Measurement of Instantaneous Rates of Mass Transfer to a Small Sink on a Wall

L. PHILIP REISS and THOMAS J. HANRATTY

University of Illinois, Urbana, Illinois

A technique has been developed for measuring the average rate of transfer and the fluctuations in the rate of transfer at a small source or sink on a wall. The transfer area consists of a small polarized electrode mounted flush with the wall. An electrochemical redox reaction whose rate is limited by mass transfer is employed. The technique can be used to study the flow pattern in the vicinity of the wall. By measuring the mass transfer simultaneously to two wall electrodes at varying distances apart the extent of unsteady flows in the vicinity of the wall can be measured.

The unsteady flow in the region of the viscous sublayer ($y^+ < 5$) close to the boundary between a turbulent fluid and a solid surface can play an important role in determining the rate of heat or mass transfer between the fluid and the solid (*5*). The unsteady nature of the viscous sublayer has been studied by Fage and Townend (*4*) who used an ultramicroscope to examine the motion of dust particles; by Laufer (*8, 9*), Sandborn (*11*), and Klebanoff (*6*) who measured velocity fluctuations with hot wire anemometer probes; and by Hama (*1*), Kline and Runstadler (*7*), and Beatty (*1*) who examined the motion of dye. None of these techniques are completely satisfactory. Visual studies have limitations in that quantitative data are difficult to obtain. Anemometer measurements are limited by the relative size of the probe to the region being studied and by the possible introduction of disturbances into the fluid. In order to circumvent these difficulties a method involving the measurement of the fluctuations in the local rate of mass transfer to a wall has been developed in this laboratory.

It has the disadvantage over techniques previously used to study the unsteady flow in the immediate vicinity of a wall in that it measures fluctuations in the flow indirectly through fluctuations in the gradient of concentration at the wall. The local rate of mass transfer is studied by measuring the average current and fluctuations in the current flowing to or from a small polarized electrode (mass transfer controlled) mounted flush with the solid boundary. By measuring the fluctuations in the rate of mass transfer simultaneously at two locations on the solid boundary the extent of the flow fluctuations close to the solid surface can be measured. The technique is a modification of methods used previously to measure average rates of mass transfer from rotating cylinders (3) and in an annulus (*10*).

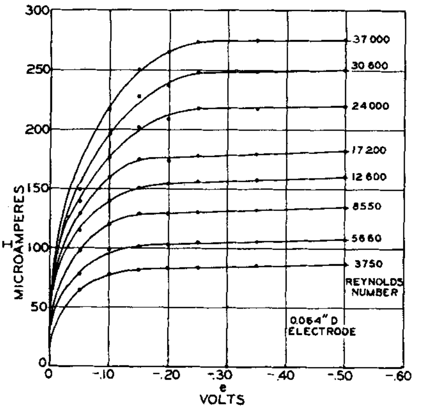

Fig. 2. Reduction of ferricyanide.

Since this technique for measuring the average rate of mass transfer and fluctuations in the rate of mass transfer to a small sink on a surface might have wider application than is indicated above, this paper has been written to describe in detail the experiments being performed. In a later paper the result of its application to the study of the unsteady nature of the viscous sublayer will be presented.

DESCRIPTION OF EXPERIMENTS

The flow system in which the studies are being conducted is shown in Figure 1. An electrolytic reaction is carried out between a small electrode mounted flush

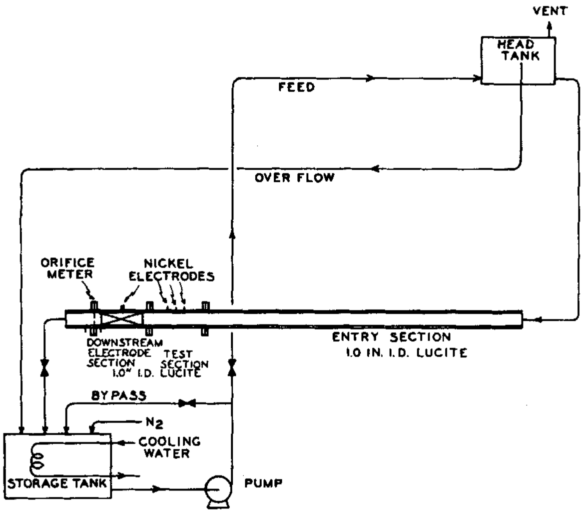

Fig. 1. Flow system.

