ChE laboratory

AN ENTRANCE REGION MASS TRANSFER EXPERIMENT

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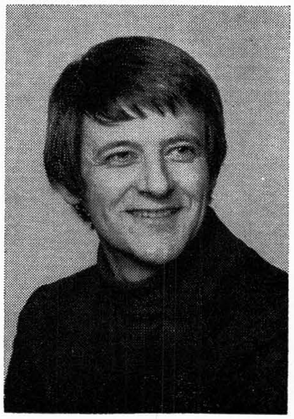

Gordon Youngquist received his BS from the University of Minnesota and his MS and PhD from the University of Illinois. Since 1962 he has been at Clarkson College of Technology where his teaching and research interests are in reactor analysis, crystallization and porous media.

This experiment is simple to carry out in the laboratory, and a large amount of good data can be obtained in a relatively short period of time.

PART OF CLARKSON'S undergraduate laboratory course is devoted to experiments which reinforce concepts introduced in earlier lecture courses. This paper describes an experiment designed to reveal the consequences of the development of a concentration boundary layer. The rate of a mass transfer limited electrochemical reaction is measured and used to obtain the dependence of average Sherwood number on Reynolds number and entrance length. The experimental results may be compared directly to theory for laminar flows and to existing correlations for turbulent flows.

When a fluid enters a section of conduit where mass is exchanged between the fluid and the conduit wall, the concentration profile in the fluid undergoes rapid change. An initially flat profile changes to one exhibiting a large concentration gradient at the wall. The shape of the concentration profile in the fluid leaving a mass transfer section will depend on the length of the section until, for sufficiently long sections, the profile becomes fully developed. As a consequence of the development of the profile, the local mass transfer coefficient decreases from a large value at the leading edge of the mass transfer section to a minimum downstream. Correspondingly, the average mass transfer coefficient decreases with increasing length for the mass transfer section. Dependence of the mass transfer coefficient on system properties and conditions is normally described as

$$Sh_{Avg.} = f\left(Re, Sc, \frac{d_e}{L} \right)$$

where

$$Sh_{Avg.} = \frac{k_{Avg.}\, d_e}{D};\ Re = \frac{d_e \langle v \rangle}{\nu};\ Sc = \frac{\nu}{D}$$

and

$k_{Avg.}$ = average mass transfer coefficient
D = diffusivity
ν = kinematic viscosity
d_e = equivalent diameter
$\langle v \rangle$ = average velocity
L = mass transfer length

For laminar flow between flat plates, Leveque analysis (Newman, 1968; Newman, 1973) gives

$$\mathrm{Sh}_{\mathrm{Avg.}} = 1.85\left(\frac{\mathrm{ReScd_e}}{\mathrm{L}}\right)^{1/3} \tag{1}$$

For turbulent flow in circular tubes, Van Shaw, et al. (1963) give

$$\mathrm{Sh}_{\mathrm{Avg.}} = 0.276\,\mathrm{Re}^{0.58}\mathrm{Sc}^{1/3}\left(\frac{\mathrm{d_e}}{\mathrm{L}}\right)^{1/3} \tag{2}$$

Electrode reactions have often been used for experimental determination of forced convection mass transfer rates in solution (Lin, et al. 1951; Van Shaw et al., 1963; Eisenberg, et al., 1955). Some of the various reactions used are:

1.) Reduction of ferricyanide ion
$\mathrm{Fe(CN)_6^{-3} + e \rightarrow Fe(CN)_6^{-4}}$
2.) Reduction of quinone
$\mathrm{C_6H_4O_2 + 2H^+ + 2e \rightarrow C_6H_4(OH)_2}$
3.) Reduction of oxygen
$\mathrm{O_2 + 4e + 2H_2O \rightarrow 4OH^{-1}}$
4.) Oxidation of ferrocyanide ion
$\mathrm{Fe(CN)_6^{-4} \rightarrow Fe(CN)_6^{-3} + e}$

