S_n = number of optimal and near optimal sequences desired
T = terminal or goal node; $T \epsilon N$; $T \neq B$
V = boil up vapor flow rate
X_i = node representing a partially completed sequence; an element of N
$\alpha_{m,n}$ = relative volatility between components m and n
$\Gamma_t^{m/n}(i, j)$ = an arc or separation operator for expanding node X_i into successor node X_j using separator type t, light key component m, and adjacent heavy key component n; an element of ϕ; acts as a pointer from node X_j back to node X_i
ϕ = complete set of feasible operators, $\{\Gamma\}$

Other Symbols

ϵ = element of
$\{ \}$ = set
$\wedge$ = and
$\forall$ = for all

LITERATURE CITED

Hart, E. H., N. J. Nilsson, and B. Raphael, "A Formal Basis for the Heuristic Determination of Minimum Cost Paths," *IEEE Trans. Systems Cybernetics*, 4, No. 2, 100 (1968).

Hendry, J. E., "Computer Aided Synthesis of Optimal Multicomponent Separation Sequences," Ph.D. thesis, Univ. Wisc., Madison (1972).

———, and R. R. Hughes, "Generating Separation Process Flowsheets," *Chem. Eng. Progr.*, **68**, No. 6, 69 (1972).

King, C. J., *Separation Processes*, McGraw-Hill, New York (1971).

Motard, R. L., M. Shacham, and E. M. Rosen, "Steady State Chemical Process Simulation," *AIChE J.*, **21**, 417-436 (1975).

Nilsson, N. J., *Problem-Solving Methods in Artificial Intelligence*, McGraw-Hill, New York (1971).

Rathore, R. N. S., K. A. Van Wormer, and G. J. Powers, "Synthesis of Distillation Systems with Energy Integration," *AIChE J.*, **20**, 940 (1974).

Robinson, C. S., and E. R. Gilliland, *Elements of Fractional Distillation*, 4 ed., McGraw-Hill, New York (1950).

Rodrigo, F. R., and J. D. Seader, "Synthesis of Separation Sequences by Ordered Branch Search," *AIChE J.*, **21**, 885 (1975).

Rudd, D. R., J. J. Siirola, and G. J. Powers, *Process Synthesis*, Prentice-Hall, Englewood Cliffs, N.J. (1973).

Seader, J. D., W. D. Seider, and A. C. Pauls, "FLOWTRAN Simulation—An Introduction," CACHE, Cambridge, Mass. (1974).

Thompson, R. W., and C. J. King, "Synthesis of Separation Schemes," Technical Report No. LBL-614, Lawrence Berkeley Laboratory (July, 1972*a*).

———, "Systematic Synthesis of Separation Schemes," *AIChE J.*, **18**, 941 (1972b).

Westerberg, A. W., and G. Stephanopoulos, "Studies in Process Synthesis-I," *Chem. Eng. Sci.*, **30**, 963 (1975).

Manuscript received May 28, 1976; revision received August 6, and accepted August 9, 1976.

Application of the Limiting Current Method to Mass Transfer in Packed Beds at Very Low Reynolds Numbers

PETER W. APPEL
and
JOHN NEWMAN

Materials and Molecular Research Division,
Lawrence Berkeley Laboratory,
and Department of Chemical Engineering,
University of California,
Berkeley, California 94720

The limiting current technique is used to obtain mass transfer coefficients at very low Reynolds numbers ($Re < 0.1$) in a packed bed consisting of stainless steel spheres. The data show that for $Re < 0.015$, the Nusselt numbers are below those predicted by existing empirical correlations. The results are discussed in the light of some mathematical models for packed beds reported in the literature and show semiquantitative agreement with the values predicted by Sorensen and Stewart (1974*a*).

