Turbulence Phenomena at Free Surfaces

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Gas absorption by eddies at the free surface of a strongly turbulent liquid is interpreted quantitatively in terms of the Levich approach. The mass transfer coefficient is calculated to vary as *Re* to a relatively high power (1.3 to 1.5).

Experiments on free turbulent jets of liquids in gas are in general accord with this theory. For turbulent films of liquids flowing over large roughness elements in "wake-interference" flow, the turbulence is anomalously effective in promoting gas absorption.

Traces of surface-active agents suppress the surface renewal. This is analyzed theoretically: the results compare favorably with gas-absorption for stirred cells and flow experiments over smooth plates. For "wake-interference" flow over rough plates, the reduction in the rate of gas absorption by surface-active material is more pronounced than predicted for ordinary turbulence. But even in the presence of a surface-active agent, the roughness still gives an advantage in mass transfer rates as compared with smooth plates.

THEORY OF MASS TRANSFER AT FREE SURFACES OF TURBULENT LIQUIDS

Mass transfer at the free surface of a turbulent liquid depends on the eddy behavior close to the surface. The word "close" (not "at") is used here, because the observed mass transfer coefficients are very much smaller than would correspond to the bulk eddy diffusivities D_E (which can be of the order 10^5 times greater than the molecular diffusivities D). Also, a dependence of k_L on $D^{0.5}$ has repeatedly been observed.

A quantitative theory of the approach of an eddy to a free surface has been put forward by Levich (*1*). His basic equations can be summarized as follows. As the eddy of liquid approaches the free surface, the latter becomes deformed. This deformation gives rise to a pressure ($2\sigma/R$, where σ is the surface tension and R the local radius of curvature) which opposes the progress of the eddy. The pressure fluctuation of the arriving eddy is ρv_0^2 (where ρ is the liquid density and v_0 is the characteristic turbulence velocity), so if the eddy is not to splash through the surface

$$2\sigma/R = \rho v_0^2 \qquad (1)$$

From a further analysis of the eddy movements near a free surface, it can be shown (*1, 2*) that there is at the surface a mathematically equivalent diffusion layer of thickness δ_2 (defined by D_E being less than D within this layer) given by

$$D = D_E = 0.8\, \delta_2^2\, v_0/R$$

Mass transfer through this layer δ_2 is essentially the rate-controlling factor, and by substituting for R from Equation (1) it follows readily (*1, 2*) that

$$k_L = 0.32\, D^{1/2}\, v_0^{3/2}\, \rho^{1/2}\, \sigma^{-1/2} \qquad (2)$$

Equation (2) should be of general application to fully developed turbulent flows.

For a free turbulent jet emerging from a tube, the eddies are initially characteristic of the developed turbulence within the tube, though the turbulence decays appreciably further along the free jet. Near the exit of the tube, however, the turbulence is essentially that obtaining in the tube, for which it is well known that v_0, the shear stress velocity, gives a good approximation to the velocity of eddy approach towards the surface. The Blasius equation can be applied to calculate v_0 for a tube of diameter d, and substitution into Equation (2) gives:

$$k_L = 0.028\, D^{1/2}\, Re^{1.31}\, \mu^{3/2}/(\rho d^{3/2}\, \sigma^{1/2}) \qquad (3)$$

In terms of dimensionless groups this becomes

$$Sh = 0.028\, Re^{5/16} We Sc^{1/2} \qquad (4)$$

where $We = v_m(\rho d/\sigma)^{1/2}$, and the other groups have their usual significance.

From Equation (3) it is clear that a rather high power dependence on *Re* is to be expected for free turbulent jets.

EXPERIMENTS ON MASS TRANSFER INTO FULLY TURBULENT LIQUIDS

To test Equation (2) experimentally, it is necessary to achieve a fairly high degree of turbulence in the vicinity of the liquid surface. This cannot be achieved readily in stirred cells (with unbroken surfaces), nor in the flow of water in a channel downstream of a grid. In these systems k_L varies as *Re* to a power usually lying in the range 0.5 to 1.1.

We have studied two methods of inducing strong turbulence near the surface: the first involves vertical turbulent jets (restrained from spreading by the forces of surface tension). The second involves flow of thin films of liquids over inclined plates with large roughness elements in various geometrical arrangements. The results of mass transfer studies on these systems will now be described.

