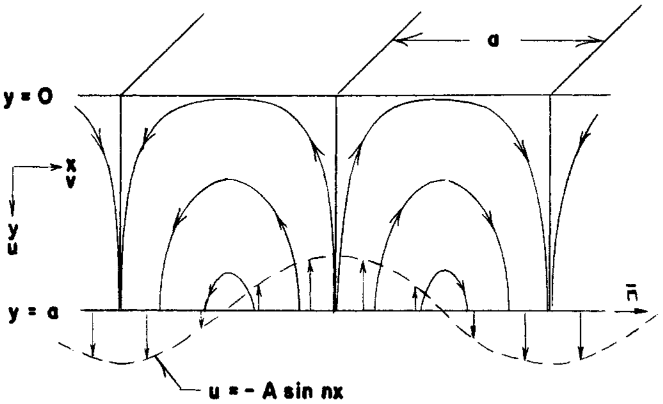
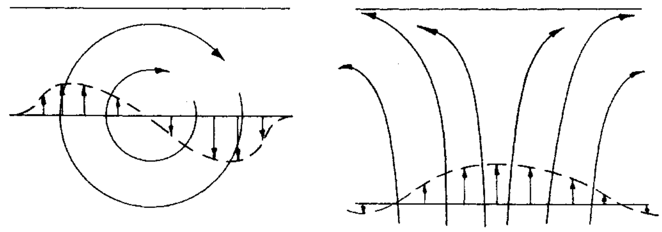


Fig. 4. Idealized viscous eddy cell.



(a) ROTATING ELEMENT (b) JET

Fig. 5. Possible eddy motions similar to the eddy cell.

The sinusoidal shearing motion is suggested by the Fourier analysis of the turbulent velocity field, in which velocities are decomposed into sinusoidal shearing motions of different amplitudes and wavelengths. The energy spectrum is based on this model of the turbulence. Real velocities in the turbulence are, in general, much more complicated than the sinusoidal shearing motion due to superposition of many components. However, in many regions the flow pattern relative to the surrounding fluid should be well represented by a single component, as indicated in Figure 5. An analysis of mass transfer rate into these regions should give a good estimate of overall mass transfer rates.

The flow within the cell is treated as viscous for ease of solution of the flow problem and in keeping with the postulate that the smallest (viscous) motions are most important for the mass transfer process. In order to further facilitate the solution of the flow and diffusion equations for the eddy cell, the motion is treated as time steady. This simplification is a reasonable approximation if the real eddy motions exist for long enough that their mass transfer behavior approaches the behavior of the ideal, steady cells. For the solid surface, the surface boundary conditions is $v = u = 0$. The free fluid surface is supposed to remain flat and to exert no force in the plane of the surface, as discussed above. Because of the very much lower viscosity of gas than liquid, no momentum is transferred across the interface. Therefore, the surface boundary conditions are $u = 0$ and $\partial v/\partial y = 0$ for the free surface. Solutions for the flow patterns and rate of solute diffusion into cells with both solid and free fluid surfaces have been obtained (*17*), and stream function results are given in Appendix A. For high N_{Pe}, the diffusion equations were solved by assuming a self-preserving concentration profile in the boundary layer to yield

$$\frac{k_L' a}{\mathcal{D}} = 0.815\ N_{Pe}^{1/3} \quad \text{(solid surface)} \tag{5}$$

$$\frac{k_L' a}{\mathcal{D}} = 0.445\ N_{Pe}^{1/2} \quad \text{(fluid surface)} \tag{6}$$

For low N_{Pe}, a finite difference estimate was made. The results are summarized in Figure 6. (Details of the lengthy derivations involved may be found in Appendix VI of reference *17*.)

The form of these two curves indicates that the absolute value of N_{Pe} for the eddy cells should have an important effect on whether the two types of surface will have similar or different mass transfer behavior. It is expected that $N_{Pe} > 100$, at least for solute diffusing through liquid ($\mathcal{D} \sim 10^{-5}$ sq.cm./sec.), and therefore it is supposed that the simple power law portion of the curves is of importance. An estimate of the size of N_{Pe} will subsequently be made.