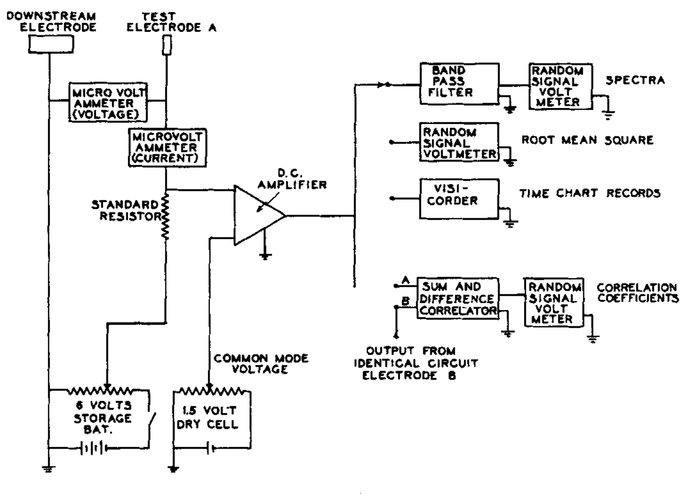

Fig. 3. Electrical circuitry.

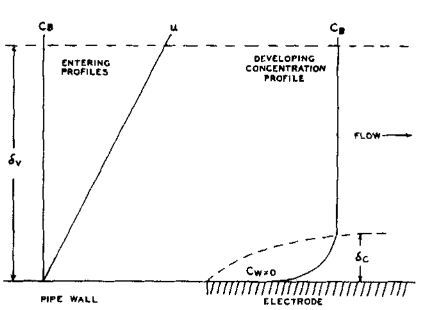

Fig. 4. Concentration and velocity profiles over the electrode surface.

with the pipe wall and a much larger electrode downstream. The electrolyte flows inside the pipe. The electrolytic reaction used in the present work is the reduction of ferricyanide ion on a nickel electrode:

$$\mathrm{Fe\,(CN)_6^{-3} + e^- \rightarrow Fe\,(CN)_6^{-4}}$$

An electric potential is applied between the test electrode and the downstream reference electrode, and the current in this circuit is measured. Plots of the average current vs. the voltage (Figure 2) show that after a certain voltage a limiting current is obtained whose magnitude is dependent on the Reynolds number. At these conditions the test electrode is polarized. The current is controlled by the rate of mass transfer of ferricyanide ions to the surface of the test electrode, and the concentration of ferricyanide ions at the surface is essentially zero. This reaction offers advantages over other reactions investigated, such as the oxidation of ferrocyanide or the reduction of dissolved oxygen, because of the large range of voltages over which the current is mass transfer controlled and over which there are no apparent side reactions.

The electrolyte consists of equal molar concentrations of potassium ferricyanide and potassium ferrocyanide and two molar sodium hydroxide. It had a kinematic viscosity of approximately 1.30 × 10^{-2} sq. cm./sec. The ferrocyanide-ferricyanide concentrations have been varied between 0.01 and 0.10 molar. The excess of sodium and hydroxide ions is used in order to keep the electrolyte electrically neutral and therefore to prevent the electric field from affecting the migration of ferricyanide ions to the electrode. In order to avoid the side reaction involving the reduction of dissolved oxygen on the negative nickel electrode, the electrolyte is saturated with nitrogen before running and a positive nitrogen pressure is maintained in the flow system while running.