SCOPE

A large number of mass transfer processes require a liquid flowing at low velocities through a porous electrode or a packed bed. At these velocities ($Re << 1$) and in the absence of natural convection, mass transfer coefficients in packed beds are only dependent upon the Péclet number. Experimental results in the low Reynolds number region, low Péclet number region are scarce and scatter widely. Therefore, reliable data in said region are important; to obtain these data the limiting current technique was used in a packed bed consisting of stainless steel spheres. For our experiments we have chosen the cathodic reduction of ferricyanide to ferrocyanide in excess supporting electrolyte. Procedures to minimize possible sources of error and design criteria are given.

CONCLUSIONS AND SIGNIFICANCE

It has been shown that the limiting current method is suitable for obtaining mass transfer coefficients in packed beds, in particular at very low Reynolds numbers, provided proper design and experimental procedures are followed.

Peter W. Appel is with Unilever Research, Vlaardingen, The Netherlands.

The correlation of Wilson and Geankoplis (1966), obtained at low Reynolds numbers, predicts values for the Nusselt number which become increasingly too high as the Péclet number drops below the value of 100. Our results, however, are in agreement with the theoretical predictions of Sörensen and Stewart (1974*a*, 1974*c*) and can be used as an aid in designing packed beds for the region investigated here.

A large number of processes have been (or are still being) developed which require a liquid flowing at low velocities through a porous electrode or a packed bed.

Processes using flow through porous electrodes are, for example, electro-organic synthesis (Davis, 1975), removal of metal ions from waste streams (Bennion and Newman, 1972; Posey, 1973), and desalination of seawater (Johnson and Newman, 1971). A variation of the porous electrode is the fluidized electrode (Fleischmann et al., 1971; Le Goff et al., 1969), where the electrode consists of spheres. This type of electrode may find applications in the removal of metal ions from waste streams containing particles which might otherwise plug up the porous electrode (Van Swaay et al., 1975).

Low velocities in packed beds are required for ion exchange processes, catalytic processes, adsorption, and chromatography.

EMPIRICAL STUDIES

Under certain conditions the reaction rate in a porous electrode may become limited by the mass transfer rate of the reactant in the solution to the electrode surface. In that case we have the same situation as in a packed bed. An exception is the ion exchange process, where migration may be important even if there is no current flowing (Van Brocklin and David, 1972), or where resistance to mass transfer inside the particles may contribute to the mass transfer coefficient (Miyauchi et al., 1975). In any case, availability of reliable mass transfer coefficients at very low Reynolds numbers is essential in the design of porous electrodes and packed beds. A large number of experimentally obtained mass transfer correlations can be found in the literature. They have been summarized by Karabelas et al. (1971).

Unfortunately, only a few researchers have extended their experiments to the region of Re' less than 0.1. Of these, Wilson and Geankoplis (1966) used the dissolution of benzoic acid spheres in water and a mixture of water and propylene glycol. They propose the following correlation to represent their data:

$$\epsilon Nu' = 1.09(Re')^{1/3} \tag{1}$$

but their experimental points scatter considerably for values of the Reynolds number less than 0.1. The same can be said about the results of Kunii and Smith (1961).

It is well known that in the limit of very low Reynolds numbers and in the absence of natural convection, the Nusselt number is only dependent on the Péclet number and the geometry of the flow system. Hence, Equation (1) suggests that natural convection has not been important in the experiments of Wilson and Geankoplis (1966). The region where natural convection becomes dominant depends, of course, on the Grashof number and the Reynolds number of the system.

Karabelas et al. (1971) used the limiting current technique (reduction of ferricyanide in the presence of excess sodium hydroxide) to investigate mass transfer in packed beds over a large range of Reynolds numbers ($0.1 < Re' < 1\,000$), including the effect of natural convection. Their electrodes, however, consisted of a single active sphere placed at different locations in the bed. There are two objections to this technique, especially if used in the low range of Reynolds numbers investigated here. The first is that the diffusion layer around a sphere is increasingly influenced by those of neighboring spheres as the Reynolds number is decreased. Secondly, if natural convection occurs, the distortion of the velocity profile near a sphere would also be influenced by natural convection effects on neighboring spheres. Also, channeling may occur.