ENERGY OF THE MOTIONS

In order to apply the results in Figure 6 to a turbulent fluid composed of a range of scales of motion, the relative energy of different sized motions must be compared. The energy spectrum of the turbulence provides a means of making this comparison. The energy spectrum is based on a Fourier decomposition of the turbulent velocity field, as discussed above. The energy spectrum indicates how the turbulent energy is distributed over the various wave numbers of the Fourier components. The function $E(n)$ is the kinetic energy per unit mass of fluid per unit increment of wave number. Certain features of the spectrum have been well established theoretically and experimentally (*19*).

For well-developed turbulence, there exists a range of small scales of motion that are isotropic and dominated by inertial forces. In this inertial subrange, the structure of the turbulence is a universal function of ϵ and the wave number n:

$$E(n) = 0.45\ \epsilon^{2/3}\ n^{-5/3} \tag{7}$$

Viscous dissipation of energy is the main feature at the smallest wave numbers and causes the spectrum to fall off more steeply than $n^{-5/3}$ beyond a value of approximately $1/3\ n_d$, where

$$n_d = (\epsilon/\nu^3)^{1/4} \tag{8}$$

The size of the idealized eddy cell corresponds to a wave number $n = \pi/a$. In the cell shown, the motion corresponds only to wave numbers which lie in a plane parallel to the surface, and so represents only an infinitesimal fraction of the total energy. However, if an analysis were made for similar motions for all wave numbers which make an angle within say 30 deg. of the surface, it seems probable that the mass transfer behavior would not be significantly different from the parallel case. The one-dimensional energy spectrum, Equation (7), represents the energy of only the components of velocity normal to a given wave number (parallel to the surface in this case). Therefore, Equation (7) is directly applicable for estimating the amplitude of the shearing motions in the idealized cells shown in Figure 4. This amplitude is proportional to the square root of the energy of motions of the size range under consideration.

If eddy motions are considered which have wave numbers within the range Δn, then the energy in these motions is $E(n)\Delta n$. To compare the mass transfer contribution due to different sized motions, the wave number increments must be a constant fraction of the wave number, that is, $\Delta n \propto n dn$, where the increment dn is constant across the spectrum. The energy within the increment Δn is proportional to $n\ E(n)$. Therefore, the amplitude A of the eddy cell velocity is proportional to $\sqrt{nE(n)}$. For the inertial subrange this results in

$$A \propto \epsilon^{1/3}\ n^{-1/3} \quad (9)$$

For an eddy motion of scale a, Levich (*21*) indicates that the characteristic velocity is of the same order as $(\epsilon\, a)^{1/3}$, a result equivalent to Equation (9) but which shows that the constant of proportionality is of the order of unity.

Approximate absolute values of the eddy cell Peclet number have been estimated from the above result (*17*). In the present pipe flow, the inertial subrange is not developed, but the size and velocity of the small scale motions should be of the same order as given by Equations (8) and (9). At $N_{Re} = 10{,}000$, a scale of wave number $1/3\, n_d$ ($a \sim 0.05$ cm.) has an amplitude $A \sim 5$ cm./sec. and $N_{Pe} \sim 3{,}000$, which gives by Equation (6) $k_L \sim 3$ cm./min. for the free fluid surface. This result is in the same range as the experimental values, which indicates that motions of this size could make a significant contribution to mass transfer if they reached the interface.

The above discussion of the energy of turbulent motions applies to the bulk fluid far from any surface, whereas the present region of interest is immediately adjacent to the surface. However, it seems reasonable that a motion of size a will not be much affected by a surface unless it is within approximately a distance a from the surface. Furthermore, the way the motion will be affected by the surface over the distance a must be more or less as described by the eddy cell model. Hence, it is supposed that the bulk turbulent energy spectrum can be applied to the eddy cell model adjacent to the surface. Fortescue and Pearson also made this assumption regarding large eddies.