Such reactions involve two steps: mass transfer of reactants from the bulk solution to the surface of the electrode and reaction at the electrode. At low cell potentials, the reaction rate is reaction limited. As the cell potential is increased, the rate increases to the point where it is mass transfer limited, the concentration of reactant at the electrode surface is essentially zero, and the limiting cell current is attained. Under these conditions, the mass transfer rate is given by

$$\mathrm{k_{Avg.}AC_{\infty}} = \frac{\mathrm{i_L}}{\mathrm{nF}} \tag{3}$$

where

A = electrode area
$\mathrm{C_{\infty}}$ = bulk reactant ion concentration
$\mathrm{i_L}$ = limiting cell current
F = Faraday's constant
n = number of electrons per ion reacted at the electrode

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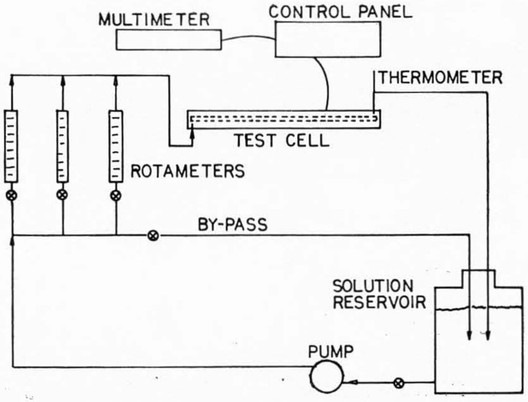

FIGURE 1. Schematic Diagram of Apparatus

By measuring the limiting current and knowing the bulk reactant concentration and the electrode area, the average mass transfer coefficient may be calculated.

APPARATUS AND TECHNIQUES

REDUCTION OF FERRICYANIDE ion in a sodium hydroxide solution on a nickel cathode is used to measure mass transfer rates in our experiment:

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

The apparatus, shown schematically in Figure 1, consists of a rectangular duct through which $\mathrm{Fe(CN)_6^{-3}/Fe(CN)_6^{-4}/NaOH}$ solution is circulated. Current is passed between the test electrodes using a 6 volt storage battery as the D.C. source. A ten-turn potentiometer is provided for cell voltage control. Current and voltage in the test section are measured with a digital multimeter. Rotameters are provided for flow measurement. PVC pipe was used for connecting lines and valves and pump body were of stainless steel.

The test cell, mounted horizontally, is made of Plexiglas with a duct 0.635 cm × 2.86 cm in cross-section and approximately 125 cm in length. Six cathodes (0.635, 1.27, 1.91, 2.54, 3.81 and 5.08 cm × 2.86 cm) are provided. Oxidation of ferrocyanide ion takes place at a large anode (30 × 2.86 cm) placed opposite to the cathodes. The electrolyte solution contains equimolar amounts of potassium ferricyanide and ferrocyanide (about 0.015 molar). Approximately 2 M. NaOH is used as an indifferent electrolyte to eliminate ionic migration effects.

To determine the limiting current, and hence the mass transfer coefficient, steady flow at a de-

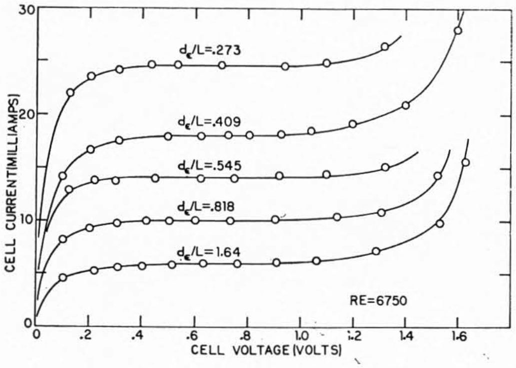

FIGURE 2. Data for Determination of Limiting Current

sired rate through the test section is established. Then, the cell current is measured as a function of applied cell voltage for a given cathode. The procedure is repeated for each cathode and over the maximum flow rate range possible.

Additional details concerning the apparatus and procedures are appended.