Since the technique used by these authors is very similar to the one used here, we are interested to see under what conditions natural convection becomes important. They obtained the dependence of the Nusselt number on the Reynolds number in the lowest range by extrapolating to the value obtained for no flow at all. The solution of the diffusion equation in the absence of convection for steady mass transfer to a particle gives a constant value for the Nusselt number; the value depends on the particle geometry. For a sphere diameter of 12.7 mm, they find that $Nu' \approx 1.5$ in the bed with no flow. Since $Nu' = 2$ for a sphere in an infinite, stagnant medium (without adjacent surfaces), this indicates that natural convection in this system is not important if spheres with a diameter smaller than 12.7 mm are used.

For $Re' < 10$ and in the absence of natural convection, they propose

$$Nu' = 4.58(Pe')^{1/3} \tag{2}$$

which has the same dependence on the Péclet number as Equation (1) but gives values of the Nusselt number which are about 10% higher for $\epsilon = 0.26$.

Almost identical experiments have been performed by Mandelbaum and Böhm (1973), who used the same electrochemical technique but employed Raschig rings instead of spheres. Mass transfer coefficients were obtained by averaging the measured currents of six randomly placed active rings.

Gracon (1974) used stacked disks of woven metal screen in studying slow flow through porous electrodes at the limiting current. Unfortunately, he did not calculate mass transfer coefficients for this system, probably because the concentration of the reacting species at the bed outlet was practically equal to zero. Under those circumstances, small uncertainties in the measured current will give rise to large uncertainties in the Nusselt number, as will be shown later.

Even though the limiting current method may be more complicated to implement than the dissolution technique, especially if the whole bed is to be active, with proper choice of reacting species it is particularly suited for measurements at low Reynolds numbers for the following reasons. First, the ferrocyanide/ferricyanide redox system in excess supporting electrolyte and with low reactant concentration level gives less natural convection effects than common dissolution techniques, since the excess of product near the electrode surface counteracts the depletion of the reactant near the surface (Selman and Newman, 1971). Of course, this is also true for the density differences between the inlet stream and the outlet stream of the bed. Second, no change in surface area occurs. This becomes particularly advantageous if long times are needed to reach steady state in the flow system. Lastly, we can calculate the mass transfer coefficients in three independent ways: from the change in reactant concentration, from the change in product concentration, and from the limiting current.

Selman (1971) gives an extensive review of limiting current methods, their reliability, and the systems for which they have been used.

MATHEMATICAL MODELS

In order to be able to predict mass transfer coefficients in packed beds from an assumed pore geometry, one first has to solve the Navier-Stokes equations with the corresponding boundary conditions. The early models of packed beds involve straight tubes and include a random orientation in the bed as well as a distribution of the tube radii (Scheidegger, 1960). Prediction of mass transfer coefficients with this model were not attempted until recently by Sörensen and Stewart (1974*a*). These authors solved the extended Graetz problem including axial diffusion in the range of Peclet numbers of interest here. An additional dimensionless variable for this model is the ratio of tube length to tube diameter, the wall beyond and before the active region being insulated. They contend that the form of the solution is applicable to mass transfer in packed beds at low Reynolds numbers where axial diffusion becomes important. For $Pe > 100$, they find that the Nusselt number has the same dependence on the Reynolds number as correlations 1 and 2, whereas for $Pe < 10$ the Nusselt number drops below the values predicted by these correlations.