The initial postulate that the mass transfer is controlled by the smallest scales of motion can now be tested. The local mass transfer coefficient k_L' will be estimated as a function of cell size over the inertial subrange to see if wave numbers close to $1/3\, n_d$ predominate. The viscous treatment is not applicable for these inertial motions, but if their mass transfer behavior is not too different from viscous eddies, then the analysis should be adequate to indicate whether the smaller scales are controlling. From Equations (5) and (9) and the definition of N_{Pe}, for the solid surface

$$k_L' \propto \mathfrak{D}^{2/3}\ \epsilon^{1/9}\ n^{5/9} \quad (10)$$

For the free fluid surface, by applying Equation (6):

$$k_L' \propto \mathfrak{D}^{1/2}\ \epsilon^{1/6}\ n^{1/3} \quad (11)$$

These expressions show that in the present model of turbulent transfer, the smaller scales (higher n) are most effective. However, the exponents on n are so low in Equations (10) and (11) that the inertial subrange cannot be ignored as was initially postulated. In fact, the inertial motions are expected to thin the concentration boundary layer more than in the viscous case, and therefore the larger scales may be of more importance than Equations (10) and (11) indicate. The only possible conclusion from the present model, therefore, is that mass transfer is not due to any narrow range of scales of motion, but is due to scales which extend from the smallest viscous motions well into the inertial motions, with only a minor preference for the smaller scales.

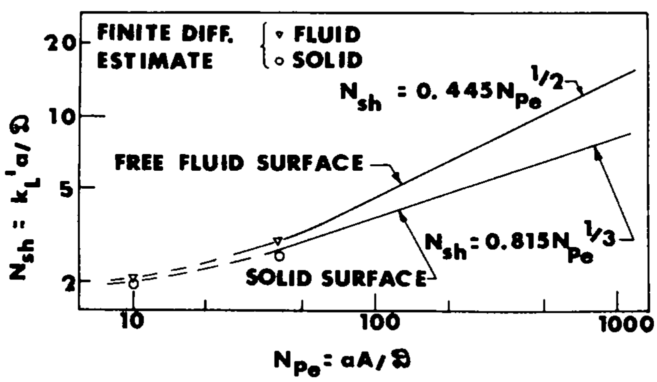


Fig. 6. Mass transfer into idealized eddy cell.

OVERALL TRANSFER RATE k_L

To determine the overall transfer coefficient, it is necessary to add up the contributions due to scales of all sizes. It has been assumed that motions of each scale behave independently. As previously discussed, this assumption is expected to be satisfactory for the small, viscous scales. However, it has been found that the larger, inertial scales may be of some importance to transfer. Therefore, the assumption of independence is of doubtful validity for the large scales. Furthermore, the viscous model is not applicable to the inertial motions. In spite of these possible weaknesses of the model, the integration will be carried out, since a large portion of the range consists of small, viscous motions. It is also possible that the mass transfer behavior of the inertial motions is not too different from the viscous motions.

The proportionalities in Equations (10) and (11) hold if increments $\Delta n \propto n dn$ are considered. In order to integrate with respect to the variable n, Equations (10) and (11) must be converted to the basis of equal increments of dn. That is, $k_L'(n) = k_L'/n$ expresses the contribution to mass transfer coefficient per unit wave number.

A number of functions have been proposed for the energy spectrum in the dissipation range. The Kovaszney spectrum (*19*) will be used for the present purpose:

$$E(n) = 0.45\ \epsilon^{2/3}\ n^{-5/3} \left[1 - \frac{0.6\nu}{\epsilon^{1/3}}\ n^{4/3}\right]^2 \quad (12)$$

This function is identical with Equation (7) in the inertial subrange and drops to zero at a value $n_0 = 1.47\ n_d$. Using Equations (5) and (12), and recalling that $A \propto \sqrt{nE(n)}$ and $N_{Pe} = aA/\mathfrak{D} = \pi A/n\mathfrak{D}$, we obtain the following relation for the solid surface:

$$k_L'(n) \propto \epsilon^{1/9}\ \mathfrak{D}^{2/3}\ n^{-4/9} \left[1 - \frac{0.6\nu}{\epsilon^{1/3}}\ n^{4/3}\right]^{1/3} \quad (13)$$

