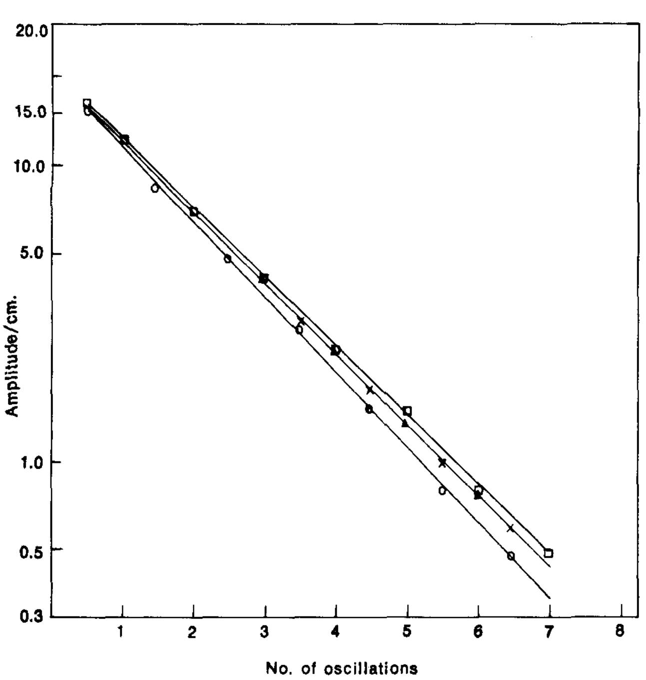

Fig. 3. Amplitude of oscillation against time for Aerosol OT in a semicircular glass tube. □ Water. △ 10 p.p.m. Polyox WSR-301. × 250 p.p.m. Aerosol OT. ○ 2 500 p.p.m. Aerosol OT.

ber of oscillations with pure water is N_w and with an additive present is N_a, the percentage increase in the number of oscillations is defined as

$$100(N_a - N_w)/N_w$$

In Figure 2 we compare the behavior of Aerosol OT with Polyox grade WSR N3000 (N3000 is a relatively inefficient grade of Polyox and only gave a peak enhancement of 50%, compared with WSR301, which gave 120%; see McComb, 1974) over a wide range of concentrations in a semicircular PVC tube. It is clear that Aerosol OT behaves very much like PEO, although the total effect at any given concentration is a lot smaller. Results are also given for Aerosol OT in a U shaped tube. It may be seen that the behavior of the surfactant is not affected much by the change of configuration. This contrasts with the behavior of PEO (McComb, 1974), where the effect in a U tube was much smaller than in the semicircular tube.

Various other tests were carried out. To test the effect of a different tube material, we used a 1.1 cm bore glass tube in the same configuration as the PVC tube. Experiments with both PEO and Aerosol OT did not show any obvious change in the wetting of the glass tube above the meniscus. The only quantitative effect was an increased damping with both additives. When Aerosol OT was used, quite large concentrations were needed to produce a measurable difference in the decay rate. Some representative results are given in Figure 3.

To exclude any sample anomaly, we tested the Aerosol OT solutions (at two different concentrations) in turbulent shear flow in a 1.9 cm bore pipe. As expected, there was no measurable effect on the pressure drop.

Finally, it appeared that the damping reduction was due to an adsorbed layer of PEO on the pipe wall (McComb, 1974). In the present case we did not find this effect. Tubes which had contained Aerosol OT solutions were emptied and refilled with clean water, but no reduction in damping then occurred.

To summarize, in some ways Aerosol OT behaved like PEO in its effect on manometer types of oscillations. It reduced the damping in a PVC tube and increased the wetting of the PVC tube above the meniscus. It did not reduce the damping in a glass tube and did not have any noticeable effect on the wetting of the glass tube above the meniscus.

In other respects the two additives behaved differently. The effect of Aerosol OT was very much smaller than that of PEO, and apparently it (unlike PEO) did not act by coating the pipe wall. Also, Aerosol OT had a roughly equal effect in both semicircular and U shaped manometers of PVC tube, with a peak enhancement of about 20 to 25%. This contrasts with the behavior of PEO. McComb (1974) showed that the enhancement due to Polyox WSR301 in the U tube was very much smaller (30%) than in the semicircular tube (120%).

The only firm conclusion we can draw is that Aerosol OT (although not a drag reducer in turbulent shear flow) does reduce the damping of manometer types of oscillations. However it has a very small effect compared to PEO. In view of this, and the other differences between the two additives, it seems quite unlikely that the wetting of the tube wall plays a major role in the phenomenon reported by McComb (1974).