The test electrodes are made of nickel wire which varies from 0.005- to 0.064-in. diameter. The electrodes are made by inserting the wire through holes in the plastic pipe wall and gluing them in place with epoxy glue. The end of the wire which protrudes into the pipe is smoothed flush with the pipe wall. This operation produces a test electrode which is a small circular nickel surface having the contour of the pipe wall. The reference electrode is a section of nickel pipe. The area of this electrode is large enough that under normal operating conditions it will not limit the electrode circuit current.

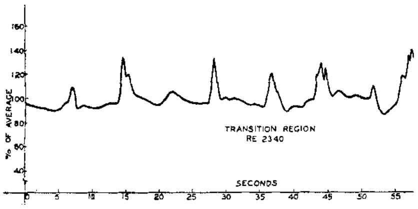

Fig. 5. Intermittancy in the rate of mass transfer noted in the transition region between laminar and turbulent flow.

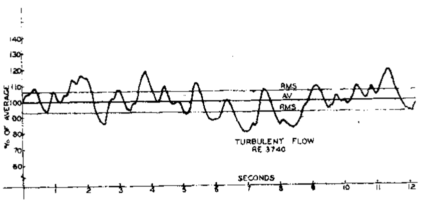

Fig. 6. Fluctuations in the rate of mass transfer for a Reynolds number of 3,740.

The flow system is constructed from materials which are inert in the presence of the electrolyte. The test section and the entry section (85-diam. long) are made of 1-in. I.D. Lucite plastic pipe. The remainder of the flow lines are Aceite hard rubber piping. The feed and constant head tanks are made of Lucite sheet, and the pump used to pump the electrolyte to the constant head tank is stainless steel.

The electric circuit being used is shown in Figure 3. The power is supplied by storage batteries. The voltage applied to the electrodes is controlled by a rheostat and can be varied from 0 to 6 v. The applied voltage and the average electrode circuit current are measured with a microvolt-ammeter. Fluctuations in the current are measured by measuring the voltage drop across a standard resistor. This voltage is amplified using a wide band differential input D.C. amplifier. The common mode rejection characteristic of this amplifier is used to eliminate the D.C. component. The output from the amplifier is recorded. The root-mean-square of the fluctuating signal is measured with a random signal voltmeter. Frequency spectra are measured by passing the amplifier output signal through an ultra-low frequency band-pass filter and then to the random signal voltmeter.

The simultaneous current fluctuations at two electrodes separated by different distances in the flow direction and around the circumference of the pipe are also being measured. Spatial correlation coefficients are obtained by using a modification of the sum and difference unit described by Sandborn (*11*).

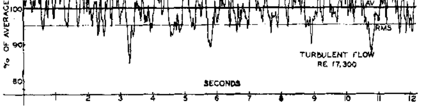

Fig. 7. Fluctuations in the rate of mass transfer for a Reynolds number of 17,300.

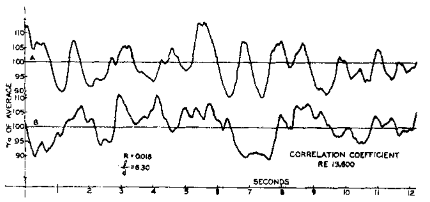

Fig. 8. Low-correlation fluctuations in the rate of mass transfer recorded simultaneously for two locations far apart.

INTERPRETATION OF THE MEASUREMENTS

The current flowing in the electrode circuit when an excess of sodium hydroxide is used and when the test electrode is polarized can be related to the rate of mass transfer to the electrode surface by the following equation:

$$N = \frac{I}{A n_e F} \tag{1}$$

Since the instantaneous rate of mass transfer is directly proportional to the concentration gradient at the surface averaged over the electrode surface

$$N = D \left\langle \frac{\partial C}{\partial y} \right\rangle_o \tag{2}$$

fluctuations in the current are directly proportional to fluctuations in $\left\langle \frac{\partial C}{\partial y} \right\rangle_o$.