The upper limit of integration is n_0. In establishing the lower limit, it is supposed that all scales smaller than the dimensions of the particle or bubble are involved. This dimension corresponds to a wave number n_B. The overall mass transfer coefficient for the solid surface is, therefore

$$k_L \propto \int_{n_B}^{n_0} \epsilon^{1/9}\ \mathfrak{D}^{2/3}\ n^{-4/9} \left[1 - \frac{0.6\nu}{\epsilon^{1/3}}\ n^{4/3}\right]^{1/3} dn \quad (14)$$

The integrand in Equation (14) can be expanded by the binomial theorem and integrated. If at least three octaves of scales exist in the inertial subrange below the particle or bubble dimension, then $n_B \sim 1/20\ n_0$, and the lower limit can be omitted from the integrated equation with only a small error. Equation (14) can be integrated and simplified to

$$k_L \propto \left(\frac{\nu}{\mathfrak{D}}\right)^{-2/3} (\epsilon\nu)^{1/4} \quad (15)$$

Similarly, for the fluid surface

$$k_L \propto \int_{n_B}^{n_0} \epsilon^{1/6}\ \mathfrak{D}^{1/2}\ n^{-2/3} \left[1 - \frac{0.6\nu}{\epsilon^{1/3}}\ n^{4/3}\right]^{1/2} dn \quad (16)$$

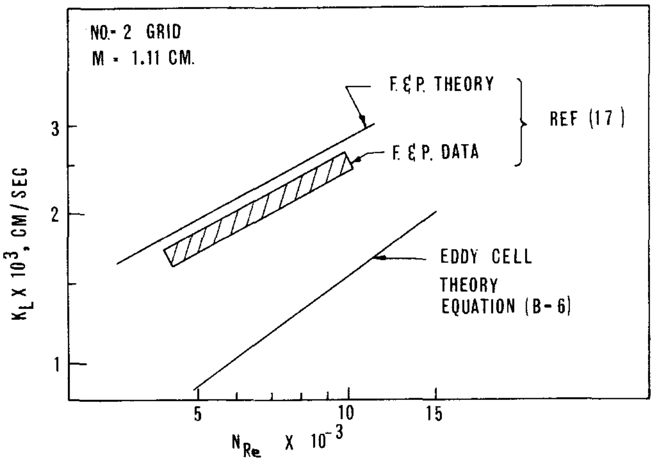


Fig. 7. Mass transfer into a turbulent channel flow.

which results in

$$k_L \propto (\nu/\mathcal{D})^{-1/2} \; (\epsilon\nu)^{1/4} \qquad (17)$$

The exponents on ϵ and ν obtained from the eddy cell model are consistent with the dimensional requirement that can be derived (*17*) from the foregoing assumptions about surface tension and the parameters controlling the turbulent structure. The Schmidt number dependence is also consistent with that found by Scott and Hayduk (*18*) for the gas-liquid interface.

COMPARISON WITH EXPERIMENTAL RESULTS

The constant of proportionality in Equation (9) is close to unity. If the constants are carried through the derivation of Equations (15) and (17), a constant of about 0.4 is obtained for each equation. The result for the solid surface is identical in form with Calderbank and Moo Young's empirical result [$k_L = 0.2\ N_{Sc}^{-2/3}\ (\epsilon\nu)^{1/4}$], and the absolute value is within about a factor of 2. This is felt to be quite good agreement, when we consider that the eddy cell model is derived entirely from first principles, using the turbulence theory to describe the velocity field.

For the fluid surface in the present bubble flow work, the mass transfer coefficient can be calculated from Equations (3) and (17). For $N_{Re} = 10{,}000$ in the 5/16-in. tube, the model predicts $k_L = 4.5$ cm./min., compared with an experimental value of 2.8 cm./min.; this agreement is quite good. However, the Reynolds number exponent ($\epsilon^{1/4} \propto N_{Re}^{0.69}$) in Equation (17) is considerably higher than the experimental exponent of 0.52. No other experimental data are available to provide a good test of the validity of the model. Situations in which well-developed scales of motion exist smaller than the surface, and in which the surface is freely transported at the mean fluid velocity, are difficult ones for which to obtain reliable mass transfer coefficients. Calderbank's data (*8*) provide one test of Equation (15), and the agreement has been noted above.

