

# Quantitation of Eddy Diffusion Using an Oxygen Microelectrode

H. R. BUNGAY, III, M. Y. HUANG,  
and W. M. SANDERS, III

Division of Interdisciplinary Studies  
Clemson University, Clemson, South Carolina 29631

Experiments with capillary microelectrodes placed near and within microbial slimes bathed in flowing nutrient medium have permitted estimation of mass transfer coefficients and of oxygen utilization rates (Sanders et al., 1971; Bungay et al., 1969). A suggestion by E. Tsivoglou of Georgia Institute of Technology that variations in the oxygen recordings were caused by eddy diffusion led to some preliminary experiments which showed that the microprobe produced an almost constant reading in a violently agitated homogeneous solution, but had a fluctuating output signal in a system with oxygen gradients (Bungay et al., 1970). The microprobe appears to be insensitive to small pressure changes and highly responsive to oxygen concentration changes.

Mass transfer by eddy renewal has been analyzed by Danckwerts (1951) who derived the relationship

$$k_L = (D \cdot \dot{s})^{1/2} \quad (1)$$

Other treatments of turbulent mass transfer theory have considered eddy renewal (Toor and Marchello, 1958; Marchello and Toor, 1963; Ruckenstein, 1971).

It is possible to estimate  $s$  by determining the number of abrupt changes in slope per unit time from the oxygen microprobe signal. This will be somewhat in error because eddies or packets of liquid can have almost the same concentration of oxygen and thus cause no detectable change in signal when one replaces another at the sensing zone of the microelectrode. Furthermore, some eddies may be oriented such that the sensing zone is averaging two or more eddies. Nevertheless, the renewal rate should be directly proportional to the inflection rate in the microprobe signal, and experiments at different intensities of turbulence with other parameters held constant should be comparable. The ability to measure  $s$  directly permits experimental confirmation of Danckwerts' theory.

## MATERIALS AND METHODS

The capillary microelectrode (Transidyne Corporation, Ann Arbor, Michigan) had a tip diameter of approximately one micron. Conventional electronic circuitry was used to impress a polarizing voltage across the microelectrode and a silver-silver chloride reference electrode, and a picoammeter was used to measure current flows.

A Plexiglas vessel constructed with an extended entry port as shown in Figure 1 was filled with nitrogen-sparged water until liquid began to rise in the port. The working volume was 400 ml, and the port cross section was 2.85 cm<sup>2</sup>. The capillary microelectrode was mounted on a micromanipulator and inserted just into the liquid. Tap water was used so that purity and conductivity of distilled water need not be considered; the circuit resistance of the microelectrode is vastly greater than that of tap water. Temperature was adjusted at the start of each run and was found to rise roughly 0.25°C

during the experiment; thus temperature control was deemed unnecessary.

Overall transfer rates to the liquid were calculated from the volume of liquid and the rate of change of oxygen concentration as determined with a commercial oxygen electrode or by occasional lowering of the microelectrode into the bulk of the liquid. Only low mixing rates were employed because fluctuations of the air-water interface would prevent accurate orientation of the microprobe. Ripples were not observed; thus the transfer area was assumed equal to the cross section of the port.

## RESULTS AND DISCUSSION

Typical results in Figure 2 show the oxygen tension variations with time in the air-water interface. Stirring was increased from its lowest level in 2A to the highest level in 2E. The surface renewal rate was determined from the number of abrupt changes per unit time in the recordings. An overall mass transfer coefficient was calculated from the overall mass transfer rate, the transfer area, and the driving force. Plots of mass transfer coefficient versus square root of the rate of inflection of the microprobe signal for two typical runs are shown in Figures 3 and 4. For a series of runs, the slopes and projected intercepts of the linear portions of the curves varied slightly. This is attributed to aging of the microelectrodes or to errors in trying to place the tip exactly in the interface. The mass transfer coefficient is almost independent of the eddy renewal rate when the bulk liquid is nearly stagnant, and diffusion is the dominant transfer mechanism. The transfer mechanism of the transition zone can be considered as a combination of film and renewal models.

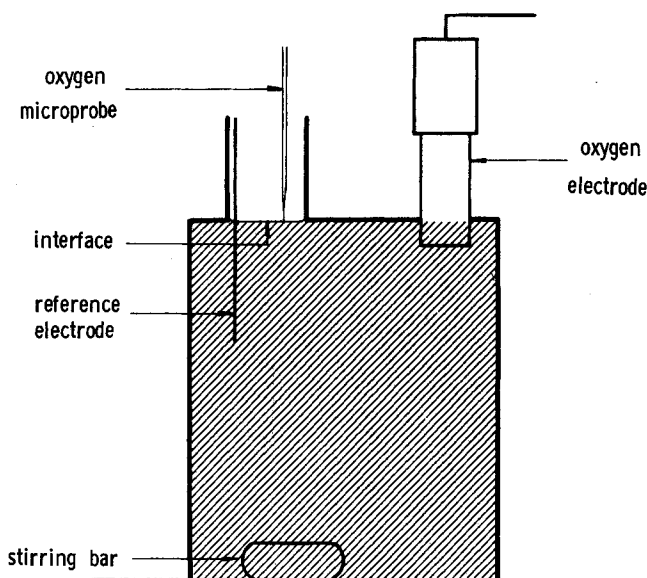


Fig. 1. Diagram of reactor.