The obvious disadvantage of the straight tube models is that they do not take into account the converging-diverging nature of actual channels in packed beds. To overcome this shortcoming, Happel (1958) developed the free surface model, which accurately predicts pressure drops in packed beds at low Reynolds numbers. Kusik and Happel (1962) used a combination of the free surface model and boundary-layer theory, valid for high Péclet numbers and for Reynolds numbers beyond the region investigated here. In order to extend the free surface model to predictions of mass transfer rates at low Reynolds numbers, Pfeffer and Happel (1964) solved the convective diffusion equation for this geometry; they assumed constant concentrations both on the surface of the sphere and at the free surface. This may be a first-order correction to the boundary-layer model, but it is not applicable to very low Péclet numbers since the concentration at the free surface becomes increasingly nonuniform. In addition, as several authors have pointed out (Nelson and Galloway, 1975; Sörensen and Stewart, 1974*a*), the boundary condition at the free surface represents a sink of material This model also predicts a one third exponent of the Péclet number for $Pe' > 100$, while for $Pe' < 100$ the Nusselt number gradually reaches a constant value. Nelson and Galloway (1975) combined the geometry of the free surface model and Danckwerts surface renewal theory to explain the low heat transfer coefficients observed at low Reynolds numbers (Kunni and Smith, 1961). Though it does remove the objection mentioned above, the concept of a surface renewal frequency is not realistic in creeping flow. El-Kaissy and Homsy (1973) modified the free cell model by assuming distorted instead of spherical cells. Since they used a boundary-layer solution, their results are valid for high Reynolds numbers.

Payatakes et al. (1973) solved the Navier-Stokes equations for a periodically constricted tube, but the pertinent solution of the convective diffusion equation has not been obtained yet.

Sörensen and Stewart (1974*b*) calculated the velocity field around a cubic array of spheres for creeping flow. Subsequently, they obtained the solution to the boundary-layer equation (1974*d*) and the convective-diffusion equation (1974*c*). The latter results are also pertinent to our experimental observations.

CALCULATION PROCEDURE

The theory of porous electrodes has been reviewed recently by Newman and Tiedemann (1975). We confine ourselves to the situation where the cell is operated at the limiting current. Averaging procedures for the pertinent quantities are given in Dunning's thesis (1971).

At the limiting current, the concentration of the reactant at the electrode surface approaches zero. Also, in the presence of supporting electrolyte, the influence of migration on the reactant may be neglected. For low Péclet numbers the axial mixing coefficient E is primarily determined by molecular diffusion:

$$E = \frac{D_R}{\tau} \tag{3}$$

where τ is a tortuosity factor about equal to 1.4. Molecular diffusion in the axial direction does not become dominant until very low values of the Péclet number are reached (Sherwood et al., 1975). With these assumptions, we define the local mass transfer coefficient k_m

$$v \frac{dc_R}{dx} = - k_m a c_R \tag{4}$$

so that k_m can be calculated by integrating Equation (4) over the length of the bed:

$$\frac{c_{R,O}}{c_{R,L}} = \exp\left(\frac{a k_m L}{v} \right) \tag{5}$$

The relation between the average current density in the solution i_2 and the reactant concentration c_R is given by Faraday's law. For the reduction of ferricyanide to ferrocyanide, it takes the form

$$v \frac{dc_R}{dx} = \frac{1}{F} \frac{di_2}{dx} \tag{6}$$

with the boundary condition

$$i_2 = 0 \quad \text{at} \quad x = L \tag{7}$$

This boundary condition implies that the counterelectrode (anode is located at $x < 0$. The limiting cell current I_{lim} (which, of course, is measured experimentally) follows from integration of Equation (6):

$$I_{\text{lim}} = vF(c_{R,O} - c_{R,L}) \tag{8}$$

In evaluating the potential distribution in the solution, we can neglect the diffusion potential and use Ohm's law

$$i_2 = - \kappa \frac{d\Phi_2}{dx} \tag{9}$$

with the boundary condition

$$\Phi_2 = 0 \quad \text{at} \quad x = 0 \tag{10}$$

The potential drop in the solution across the bed $\Delta\Phi_2$ is then given by

$$\Delta\Phi_2 = vF\frac{c_{R,O}}{\alpha\kappa}[-1 + (1 + \alpha L)e^{-\alpha L}] \qquad (11)$$

where

$$\alpha = ak_m/v \qquad (12)$$

The equations presented here (and derived by Bennion and Newman, 1972) serve as a basis for the design of a porous electrode which can be used for mass transfer studies.