Fortescue and Pearson (*16*) have provided data for gas absorbing into the surface of a turbulent channel flow. The turbulence was generated by flow through a grid and is well characterized by Batchelor and Townsend's measurements on decaying turbulence (*22*). In Appendix B, the energy dissipation ϵ is estimated for the channel from Batchelor's theory, and this is applied to Fortescue's experimental conditions to predict the mass transfer coefficient from Equation (17). The predicted values are summarized in Figure 7 along with the experimental data and Fortescue's theoretical values. The agreement with experiment is not as good for the eddy cell theory as for Fortescue's theory. However, the former theory is still within a factor of less than 2 of the measured values. As in the case of bubble flow, the N_{Re} exponent (0.5) is less than the eddy cell theory predicts.

DISCUSSION

The number of situations in which the eddy cell model is applicable is uncertain. For channel flow, Fortescue's theory gives better agreement with the measurements. However, the eddy cell theory, which is able to predict mass transfer coefficients to within a factor of 2, for three widely different situations, appears to possess a good deal of potential merit. Clearly, the basic concents on which this model rests cannot be confirmed solely by the degree of agreement with mass transfer results, but from this order of magnitude agreement it can be inferred that the concepts used are reasonable and show a promising potential.

The two models are very similar but differ in the size of eddies considered to be controlling. Fortescue has chosen the large eddies because they contain the majority of the turbulent energy. The mixing length model proposed by the present authors previously (*1*) is based on the same idea and yields a similar result. However, it is felt that even a very weak eddy at the surface of a large eddy would greatly increase the absorption rate over that occurring if molecular diffusion only were acting at the surface of the large eddy, and therefore small scale motions should be most important. Our analysis indicated [Equations (10) and (11)] that the smaller scales contribute the most to the mass transfer process but that the contributions extend well into the larger scales. The main assumption of the eddy cell theory as well as of the theory presented by Fortescue and Pearson lies in applying a viscous velocity profile to motions where inertial forces are very important, and where smaller motions result in a complex effective viscosity.

It might be argued that the small scale motions proposed as a controlling mechanism in the eddy cell theory might be damped out by the surface. However, there is no force available to restrain motion parallel to the surface unless the surface is solid or has a contaminating film. Experiments similar to those reported in the present work, with large solid spheres or contaminated bubbles used, could provide a useful test of the model, since Equations (15) and (17) predict that the coefficients for solid and free fluid surfaces should differ as a result of the Schmidt number only. A large difference in coefficient for clean and contaminated bubbles would indicate that damping of the eddies by the contaminated surface is an important factor.

The question of the size of motions that are important is a possible area for further research. Careful measurement of the velocity field close to fluid and solid surfaces that are moving with the mean fluid velocities should be the next step in studying this question. Such measurements would fill a gap in the knowledge of turbulence and should be of value to other fields in addition to mass transfer. Alternately, some optical means might be devised to study the structure of fluctuations in mass transfer rate on a turbulent surface undergoing mass transfer. For example, the total solute in a layer beneath the surface is a measure of concentration boundary-layer thickness, and therefore transfer rate might be estimated by the absorption of light by some component in solution. Velocity field measurements of this kind are currently being carried out by the authors.

The potential usefulness of the eddy cell model is great if it can be confirmed because it provides a unified theory to cover different types of interface and because it uses the fundamental energy dissipation rate ϵ as a link to the theory of fluid flow for turbulent fields which are not well characterized. Furthermore, it provides a clear and hydrodynamically realistic picture of the transfer process near the surface as a basis for further theoretical developments and measurements.