RESULTS

FIGURE 2 SHOWS cell current vs cell voltage data acquired for determination of limiting current for several electrodes at constant flow rate. Some care must be taken to clean and activate the electrodes properly and to avoid dissolved oxygen (see Appendix) or the limiting current will not be well defined. It is apparent that the limiting current is attained for each of the electrodes in the cell voltage range 0.4-1.0 volts. Similar behavior is observed at various flow rates. Once this cell voltage range has been determined, limiting current data may be obtained quickly for the various electrodes and flow rates without changing the cell voltage. The rapid increase of the current at high voltages is caused by a second electrode reaction which results in hydrogen evolution. Naturally, the data of interest are in a cell voltage range below the point where this reaction becomes of importance.

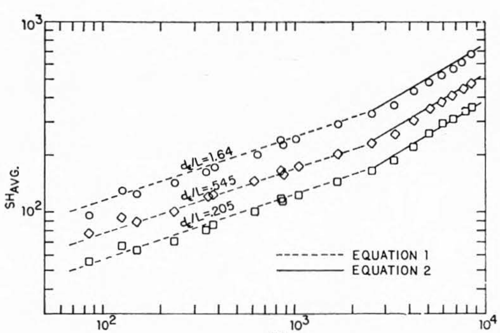

FIGURE 3. Dependence of Average Sherwood Number on Reynolds Number

From the limiting current, the average mass transfer coefficient may be calculated by rearrangement of Equation 3 according to

$$k_{Avg.} = \frac{i_L}{nFAC_\infty}$$

These data then may be compared to the predictions of Equations 1 and 2. For calculation of the Sherwood number, the diffusivity of ferricyanide ion is necessary. Van Shaw, et al. (1963) give a value of 5.2×10^{-6} cm²/sec. Alternatively, the diffusivity might be estimated from the Nernst equation:

The experimental results here provide clear confirmation of several qualitative cause-effect relationships commonly used in introducing boundary layer theory.

$$D = \frac{RT\overset{o}{\lambda_i}}{Z_i F^2}$$

where

$\overset{o}{\lambda_i}$ = equivalent conductance at infinite dilution

Z_i = ion valence

For calculation of the Reynolds number and Schmidt number, the kinematic viscosity also is needed and is easily determined by experiment.

Figure 3 depicts laboratory data for the dependence of average Sherwood number on Reynolds number for several electrode lengths. Transport properties used for calculation are

$D = 5.2 \times 10^{-6}$ cm²/sec (Van Shaw, et al., 1963)

$\nu = 8.1 \times 10^{-3}$ cm²/sec (determined experimentally @ 31°C)

Figure 4 shows data for the dependence of average Sherwood number on entrance length. The transition from laminar flow appears clearly as a change in slope on the Reynolds number plot at Re ≈ 2400, and the Sherwood number decreases with length as anticipated. The lines through the data on each figure represent the predictions of Equations 1 and 2. The agreement between experiment and prediction is very good. The good agreement with Equation 2 is somewhat surprising since the corresponding experimental data were

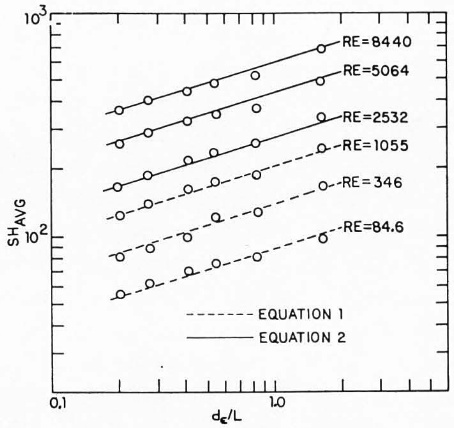

FIGURE 4. Dependence of Average Sherwood Number on Entrance Length

all in the transition region. The average deviation is 4.9% for the laminar flow data (72 data points) and 5.9% for the turbulent flow data (48 data points).

The data also were correlated using a least squares technique. Using the functional form of Equations 1 and 2,

$$Sh_{Avg.} = aSc^bRe^c\left(\frac{d_e}{L}\right)^d \qquad (4)$$

where a, b, c, and d are unknown constants. Linearizing,

$$\ln(Sh_{Avg.}) = \ln(a) + b\ln(Sc) + c\ln(Re) + d\ln\left(\frac{d_e}{L}\right) \qquad (5)$$

Since it was not feasible to vary the Schmidt number experimentally, Equation 5 is of the form

$$y = A + cx_1 + dx_2 \qquad (6)$$

where

$$y = \ln(Sh_{Avg.})$$
$$A = \ln(a) + b\ln(Sc)$$
$$x_1 = \ln(Re)$$
$$x_2 = \ln\left(\frac{d_e}{L}\right)$$

Good agreement of experimental data with the predictions of theory and/or existing correlations is often satisfying to the students, although most tend to need considerable guidance in examining the data.