Mass Transfer to Turbulent Restrained Jets

If liquid at $25{,}000 > Re > 7{,}000$ emerges from a tube into a gas, the jet remains intact for some distance, without breaking up into drops (*3*). This is because the random eddy movements in the surface break the pattern of coherent, periodic movements tending to pinch the liquid stream into discrete drops. Such a turbulent jet offers an opportunity to test Equations (3) and (4) rigorously. For the absorption of different gases into turbulent jets of water, it has been found (*3*) from direct analysis of the dissolved gas in the liquid jet that $k_L \propto D^{0.55} Re^{1.34}$, in good agreement with the predictions of Equation (3).

In terms of the dimensionless groups of Equation (4), the results of Davies and Ting (*3*) are as shown in Figure 1. A line of slope 1.0 has been drawn through the points

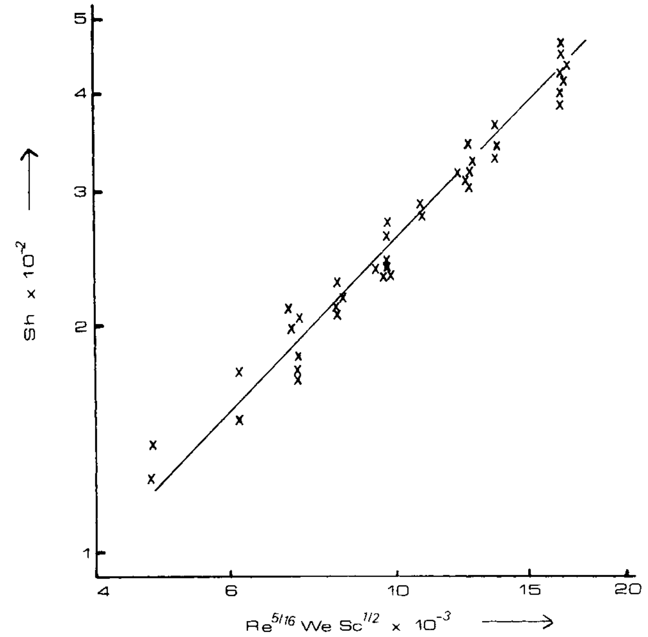

Fig. 1. Absorption of carbon dioxide and of hydrogen into turbulent jets of water, plotted on a log-log scale in terms of dimensionless groups. The original data of Davies and Ting (3) are corrected here for surface area changes due to the eddy protrusions.

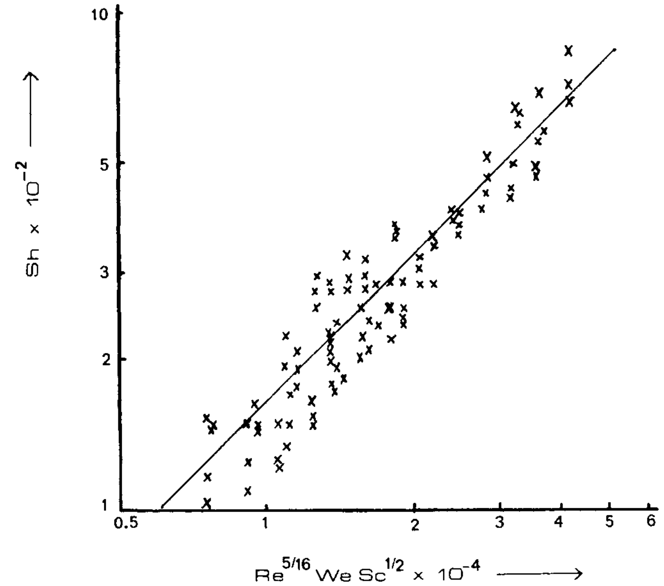

Fig. 2. Absorption of carbon dioxide, hydrogen, and helium into turbulent jets of kerosene, for various jet lengths and 2 nozzle diameters (*4*). A straight line of slope unity has been drawn through the points: it corresponds to $Sh = 0.016\ Re^{5/16}WeSc^{1/2}$. The reproducibility of the numerical factor is ± 0.003.

on this log-log plot to check Equation (4). The numerical factor is found from the graph to be 0.025 ± 0.002, slightly below the theoretical value. Jets of water from other nozzles gave numerical factors of 0.03 and 0.02.