Correspondence concerning this note should be addressed to H. R. Bungay, III. W. M. Sanders, III is with the Southeast Environmental Research Laboratory, National Environmental Research Center-Corvallis, U. S. Environmental Protection Agency, Athens, Georgia.

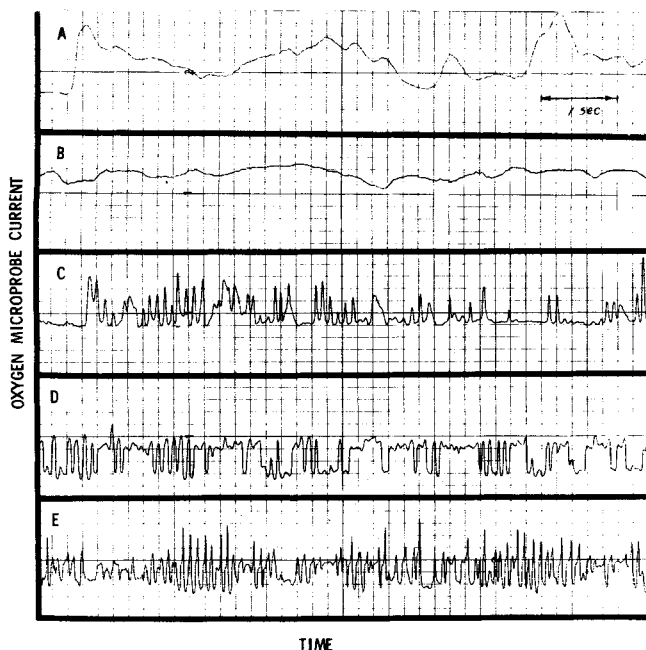


Fig. 2. Strip chart recordings of oxygen tension at the air-water interface (various turbulence levels at 23.5°C).

There was eddy renewal even with no stirring. This should be true in many real systems because of thermal convection arising from evaporation or uneven heating. Eddy renewal was observed in our studies of microbial slime films at flow rates that were calculated to be in the laminar range (Sanders et al., 1971).

Fluctuations in the current recordings shown in Figure 2 oscillate in a certain range. The lowest reading of each run is about that of the bulk concentration. An inflection in the recording down to the lowest reading is regarded as a fresh eddy arriving at the interface. Inflection to an intermediate value implies that an old element has mixed with or exchanged with a fresh incoming eddy as predicted by Marchello and Toor (1963). It is also possible that a displaced element rich in oxygen is only partly mixed by the bulk liquid before it returns to the interface.

Although the experiments were not performed in a manner which allows meaningful statistical treatment, it is possible to estimate the efficiency of the microprobe in detecting eddies. Assuming the renewal rate to be equal to the fluctuation rate of the microprobe signal, based on Equation (1) calculated diffusivities for different runs ranged from  $1.6$  to  $7.7 \times 10^{-5}$  cm<sup>2</sup>/sec. which is of the correct order of magnitude for the diffusivity of oxygen in water at these temperatures. It would thus seem that the microprobe is highly efficient in detecting eddies.

## CONCLUSION

The effects of surface renewal have been observed directly at an air-water interface. A linear dependence of mass transfer coefficient on square root of renewal rate at very low turbulence levels has been confirmed.

## NOTATION

- $D$  = diffusivity of oxygen in water
- $k_L$  = mass transfer coefficient
- $s$  = rate of surface renewal by eddies