Fluctuations in the current therefore reflect fluctuations in the flow field in the region in which there are significant concentration gradients. Because of the small size of the electrodes and the small value of the molecular diffusion coefficient for ferricyanide ions this is a relatively small region. If δ_v is defined as the thickness of the viscous sublayer, and if δ_c is defined as the thickness of the concentration boundary layer, then at any instant of time a profile down the center of the electrode might be represented as shown in Figure 4. The boundary defining δ_c should be varying with time. The diffusion-layer thickness on an average increases with electrode length; however for the systems considered $\delta_c << \delta_v$. When one uses the Nernst diffusion layer concept (*2*), δ_c is estimated to be 6.5 × 10^{-4} in. at a Reynolds number* of 10,000 and 3.2 × 10^{-4} in. at a Reynolds number of 50,000 for a 0.064-in. diameter electrode. These would correspond to values of δ_c/δ_v of 0.082 and 0.16. Therefore fluctuations in the current reflect velocity fluctuations in a region well within the viscous sublayer.

---

* The Reynolds number throughout this paper is based on the pipe diameter and the mean velocity.

Because of the very large rate of reaction on the surface of the electrode and because of the relative small frequency of the fluctuations it is felt that the kinetics of the electrode reaction were not affecting the measurements. However this matter will be given further consideration in future work.

MEASUREMENTS

The measurements are presented in terms of a mass transfer coefficient defined as

$$K = N/(C_B - C_W) \qquad (3)$$

which may be related to the current through Equation (1). If average and fluctuating values of K and I may be defined as

$$I = \overline{I} + i \qquad (4)$$

$$K = \overline{K} + k \qquad (5)$$

then fluctuations in the current are related to fluctuations in the mass transfer coefficient by the following equation:

$$k = \frac{i}{A n_e F C_B} \qquad (6)$$

Figures 5 to 9 show the variation of $(1 + k/\overline{K})$ with time for a 0.064-in. electrode at different Reynolds numbers. The root-mean-square value of k measured with the random signal voltmeter is also shown in these figures. At low Reynolds numbers the flow is laminar and there are no recorded fluctuations. At a Reynolds number of 2,140 a slight wavy disturbance is noted. At a slightly larger Reynolds number, Figure 5, intermittant patches of turbulent flow and nonturbulent flow are indicated. The frequency of occurrence of the turbulent patches increases with Reynolds number. At a Reynolds number of 3,740 the field is completely turbulent as indicated in Figure 6. Further increase in Reynolds number increases the frequency of the fluctuations of the mass transfer coefficient, Figure 7.

Simultaneous records at a Reynolds number of 13,600 of the signals from two 0.064-in. electrodes located downstream of one another are shown in Figures 8 and 9. In Figure 8 the electrodes are spaced 6.30 pipe diameters apart, and there is a low degree of correlation between the two signals. In Figure 9 the spacing was 0.197 pipe diameters, and there is a high degree of correlation. A correlation coefficient may be defined as

$$R = \frac{\overline{k_A k_B}}{\sqrt{\overline{k^2_A}}\sqrt{\overline{k^2_B}}} \qquad (7)$$

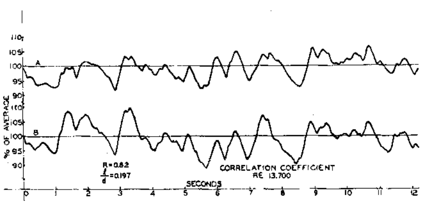

Fig. 9. High-correlation fluctuations in the rate of mass transfer recorded simultaneously for two locations close together.

For the arrangement shown in Figure 8 R = 0.018, while for Figure 9 R = 0.815.

A frequency spectrum may be defined as

$$\overline{k^2} = \int_0^\infty W\,df \qquad (8)$$

Measurements of W for Reynolds numbers of 34,200 and 3,280 with a 0.064-in. electrode are shown in Figure 10.