To study a liquid of different surface tension σ, Davies and Hameed (*4*) used turbulent jets of kerosene. The results for the absorption of several gases were that $k_L \propto D^{0.54}Re^{1.4}$. Results (on a log-log scale) are shown in Figure 2: again a line of slope 1.0 drawn through the points is satisfactory. The numerical factor is found from the data of this figure to be 0.016 ± 0.003, rather below the theoretical value.

Eddy Promotion by Large Roughness Elements

A film of liquid flowing down a *smooth* vertical plate departs from purely laminar flow when $Re > 500$. Here Re is defined by

$$Re = \frac{v_m B_f}{\nu} = \frac{V_b}{\nu} \tag{5}$$

where v_m is the mean linear velocity of flow, B_f is the mean thickness of the liquid film, V_b is the volumetric flow rate per unit width of plate, and ν is the kinematic viscosity of the liquid. Even at $Re = 1500$ the turbulence over a smooth plate is transitional rather than fully developed.

To promote turbulence when Re is as low as 200, various types of *roughness* can be utilized. Davies and Warner (*5*) explored the most effective form of roughness to promote turbulence and so enhance the rate of gas absorption into the falling film. The sharp-edged roughness elements were cut in various geometrical arrangements, as shown in Figure 3. Plates were positioned at various angles θ to the horizontal.

The rate of absorption of a gas (for example, carbon dioxide) into the film of water is best determined by analysis of the water, using gas-solid chromatography (*5*). The rates were up to 3.6 times faster than for smooth plates, as is shown in Figure 4. The greatest enhancement in the mass transfer ratio is found when s_1/e lies between 5 and 6.7, and $Re = 700$: at this Reynolds number the flow over a *smooth* plate is still essentially laminar, but the geometry of the *rough* plate induces the so-called wake-interference flow. The latter (Figure 3c) occurs

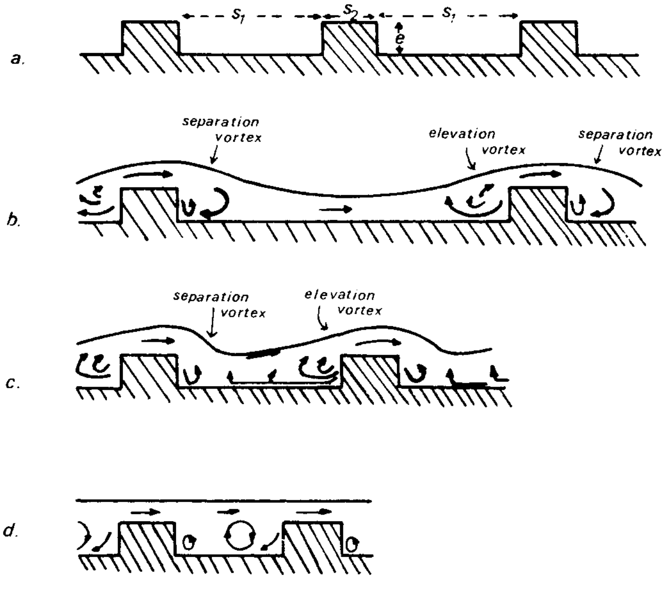

Fig. 3. Ridge dimensions and the three regimes of roughness flow on base plates. a. Typical base plate showing dimensions s_1, s_2 and e. For all the plates s_2/e was constant at 1.67, and the profile of the ridges (running across the plate) was rectangular. b. Flow pattern of "isolated roughness" flow. This occurs when $s_1/e \geqq 10$, $\theta = 24°56'$, $Re = 400$ to 500, e = 1.9 mm. Here the separation and the approach vortices are quite separate. Water flow is from left to right in all figures. c. "Wake interference" flow, occurring when $6.7 \geqq (s_1/e) \geqq 5$, other parameters being as above. Here the approach vortex interferes with the separation vortex (or "wake"), leading to an appreciable reverse flow and intense oscillatory vorticity between the ridges. The mass-transfer coefficient is particularly great under these conditions. d. "Quasi-smooth" flow, occurring when $s_1/e = 3.3$, other parameters being as above. The liquid is essentially skimming over the crests of the ridges and over the stable vortices in the grooves.

when the vortices interfere with each other strongly, causing oscillations across the span of the plate, giving the liquid surface a flickering, lattice-like appearance. The period of these spontaneous pulsations is of the order 0.1 sec.