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Enhancement and Effectiveness Factors in Gas-Liquid Absorbers and Reactors

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The rates of chemical processes in two phase systems are customarily expressed as a ratio of the rate under influence of the interphase mass transfer to the rate to be expected in a mass transfer, free reference condition. Thus, in heterogeneous catalysis, the effectiveness factor (Thiele, 1939) is the ratio of the rate of reaction in a catalyst pore to the rate expected if the full pore surface were in contact with gas at the temperature, pressure, and composition of the gas at the pore mouth or catalyst pellet surface. Recently, Kulkarni and Doraiswamy (1975) have extended this idea to bubbling gas-liquid reactors. In gas-liquid absorption accompanied by chemical reaction, the enhancement factor (Danckwerts, 1950) is the ratio of the rate of absorption under reacting conditions to the rate to be expected in the absence of chemical reaction. This note is to draw attention to the symmetrical nature of these definitions and to show that both enhancement factors and effectiveness factors are alternative expressions for the same phenomenon.

All of the simplified models used to date to calculate the interaction effects of mass transfer and chemical reaction consider a one-dimensional transport perpendicular to the phase interface (bubble surface, drop surface, catalyst pellet surface) in which the region interior to the phase in which reaction occurs (henceforth called the reaction phase) is divided into two zones. The film adjacent to the interface includes the entire region within which appreciable composition and/or temperature gradients are considered to exist. The balance of the reaction phase is supposed to have uniform composition and properties. One then postulates for each component a dispersion limited transfer equation, in steady state:

$$D_i \frac{\partial^2 C_i}{\partial x^2} + R_i = 0 \tag{1}$$

We assume no convection of bulk fluid perpendicular to the interface and constant pressure in the reacting phase. For gases reacting in catalyst pores with a net change in the number of moles, these assumptions will need revision, but the more general case will not be treated here.

For a first-order disappearance of a single diffusing species

$$D \frac{d^2C}{dx^2} = k_1 C \tag{2}$$

At the interface

$$C(0) = C^* \qquad (x = 0) \tag{3}$$

At the other boundary of the film, $x = \delta$, we impose continuity of flux:

$$-aD \frac{dC}{dx}\bigg|_{x=\delta-} = N(\delta) \qquad (\text{kg moles/m}^3\ \text{s}) \tag{4}$$

If the region outside the film ($x > \delta$) has uniform composition, the flux of reactant into the uniform region must just balance the rate of disappearance by reaction in that region. Hence

$$N(\delta) = +\, k_1(\Delta - \delta) a C(\delta) \tag{5}$$

Note that $a\Delta$ is the volume of reaction phase per unit volume of reactor. If the reaction phase is a liquid in contact with a gas, $a\Delta$ is the liquid holdup in the reactor. For a catalyst, the entire pellet is reaction phase, and $a\Delta$ is the pellet volume per unit volume of reactor.

Equation (2) is readily integrated for boundary conditions, Equations (3) and (4), to give

$$\frac{C}{C^*} = \frac{\beta \cosh m(x-\delta) - m\delta \sinh m(x-\delta)}{\beta \cosh m\delta + m\delta \sinh m\delta} \tag{6}$$

where

$$\beta = \delta/(\Delta - \delta) \tag{7}$$

$$m = (k_1/D)^{1/2} \tag{8}$$

The flux at the phase interface is

$$N(0) = -Da \frac{dC}{dx}\bigg|_{x=0} = \frac{Da}{\delta} C^* \left\{ \frac{\beta \tanh m\delta + m\delta}{\beta + m\delta \tanh m\delta} \right\} (m\delta) \tag{9}$$

This result is readily expressed in the form

$$N(0) = E\, k_L{}^o a\, C^* \tag{10}$$

or

$$N(0) = E_1 k_1 C^* a\Delta \tag{11}$$

where

$$k_L{}^o = D/\delta \tag{12}$$

Thus, one finds

$$E_1 = \frac{k_L{}^o a}{k_1 a \Delta} E = \left(\frac{\delta}{\Delta}\right) \frac{E}{(m\delta)^2} = \left(\frac{\delta}{\Delta}\right) \frac{1}{m\delta} \left[\frac{\beta \tanh m\delta + m\delta}{\beta + m\delta \tanh m\delta} \right] \tag{13}$$

This result is equivalent to Equation (19) of Kulkarni and Doraiswamy (1975) for the same kinetics but is expressed somewhat more compactly. Note, however, that Kulkarni and Doraiswamy use a as interfacial area per unit volume of bulk liquid, whereas here it is referred to the volume of gas plus liquid.