Using least squares, best values of A, c, and d were determined from the data, separately for the laminar and turbulent flow ranges. The results were

$$Sh_{Avg.} = 20.1\,Re^{0.336}\left(\frac{d_e}{L}\right)^{0.317} \quad \text{for laminar flow} \qquad (7)$$

and

$$Sh_{Avg.} = 1.94\,Re^{0.628}\left(\frac{d_e}{L}\right)^{0.291} \quad \text{for turbulent flow} \qquad (8)$$

which compare favorably with Equations 1 and 2. Using these correlations, the average deviations are 3.5% and 3.6% for laminar and turbulent flow, respectively. The results of the correlation are shown in Figures 5 and 6.

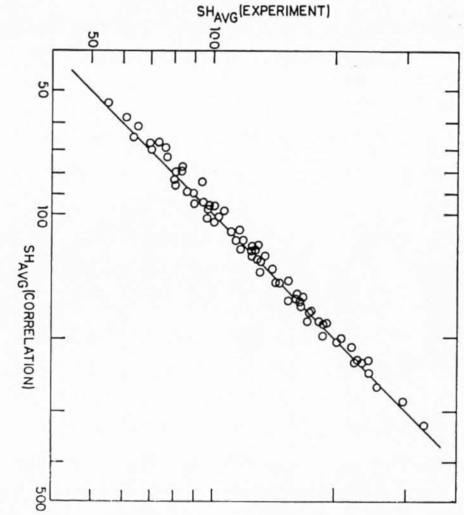

FIGURE 5. Comparison of Experimental Data with Correlation (Laminar Flow)

DISCUSSION

THIS EXPERIMENT IS simple to carry out in the laboratory, and a large amount of good quality data can be obtained in a relatively short period of time. (The data shown in this paper were obtained in about three hours.) Students tend to find the data acquisition somewhat boring, since this largely consists of reading the rotameter and multimeter while making occasional valve and potentiometer adjustments. The real challenge lies in developing some understanding of the physics implicit in the data and in doing the data correlation.

For many students, the notions of boundary

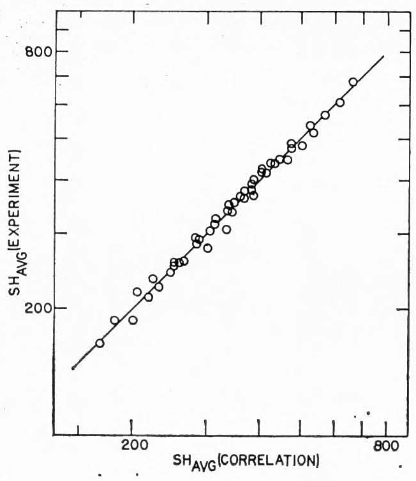

FIGURE 6. Comparison of Experimental Data with Correlation (Turbulent Flow)

layer development are difficult to grasp. The experimental results here provide clear confirmation of several qualitative cause-effect relationships commonly used in introducing boundary layer theory. Good agreement of experimental data with the predictions of theory and/or existing correlations is often satisfying to the students, although most tend to need considerable guidance in examining the data. Exposure to an electrochemical reaction is educationally useful. Moreover, the transition from reaction control to mass transfer control observed in determining the limiting current reinforces the importance of mass transfer to many chemically reacting systems.