For the rough plates with $e = 1.9$ mm., k_L increases as $Re^{0.44}$ in the range $200 < Re < 2{,}000$. A typical log-log plot is shown in Figure 5, for water passing at different flow rates V_b down the rough plate. For plates with e only 0.9 mm., k_L increases as $Re^{0.36}$.

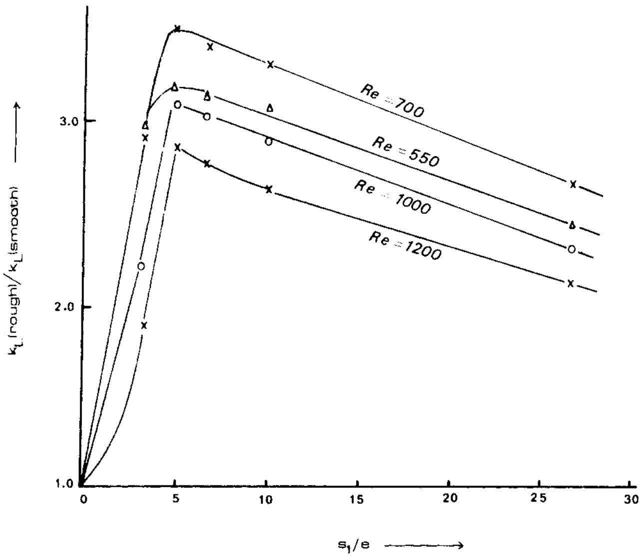

Fig. 4. Mass transfer coefficients for carbon dioxide gas dissolving into a film of pure water over roughness elements at various values of s_1/e, relative to the mass transfer coefficients for flow over a smooth plate (5). Here $\theta = 25°$, and the Reynolds number is written against each curve. The plates are effectively smooth when either $s_1 \rightarrow 0$ or $s_1 \rightarrow \infty$, for a given value of e, as inspection of Figure 3 shows.

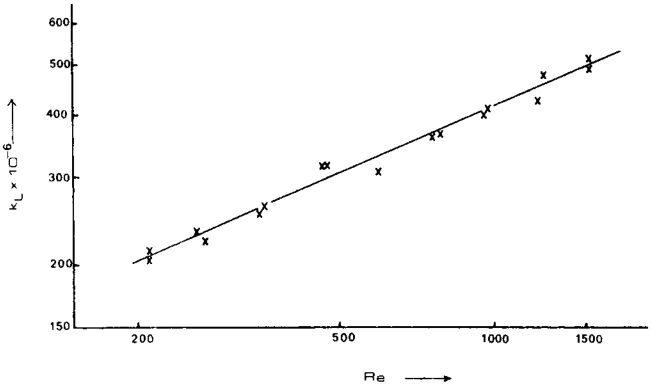

Fig. 5. Log-log plot (5) of k_L (in m./sec.) for carbon dioxide absorption into water at various Re values over rough plate with e = 1.9 mm., $s_1/e = 6.7$, and $\theta = 25°$. Slope of line drawn through points is 0.44.

To compare these observed dependences of k_L on Re with theory [that is, Equation (2)], we need to evaluate v_0 from the force balance equation

$$\tau_0 = B_f \, \rho \, g \sin \theta \qquad (6)$$

that is

$$v_0 = (\tau_0/\rho)^{1/2} = (B_f g \sin \theta)^{1/2} \qquad (7)$$

Hence the theoretical Equation (2) becomes

$$k_L = 0.32 \, D^{1/2} \, B_f^{3/4} \, g^{3/4} \, (\sin \theta)^{3/4} \, \rho^{1/2} \, \sigma^{-1/2} \qquad (8)$$

The film thickness B_f increases with Re: the exact relation is found using Equation (5), substituting for v_m values measured directly in photographic studies of the liquid film. This technique (5) involves a frame-by-frame analysis of high speed photographs of solid particles sprinkled on to the surface. For such a strong turbulence over very rough plates, we have equated the measured surface velocities to the mean velocity in the liquid film. Such experiments show (5) that $v_m \propto Re^{0.48}$, whence one deduces that $B_f \propto Re^{0.52}$. Hence Equation (8) predicts that for a falling liquid film $k_L \propto Re^{0.39}$. The experimental exponents (0.36 to 0.44) are thus in general accord with theory.