The enhancement factor defined by Equation (10) depends upon the reference state implied by setting the bulk concentration equal to zero in the usual expression for pure absorption:

$$N(0) = k_L{}^o a\, (C^* - C_{\text{bulk}})$$

Physically, this reference state is that of purely physical absorption into a fully stripped absorbent in the first moment before any back pressure can build up.

When $k_L{}^o a < k_1 a \Delta$, the effectiveness factor is less than the enhancement factor. Since E_1 is at most equal to unity, the enhancement factor can exceed unity, but for $k_L{}^o a$ sufficiently greater than $k_1 a\Delta$, the enhancement factor will fall below unity. This only means that mass transfer is so rapid at the reference conditions of Equation (10) (saturation at the interface and zero solute in liquid phase) that the chemical reaction is limiting and is in fact slow enough to permit a solute reactant level to build up so that the mass transfer rate falls below its reference value.

These results are, of course, based on a film model. It is well known that a surface renewal model is physically more acceptable. However, the recent book by Danckwerts (1970) comparing the results of both models for a variety of kinetic and mass transfer situations makes it clear that if one interprets the film thickness δ to represent a mean penetration distance during a mean surface renewal interval, the numerical results of the two models agree within 10 to 12%. Furthermore, for quasielementary kinetics of the form

$$R = k_n C^n \tag{14}$$

similar numerical agreement is achieved if one takes

$$k_1 = k_n C^{*n-1} \tag{15}$$

in Equation (13). These circumstances make Equation (13) very useful for design purposes where a more accurate estimate of the absorption or reaction rate is often not required.

Equation (13) is relatively simple to use in computer programs but can be considerably simplified in several limiting cases. These arise from the approximations

$$\tanh x = 1 \qquad (x > 2.5) \tag{16}$$

$$\tanh x = x \qquad (0 < x < 0.5) \tag{17}$$

The parameter β, the ratio of film volume to nonfilm volume in the reaction phase, ranges from very small values for wetted packing to an infinite value for a porous catalyst, which by definition has no nonfilm volume. Figure 1 shows the regions of parameter space in which simplifications can be made. For large β, at all values of $m\delta$, one recovers the original Thiele effectiveness factor. For large values of $m\delta$ ($m\delta > 0.5$), one recovers the fast reaction regime for the enhancement factor. For very small β, and $m\delta < 2.5$, one recovers pure diffusion control, since then the film is so thin that regardless of the reaction rate (up to the limits of $m\delta \leqq 0.5$) no effective reaction occurs in the film even though the kinetics is fast enough to deplete reactant nearly completely outside the film. For very small $m\delta$, one recovers the case of pure kinetic control. The enhancement factor is much less than unity, although the effectiveness factor is near 1.0. There is an intermediate range of small β and moderately small $m\delta$ for which one recovers the familiar resistance in series model. No substantial reaction occurs in the film, but the reactant is not fully depleted outside the film.

Although it is not always easy to estimate the values of $m\delta$ and β in specific cases, even rough evaluations can be useful. For example, if experimentation shows the enhancement factor to be less than unity, the fast reaction model is surely inapplicable. In liquids, the diffusivity D seldom departs by more than an order of magnitude from 10^{-9} m²/s. Literature data (Danckwerts, 1970) show $k_L{}^o$ to be approximately 10^{-4} to 10^{-3} m/s for a wide variety of contactors. This leads to the estimate

$$m\delta = \frac{1}{k_L'}\sqrt{\frac{D'}{10\,t_{1/2}}} \tag{18}$$

where

$D' = D \times 10^9$ (m²/s)

$k_L' = k_L{}^o \times 10^4$ (m/s)

$t_{1/2}$ = reaction half-life (s)

If D' and k_L' are of equal order of magnitude and taken to be ~ 5.0, one sees that reaction will be complete in the film ($m\delta > 2.5$) if $t_{1/2} < \sim 3 \times 10^{-3}$ s. The pure kinetic regime will hold ($m\delta < 0.01$) if $t_{1/2} > \sim 3.5$ min. The resistances-in-series model will be valid for $0.01 < m\delta < 0.5$, or $0.1 \text{ s} < t_{1/2} < 3.5$ min. The factor β can often be estimated from holdup measurements:

$$\beta = \frac{\delta}{\Delta - \delta} = \frac{D}{k_L{}^o\left(\Delta - \dfrac{D}{k_L{}^o}\right)} = \frac{D}{k_L{}^o\,\Delta - D} \tag{19}$$