ACKNOWLEDGMENT

Fellowship support for one of the authors was received from the National Science Foundation, The Visking Corporation, and the Monsanto Chemical Company.

NOTATION

A = area of the electrode surface
C = concentration of ferricyanide ions
D = diffusion coefficient
d = diameter of the pipe
e = electrode voltage
F = Faraday's constant
f = frequency in cycles/sec.
I = instantaneous electrode current
$\overline{I}$ = time average value of I
i = fluctuation in the current
K = instantaneous value of the mass transfer coefficient
$\overline{K}$ = time average of the mass transfer coefficient
k = fluctuation of the mass transfer coefficient
l = distance between the test electrodes center to center
N = rate of transfer ferricyanide ions to the electrode surface per unit area
n_e = number of electrons involved in the electrode reaction
R = correlation coefficient defined by Equation (7)
u = local fluid velocity
u^* = friction velocity
W = frequency spectrum distribution function defined by Equation (8)
y = distance from the wall
y^+ = dimensionless distance = $(y u^*)/(\nu)$
δ_c = thickness of the concentration boundary layer
δ_v = thickness of the viscous sublayer
ν = kinematic viscosity

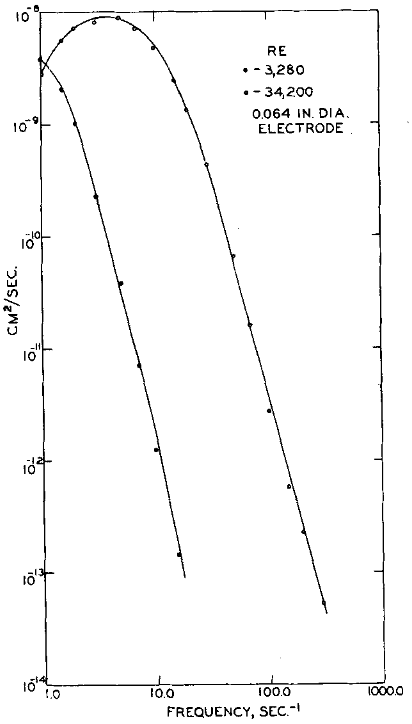

Fig. 10. Frequency spectrum.

LITERATURE CITED

1. Corrsin, Stanley, "Some Current Problems in Turbulent Shear Flow," Chap. XV, Naval Hydrodynamics, Publication 515, National Academy of Sciences—National Research Council, Washington, D. C. (1957).
2. Delahay, Paul, "New Instrumental Methods in Electrochemistry," p. 217 Interscience, New York (1954).
3. Eisenburg, Morris, C. W. Tobias, and C. R. Wilke, *Chem. Eng. Progr. Symposium Ser. No. 16*, **51**, p. 1 (1955); *J. Electrochem. Soc.*, **103**, 413 (1955).
4. Fage, A., and H. C. H. Townend, *Proc. Roy. Soc. London*, **135A**, 656 (1932).
5. Hanratty, T. J., *A.I.Ch.E. Journal*, **2**, 359 (1956).
6. Klebanoff, P. S., *Natl. Advisory Comm. Aeronaut. Tech. Note 3178* (1954).
7. Kline, S. J., and P. W. Runstadler, *Report MD-3*, Dept. of Mech Eng., Stanford University, Stanford, California (1958).
8. Laufer, John, *Natl. Advisory Comm. Aeronaut. Tech. Rept. 1053* (1951).
9. *Ibid.*, *Tech. Rept. 1174* (1953).
10. Lin, C. S., E. B. Denton, H. S. Caskill, and G. L. Putnam, *Ind. Eng. Chem.*, 43, 2136 (1951).
11. Sandborn, V. A., *Natl. Advisory Comm. Aeronaut. Tech. Note 3266* (1955).

Manuscript received June 29, 1961; revision received September 18, 1961; paper accepted September 19, 1961.