The numerical values of k_L calculated by substituting v_0 [determined by Equation (7)] into Equation (2) are, however, considerably lower than those measured. Typical values for the absorption of carbon dioxide are shown in Table 1, columns 5 and 6. The reason for the discrepancy is that the eddy flow pattern about the large, sharp-edged, roughness elements is of a very special type: the velocity fluctuations towards the surface are much greater than in isotropic or pipe-flow turbulence. A recent visualization examination (6) showed that the local eddy velocities v' could be as great as 41% of v_m (compared with v_0 being about 10% of v_m). Thus to use $v_0^{3/2}$ would be expected to give results which are too low by a factor of $4^{3/2}$, that is, by a factor of 8. The calculated values of k_L thus derived (2) are shown in Table 1, column 7: agreement with experiment is reasonable in view of the simplicity of the correction for what is, in reality, a very complicated turbulent flow pattern.

EDDY SUPPRESSION BY SURFACE-ACTIVE AGENTS

At a clean surface (having no adsorbed surface-active impurities) there can be no tangential stress to oppose the turbulent fluctuations in the plane of the surface, that is, surface renewal is unimpeded. If a *little* surface-active material adsorbed at the surface, the surface film must be locally compressed as fresh eddies sweep into the surface, as Figure 6 shows. With *considerable* adsorption of sur-

Table 1. Velocities, Derived Film Thicknesses, and Calculated and Experimental k_L Values, for Carbon Dioxide Absorption into Water Flowing Over a Plate of $e = 1.9$ mm., $s_1/e = 6.7$, $\theta = 24°56'$

Re, from Equation (5)	v_m as measured m./sec.	B_f, from Equation (5), mm.	v_0 calculated from Equation (7), m./sec.	k calc. from Equation (8), m./sec.	k for CO_2, experimental (5), m./sec.	k calc. (2), allowing for $v'/v_0 = 4$
170	0.33	0.46	0.044	16×10^{-6}	190×10^{-6}	130×10^{-6}
400	0.50	0.72	0.055	22×10^{-6}	270×10^{-6}	170×10^{-6}
700	0.66	0.95	0.063	27×10^{-6}	350×10^{-6}	220×10^{-6}
1000	0.78	1.2	0.071	31×10^{-6}	400×10^{-6}	250×10^{-6}
1500	0.94	1.4	0.077	36×10^{-6}	480×10^{-6}	280×10^{-6}

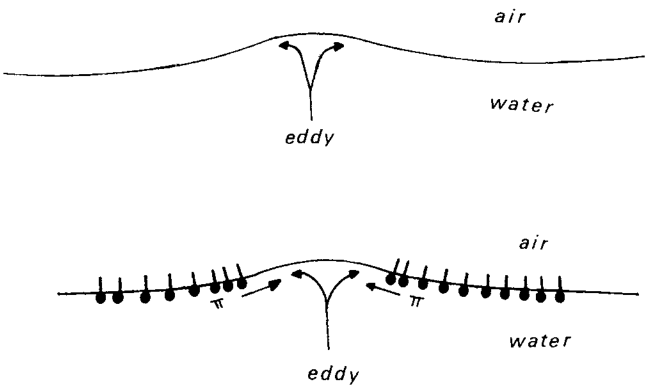

Fig. 6. Approach of eddy to (a) clean surface; and (b) to surface with film of surface-active agent present. For the film-covered surface, an additional force (arising from the reverse spreading pressure Π) opposes the eddy as in Equation (9).

face-active material, the surface becomes immobilized, and is then effectively solid in that eddies of moderate velocity will have their velocities in the plane of the surface reduced to zero. This phenomenon has been discussed elsewhere (7).