When $D \approx 10^{-9}$, $k_L{}^o \sim 10^{-4}$, any reasonable value of holdup, $a\Delta$, leads to

$$\beta \approx \frac{D}{k_L{}^o\,\Delta} = \frac{aD}{k_L{}^o\,(a\Delta)} \approx a\,\frac{10^{-9}}{10^{-5}} = 10^{-4}\,a \tag{20}$$

The interfacial area per unit volume a is thus a crucial quantity in determining the regime of the absorber/reactor operation. For porous pellets, the entire porous phase sustains a concentration gradient. Hence, $\Delta = \delta$ and $\beta \to \infty$.

The parameter $m\delta$ is more difficult to estimate when the regime is unknown, since usually k_1, the effective first-order rate constant in the reaction phase, is not known either. It certainly cannot be less than $1/\tau$, the reciprocal residence time of the liquid in the vessel, but this is not often a useful limit. It is of some interest that the rather complete study by Desai and Viswanath (1972) of the chlorination of acetylene in tetrachlorethylene clearly shows an experimentally determined enhancement factor less than unity. The fast reaction model used to interpret the data is thus clearly inappropriate.

The kinetics assumed in Equations (2) and (15) refer to the disappearance of a single reactant in an excess of solvent and other possible reactants. If more than one reactant is depleted in the film, a bimolecular kinetics must be used, and there will be an equation analogous to Equation (2) for each species. Each nonvolatile species k will satisfy a boundary condition

$$\frac{dC_k}{dx} = 0 \qquad (x = 0) \tag{21}$$

in place of Equation (3), satisfied for the volatile species. The simple case of two reacting species, one volatile and one nonvolatile, according to the equation

$$A + zB \rightarrow P \tag{22}$$

has been solved analytically only for the instantaneous reaction regime, but approximate solutions and numerical results for the fast reaction regime are summarized by Danckwerts (1970). Extension to the intermediate regimes and the general case of Figure 1 remain fields for future investigation. Such studies will also reveal the extent to which more complex kinetics modifies the enhancement/effectiveness factors.

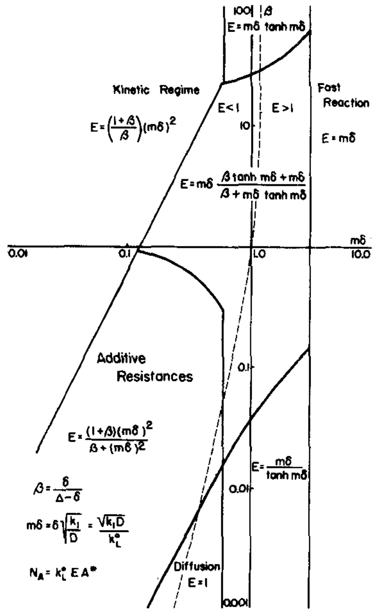

Fig. 1. Enhancement factors—parameter values for which exact and simplified expressions are valid.

NOTATION

a = interfacial area per reactor volume (m^{-1})
C or C_i = concentration of species i (kg-moles/m³)
C^* = concentration at interface (kg-moles/m³)
D or D_i = dispersion coefficient (m²/s)
E = enhancement factor, Equation (10)
E_1 = effectiveness factor, Equation (11)
k_1 = specific first-order rate constant (s^{-1})
$k_L{}^o$ = mass transfer coefficient in absence of reaction (m/s)
N = flux of adsorbate (kg-moles/m² s)
R_i = local chemical production rate of species i (kg-moles/m³ s)
t = time (s)
$t_{1/2}$ = time for 50% conversion of reactant (half-life), (s)
x = distance from interface (m)
z = stoichiometric coefficient
β = film volume/nonfilm volume (dimensionless)
Δ = film thickness (m)
δ = reaction phase thickness (m)

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Turbulent Mass Transfer in Jet Flow and Bubble Flow: A Reappraisal of Levich's Theory

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In a recent paper, Davies (1972*a*) used a modified Levich theory to obtain a prediction of the rate of gas absorption by turbulent water jets (Ting, 1967; Davies and Ting, 1967) and kerosene jets (Hameed, 1969; Davies and Hameed, 1971). Davies' predictive equation for the mass transfer coefficient was