The equipment has been relatively maintenance free, although some difficulty was experienced initially in finding a suitable technique for bonding the nickel electrodes to the Plexiglas duct. Prolonged exposure to the NaOH solution being circulated tends to weaken the adhesive bond of many cements. Flushing the duct with water after each use minimizes this effect. Care must be taken to keep the electrodes clean and properly activated (see Appendix) or the limiting current will be ill-defined. This may require occasional disassembly of the duct. Bubbling nitrogen into the feed storage tank for several hours prior to the start of the experiment serves to remove dissolved oxygen, another cause of an ill-defined limiting current. The electrolyte solution is stable, provided direct exposure to ultraviolet light which catalyzes decomposition reactions of the cyanides is avoided. Use of an opaque feed tank and plumbing and flushing the Plexiglas duct and rotameters after use solves the problem. Fresh electrolyte solution is normally prepared but once per semester. Concentrations are checked periodically using iodometric analysis for ferricyanide and permanganate titration for ferrocyanide (Kolthoff and Sandell, 1952). Ordinarily these concentrations do not change significantly over the course of a semester.

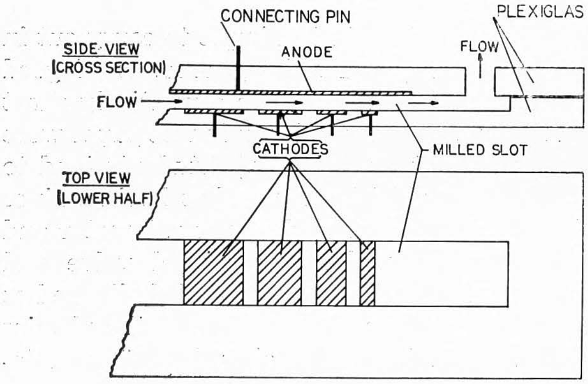

FIGURE 7. Detail of Test Cell Construction

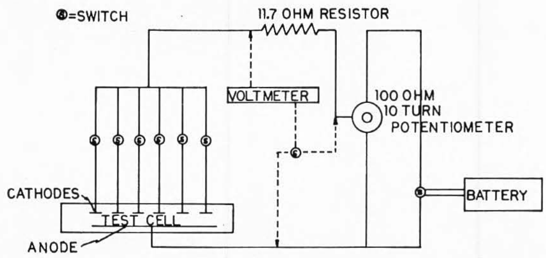

FIGURE 8. Schematic of Control and Measuring Circuit

ACKNOWLEDGMENT

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APPENDIX

Test Cell Assembly: The test cell was made from two pieces of 1/2 inch Plexiglas sheet approximately 10 x 125 cm (4 x 48 inches) as detailed in Figure 7. A slot 0.635 cm deep x 2.86 cm wide (1/4 x 1 1/8 inches) was milled in one piece to form the flow duct. 22 gage nickel sheet was used for the electrodes which covered the width of the duct. Each piece of Plexiglas was additionally milled to accommodate the thickness of the electrodes (secured using "Krazy Glue") so that a smooth flow channel was obtained. Electrical connecting pins were made by silver soldering a small brass machine screw to the back side of each electrode. The access hole through the Plexiglas for each pin was backfilled using Epoxy Cement. The halves of the cell were bolted together using Parafilm sheet as a gasket.

Some considerable care must be taken in attaching the cell electrodes. Many glues do not provide a strong adhesive bond between the nickel electrodes and the Plexiglas which is also resistant to attack by NaOH. Flushing the cell with water after use extends the useful life of the bond.

After attaching the electrodes and before bolting the cell together, the electrodes should be cleaned and activated. The electrode surfaces should be polished with fine emery cloth, followed by washing with detergent. To activate the electrodes, the test section is placed in approximately 2 M NaOH solution. A cell formed using a strip of nickel as the anode and each electrode in turn as the cathode is connected to a 6 volt D.C. source for 4 to 5 minutes. Caution should be used, as hydrogen evolution is considerable. Finally, the test section is rinsed with distilled water and the cell assembled.

Control and Measuring Circuit: A schematic of the control and measuring circuit is given in Figure 8. The cell voltage and current were determined using a digital voltmeter which could be switched alternately to measure the voltage drop across the cell and across a standard resistor placed in series with the cell. The cathodes were wired in parallel with an isolating switch for each. A 6 volt storage battery was used as the power source, and cell voltage was controlled using a 100 ohm, 10-turn potentiometer. □