If the adsorption of a *little* surface-active agent on to the mobile surface lowers the surface tension by an amount Π dynes/cm. the tangential stress opposing the surface renewal is Π/δ_1, where δ_1 is the thickness of the mathematically equivalent viscous layer at the surface.

Equation (1) then becomes [following Davies (2, 8)]:

$$\frac{2\sigma}{R} + \frac{\Pi}{\delta_1} = \rho v_0^2 \qquad (9)$$

This equation implies that δ_1 will increase with Π; and since δ_2 will likewise increase, k_L will be decreased. Since $1/\delta_1$ is typically of the order of 0.5 mm.$^{-1}$, compared with 0.02 mm.$^{-1}$ for $2/R$, the presence of a surface film of Π only 3 dynes/cm. will make the two eddy-opposing terms on the left side approximately equal. The surface film, because of its surface-tension *gradients*, thus acts strongly in increasing δ_1 and δ_2, and so decreasing k_L. The widely reported sensitivity of mass transfer rates at free surfaces to very small amounts of surface-active matter is thus explicable.

The detailed solution of Equation (9) is as follows. To eliminate R one substitutes

$$\nu = \nu_E = 0.8\,\delta_1^2\,v_0/R \qquad (10)$$

This latter expression (2) follows from the surface layer δ_1 being defined as the region where ν_E has fallen below ν, that is, where viscous forces are dominant. Substitution of R from Equation (10) into Equation (9) gives

$$\delta_1^2(v_0^3\rho) - \delta_1(v_0\Pi) - 2.5\nu\sigma = 0 \qquad (11)$$

The solution of this equation gives δ_1 as a function of Π: a mobile surface is implicitly assumed in the derivation, so Equation (11) cannot be expected to hold if Π exceeds about 5 dynes/cm. From the δ_1 values derived from Equation (11), δ_2 may be easily calculated since $\delta_2/\delta_1 = (D/\nu)^{1/2}$. Hence k_L (which is inversely proportional to δ_2) can be obtained as a function of Π. The stronger the turbulence (that is, the higher is v_0) the steeper is the percentage reduction of k_L as a function of Π.

Numerical substitution into Equation (11) gives the data shown by the full lines in Figures 7 and 8. Figure 7 refers to water in a stirred cell, and Figure 8 to water flowing over plates (smooth and also roughened to give wake-interference flow). For even relatively small lowerings of the surface tension (for example, from 72 dynes/cm. to 70 dynes/cm.) there is a marked reduction in the rate of carbon dioxide absorption into the water in all these examples. Agreement with the theory of Equation

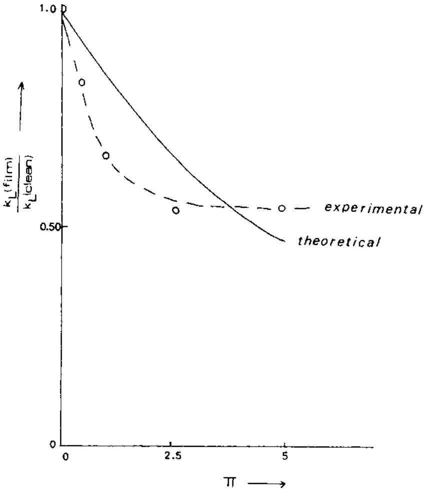

Fig. 7. Relative reduction of k_L for the uptake of carbon dioxide into water, in a stirred cell with a plane interface, as a function of Π. The full line represents the theoretical predictions from Equation (11) with $v_0 = 0.052$ m./sec., as derived from k_L (clean) $= 20 \times 10^{-6}$ m./sec. and equation (2) with $\sigma = 72$ dynes/cm. Points (and the broken line) refer to the experimental reduction of k_L when an insoluble monolayer of protein is spread on the surface, the stirring rate being constant at 437 rev./min. (9).