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

where V_O is the characteristic turbulence velocity. Although Davies (1972*a*) mentioned that the liquid turbulence decays appreciably along the free jet, he neglected this effect in the mass transfer calculations and took V_O to be equal to the shear velocity in the tube:

$$V_O = V_* = 0.2\overline{V}\,Re^{-1/8} \qquad (2)$$

The mass transfer, then, was assumed to be governed by the developed turbulence within the tube. If this were a good assumption, Equations (1) and (2) would also be expected to provide a prediction of the gas absorption rate by discrete bubbles transported in turbulent pipe flow of water (Lamont, 1966; Lamont and Scott, 1966, 1970). Here the turbulence within the tube is controlling the mass transfer process. However, this expectation is not met. In Table 1, the jet flow and bubble flow data are interpreted by an equation of the form

$$k_L = C_L(D\,\rho\,V_O{}^3/\sigma)^{1/2} \qquad (3)$$

where V_O is calculated from Equation (2), and C_L is the constant which gives the best agreement (mean-square criterion) between the measured and predicted mass transfer coefficients for a given physical system. It is seen that Equation (1) underestimates the bubble flow data by a factor of 10. In addition, while Equation (1) is in excellent agreement with the water-jet data, it overestimates the kerosene-jet data by about 50%.

Davies and Hameed (1971) were unable to explain the low C_L value for their kerosene jets and suggested that the absolute values of the proportionality constants in the Levich theory need reexamining. Also, Coeuret and Ronco (1973) could not explain the C_L variation between the water-jet and kerosene-jet results. They concluded that the Levich theory interpretation of the turbulent mass transfer process is not yet sufficient. The present paper investigates the possibility that the C_L variation in the jet flow case might be due to the incorrect specification of V_O (due to the neglect of turbulence decay) rather than to an implied limitation in the Levich theory. The motivation, then, is to allow an assessment of the Levich theory on a more realistic and uniform basis. It is shown that if the effects of turbulence decay are included for the liquid jets, a new and more invariant value of the Levich constant C_L results.

REPRESENTATION OF TURBULENCE DECAY IN LIQUID JETS

The bulk turbulence properties of the free jet, which are initially characteristic of the nearly isotropic conditions in the core of the nozzle, are assumed to follow the decay laws describing the turbulent flow downstream of a grid (Batchelor and Townsend, 1948; Batchelor, 1967). For a region downstream of the nozzle, the turbulence energy is taken to decay according to the law of the initial period, while for larger distances downstream, the law of the final period is applied. The short transition region which separates these two periods of decay will be neglected. The length of duration of the initial period t^* is of the order of a few characteristic eddy times during the early stages of decay (Batchelor, 1967). Since the experimental data of Batchelor and Townsend (1948) indicate that $t^* \sim 10T$, it is reasonable to take $t^* = 10L(x = 0)/V(x = 0)$ for jet flow.

The initial period of decay is characterized by $V^{-2} = C_1(t - t_1)$ and $\lambda^2 = 10\nu(t - t_1)$, where $t = x/\overline{V}$ and $\lambda^2 = 10\nu\,L/V$, and the constants C_1 and t_1 are determined by requiring continuity of L and V at $x = 0$. The results are

$$V = V(x=0)\left\{ 1 + \frac{V(x=0)}{L(x=0)}\,t \right\}^{-1/2}$$

TABLE 1. MASS TRANSFER DATA FOR JET FLOW AND BUBBLE FLOW AS DESCRIBED BY EQUATION (3)

Jet flow		Discrete bubble flow in pipes
Ting, 1967; Davies and Ting, 1967	Hameed, 1969; Davies and Hameed, 1971	Lamont, 1966; Lamont and Scott, 1966, 1970
Liquid: water	Liquid: kerosene	Liquid: water
Gas: CO_2, H_2	Gas: CO_2, H_2, He	Gas: CO_2
$C_L = 0.32$	$C_L = 0.20$	$C_L = 3.2$
$E = 15\%$	$E = 24\%$	$E = 48\%$
$S = 0.81$	$S = 0.67$	$S = 1.7$

C_L is the constant minimizing the sum of the squares of the deviations between the measured and predicted mass transfer coefficients.
E is the average percentage error between the measured and predicted mass transfer coefficients.
S is the slope of the least-squares line through the points on a plot of the predicted vs. measured mass transfer coefficient.

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