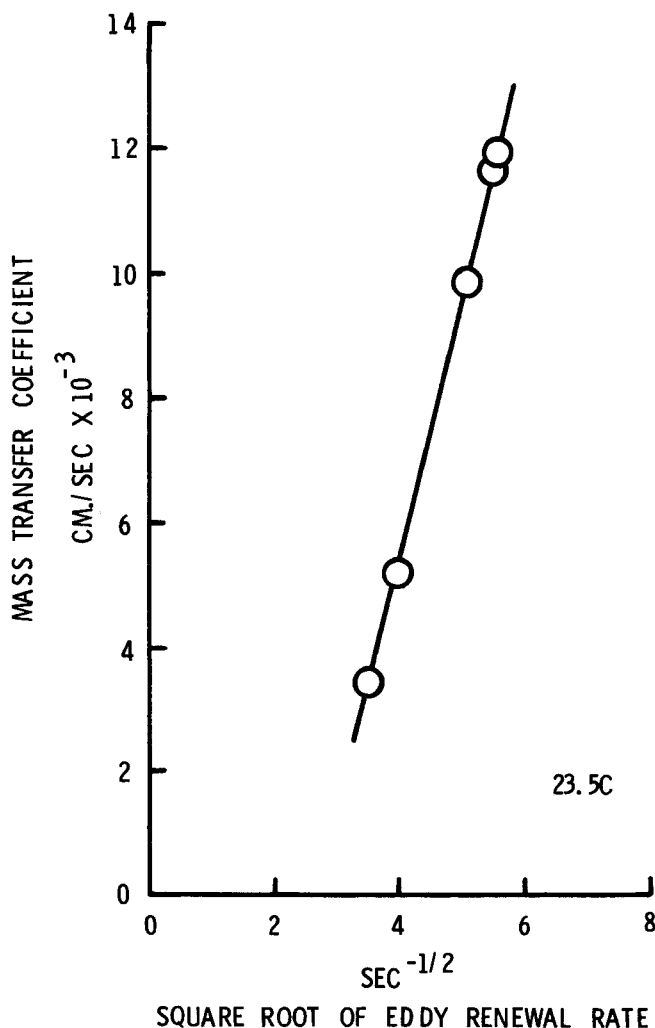


Fig. 3. Plot of mass transfer coefficient versus square root of eddy renewal rate (23.5°C).

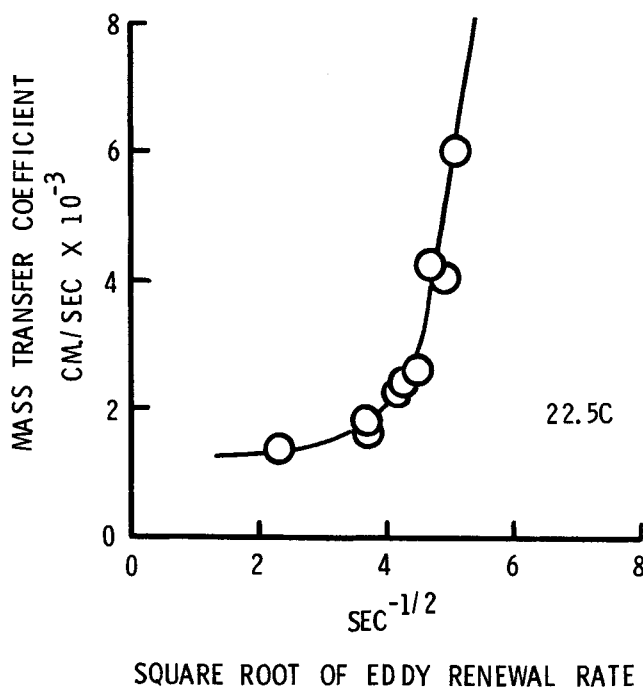


Fig. 4. Plot of mass transfer coefficient versus square root of eddy renewal rate (22.5°C).

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# Empirical Expressions for the Shear Stress in Turbulent Flow in Commercial Pipe

STUART W. CHURCHILL

School of Chemical Engineering  
University of Pennsylvania,  
Philadelphia, Pennsylvania 19104

The method of Churchill and Usagi (1972) is used herein to develop expressions for the shear stress on the wall in turbulent flow in commercial pipe at all Reynolds numbers and all roughness ratios. In this application the objective is to derive an equation for interpolation between the empirical correlations which have previously been developed for smooth pipe and for fully developed turbulence at very large Reynolds number in rough pipe. The method itself is straightforward, but the simplicity and accuracy of the final expression depends not only on the choice of the limiting correlations but also on the form in which they are arranged. Several such alternatives are examined.

Nikuradse (1932) developed the following correlations for his own precise experimental measurements of the pressure drop in turbulent flow in smooth pipes and in fully developed turbulent flow in pipes with uniform, artificial roughness:

$$\frac{u}{\sqrt{\tau/\rho}} = 2.46 \ln \left( \frac{D}{\nu} \sqrt{\frac{\tau}{\rho}} \right) + 0.30 \quad (1)$$

and

$$\frac{u}{\sqrt{\tau/\rho}} = 2.46 \ln \left( \frac{D}{\epsilon} \right) + 3.22 \quad (2)$$

The roughness of commercial pipes is not uniform and hence is not uniquely defined. Colebrook (1938-1939)

proposed that this roughness be defined arbitrarily as the effective value such that the experimental measurements of pressure drop at very large Reynolds number fit Equation (2). He further observed that when expressed in this form the experimental data for commercial pipes vary uniformly between the limiting behavior represented by Equations (1) and (2). This is a necessary condition for application of the method of Churchill and Usagi.

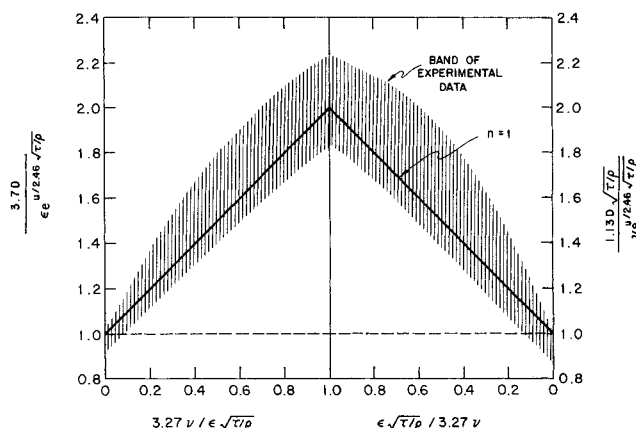


Fig. 1. Graphical construction of correlation.