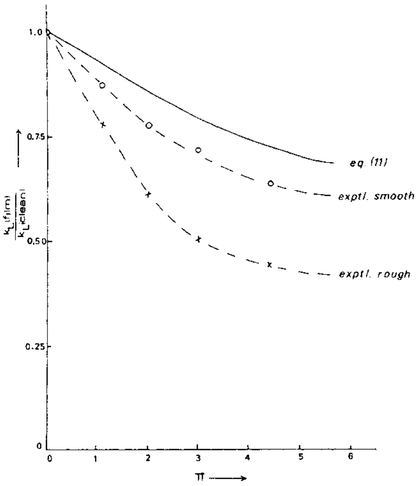

Fig. 8. Experimental relative reductions—in the presence of a surface-active agent—in k_L (for carbon dioxide absorption) below the value for clean water. Experimental points (10) are plotted as a function of Π: circles (and the broken line through them) refer to the flow of water film over a smooth surface. Crosses (and the lower broken line) refer to wake-interference flow over the rough surface (for details of the latter see legend to Table 1). The respective Reynolds numbers are 1400 and 450, corresponding in each case to an experimental k_L (clean) $= 300 \times 10^{-6}$ m./sec. The surface-active agent is dissolved sodium dioctyl sulfosuccinate. The full line is the theoretical prediction from Equation (11) (with $v_0 = 0.32$ m./sec., as deduced from Equation (2)).

(11) is fairly satisfactory for the stirred cell at 437 rev./min. and for water flowing over the smooth plate.

For the wake-interference flow, however, with its apparently anomalously efficient mass transfer, the reduction of k_L by surface-active agent is particularly marked, and is considerably more pronounced than is expected from the theory of Equation (11). This is evidently due to some inhibition of the wake-interference flow pattern by the local surface tension gradients. Indeed, the surface becomes appreciably smoother. However, k_L for *clean* surfaces in the wake-interference flow is about 3 times greater than for flow over the smooth plate if Re is the same. Hence k_L for wake-interference flow is still about twice as great in the presence of surface-active agent at $\Pi = 5$ dynes/cm., that is, though the surface-active material reduces the advantage of the eddy-promoting roughness, it does not eliminate this advantage.

In the present experiments the adsorbed film behaves as if insoluble, because there is no large-scale renewal and removal of the surface, but only local elastic clearings.

NOTATION

B_f = film thickness
d = internal diameter of tube
D = molecular diffusivity
D_E = eddy diffusivity
e = height of roughness element
g = gravitational acceleration
k_L = mass transfer coefficient in liquid phase
R = radius of curvature
Re = Reynolds number
s_1 = separation between ridges
s_2 = thickness of ridge
Sc = Schmidt number
Sh = Sherwood number ($= k_L d/D$)
v_0 = characteristic shear stress velocity of turbulent flow
v_m = mean linear flow velocity
v' = eddy fluctuation velocity
V_b = volumetric flow rate per unit width of plate
We = Weber number ($We = v_m(\rho d/\sigma)^{1/2}$)

Greek Letters

δ_1 = thickness of mathematically equivalent viscous layer near surface
δ_2 = thickness of mathematically equivalent diffusion layer near surface
θ = angle of inclination to horizontal
μ = viscosity of liquid
ν = kinematic viscosity of liquid
Π = lowering of surface tension
ρ = density
σ = surface tension
τ_0 = wall stress

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Manuscript received April 9, 1971; revision received August 9, 1971; paper accepted August 15, 1971.

Thermodynamics of Multicomponent Reactive Nonuniform Systems (Adsorption)

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Certain systems are characterized by a nonuniform distribution of matter in space. Examples of such systems are liquid-fluid *(1 to 3)* and the solid-fluid interfaces *(4)*. It is the main purpose of this paper to extend the thermodynamics of nonuniform systems to multicomponent reactive mixtures in the presence of an external field and to apply the above formalism to physical adsorption. This amounts to an extension of Hart's original analysis *(5 to 7)* as well as an improved analysis of the solid-fluid interface presented recently by Metiu and Ruckenstein *(8)*. Furthermore, various approximate solutions for the solid-fluid interface are considered, all of which reduce properly to known results.

The characterization of the thermodynamic state of an inhomogeneous system in which nonuniformity is associated with the distribution of mass over space can be done in two different ways. In the first approach one can calculate a potential $\varphi(r)$ created by a variation of density with position and deduce in this fashion a relationship be-