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NOTATION

A = velocity amplitude in idealized eddy cell, cm./sec.
a = width of idealized eddy cell, cm.
D = tube diameter, cm.
$\mathcal{D}$ = diffusivity of carbon dioxide in water, sq.cm./sec.
d_B = bubble diameter, cm.
$E(n)$ = turbulent energy spectrum (three dimensional) function, cc./sec.^{2}
k_L = liquid-phase controlled mass transfer coefficient, cm./min.
k_L' = mass transfer coefficient for an idealized eddy cell; $k_L'(n)$, contribution to overall coefficient, on the basis of unit wave number
L = length of test section, ft.
M = rod spacing in turbulence generating grid, cm.
N_{Pe} = Peclet number for idealized eddy cell, $aA/\mathcal{D}$
N_{Re} = Reynolds number for single-phase pipe flow; superficial N_{Re} where used for bubble flow
n = wave number, cm.$^{-1}$; n_B wave number of bubble dimension; n_d, wave number range of main dissipation; n_0, wave number at which $E(n) = 0$ in Kovasznay spectrum
P = pressure
s = surface renewal rate, sec.$^{-1}$
t = time
U = mean flow velocity, cm./sec.
u = velocity normal to surface in eddy cell, cm./sec.
v = velocity parallel to surface, cm./sec.
X = distance downstream of grid in channel flow, cm.
x, y = coordinates in eddy cell
ϵ = rate of energy dissipation by turbulence per unit mass, sq.cm./sec.^{3}
ν = liquid kinematic viscosity, sq.cm./sec.
Ψ = stream function for eddy cell, sq.cm./sec.

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APPENDIX A: EDDY CELL VELOCITY PROFILES

In terms of the stream function Ψ:
For the solid surface

$$\Psi = a\left[\left(-0.124 - 0.0935\frac{\pi}{a}y\right)\sinh\left(\frac{\pi}{a}y\right) + 0.124\frac{\pi}{a}y\cosh\left(\frac{\pi}{a}y\right)\right]\cos\left(\frac{\pi}{a}x\right) \quad \text{(A1)}$$

For the free fluid interface

$$\Psi = aA\left[0.0282\frac{\pi}{a}y\cosh\left(\frac{\pi}{a}y\right) - 0.117\sinh\left(\frac{\pi}{a}y\right)\right]\cos\left(\frac{\pi}{a}x\right) \quad \text{(A2)}$$

The constants in these equations are applicable only for a square cell.

APPENDIX B: EDDY CELL THEORY APPLIED TO CHANNEL FLOW TURBULENCE

By definition

$$\epsilon = -\frac{3}{2}\frac{\partial u^2}{\partial t} \quad \text{(B1)}$$

From Batchelor's measurements on decay of turbulence downstream of a grid in a wind tunnel (*24*)

$$\overline{u^2} = \frac{0.008\,U^2}{\dfrac{X}{m} - 10} \quad \text{(B2)}$$

t = decay time of fluid after passing through grid = X/U. Therefore, from (B1) and (B2)

$$\epsilon = \frac{0.012\,U^3 M}{(X - 10M)^2} \quad \text{(B3)}$$

This result applies to channel flow of liquid because of the universal nature of (B2) for a given type of mesh.

The dimensions of Fortescue's apparatus provide a conversion from channel flow Reynolds Number N_{Re} to mean flow velocity U:

$$U = 7.25\,(10^{-4})\,N_{Re} \quad \text{(B4)}$$

From Equations (B3), (B4), and (21), with constant $\cong 0.4$, the mass transfer coefficient is obtained as a function of X. For Fortescue's grid No. 2 with $M = 1.11$ cm. and ν and $\mathcal{D}$ for the system water — carbon dioxide

$$k_L(X) = 0.78\,(10^{-5})\frac{N_{Re}^{0.75}}{(X - 11)^{1/2}}\ \text{cm./sec.} \quad \text{(B5)}$$

Overall k_L is obtained by integrating over the exposed channel length

$$k_L = \frac{\int_{L_0}^{L} k_L(X)\,dx}{L - L_0} = 1.5\,(10^{-6})\,N_{Re}^{0.75}\ \text{cm./sec.} \quad \text{(B6)}$$