DESIGN CONSIDERATIONS

In choosing a porous electrode suitable for studying mass transfer rates in packed beds, several criteria have to be met:

1. The solid matrix should be representative of common packing material in packed beds yet should have a low resistivity between all parts of the solid matrix.
2. The electrochemical reaction rate should be fast with respect to the transfer rate of reacting species from the bulk solution to the electrode surface.
3. A long limiting current plateau should be obtained. This enables accurate evaluation of the limiting current.
4. The electrode surface should not change with time due to deposition or dissolution reactions.
5. No side reactions may occur.

For our experiments we have chosen the reduction of ferricyanide. This reaction has been used in numerous mass transfer experiments because the reaction is fast (if the electrode surface is properly treated), it does not change the electrode surface, and it gives a long limiting current plateau before hydrogen starts to evolve. Actually, the length of the plateau will appear to decrease as the flow rate through the bed is increased, since a higher ohmic potential drop is included before the limiting current is reached. This can be seen from Equation (11). The same equation also shows that the ohmic potential drop can be reduced by decreasing the ratio of the reactant concentration to the concentration of the supporting electrolyte. On the other hand, a decrease in reactant concentration will decrease the limiting current [see Equation (8)] and hence the accuracy of the current measurement. Similarly, the accuracy with which the reactant concentration can be determined by analytical methods will diminish. Hence, there is a maximum permissible flow rate for any design, dependent upon the current density and ohmic potential drop in the solution, the height of the bed, and the distance between cathode and anode.

If hydrogen starts to evolve, it will occur first at the front of the electrode since the potential difference between electrode and solution is largest at the front [see Equation (11)]. It is also possible that oxygen will be produced at the anode. Whether hydrogen or oxygen is produced first depends upon the pH of the solution. Consequently, our desire to obtain a limiting current and hence a large potential difference between cathode and solution everywhere in the bed must be balanced against our wish to avoid hydrogen evolution or any other side reaction.

The reliability of the data is strongly dependent upon the ratio of the inlet to the outlet concentrations. This ratio may be neither too small nor too large. In either case, small inaccuracies in determining the concentrations or the limiting current will have a large effect on the mass transfer coefficient calculated from Equation (5). Moreover, if this ratio is close to unity, Equation (8) shows that the limiting current becomes too small to be measured accurately at all. These considerations set a lower as well as a higher limit on the allowable flow rates through the bed.

Mass transfer coefficients calculated from Equation (5) do not reflect the influence of axial dispersion upon the overall bed behavior. It is possible, however, to include this influence in the calculations of the mass transfer coefficients (Wehner and Wilhelm, 1956). We have not done so in view of Equation (3) and the findings of Wilson and Geankoplis (1966) that in the range of Péclet numbers investigated here, no axial mixing effects could be detected. An alternative, and perhaps more valid, interpretation is that Equation (5) defines an average overall mass transfer coefficient describing the actual behavior of a packed bed at limiting current.

EXPERIMENTAL

Details of the experimental apparatus and procedure can be found in Appel's thesis (1976) and will not be given here.

The electrochemical cell used for the determination of mass transfer coefficients in packed beds was a modified version of the cells used by Bennion and Newman (1972) and by Yip (1973). These modifications were made to reduce entrance and exit effects. The bed diameter was 8.8 cm, and the packing consisted of 3.97 mm stainless steel spheres. To avoid channeling, the spheres were packed such that a rhombohedral or hexagonal close packing was obtained. The anode was placed above the cathode, with the feed inlet placed in between. Part of the feed stream flowed through the cathode, part through the anode; the flow rate through the anode was always about 20% higher than the flow rate through the cathode. In addition, the anode consisted of four layers of spheres, and the cathode consisted of three layers, so that a limiting current was insured at the cathode. The cathode contained 1 259 ± 1 spheres and had a porosity of 0.372, a specific interfacial area of 9.50 cm^{-1}, and a thickness of 1.06 cm.

The electrolyte was an equimolar solution (0.01 M) of ferrocyanide and ferricyanide with potassium nitrate (0.950 ± 0.005 M) as supporting electrolyte. This solution was supplied from a constant head tank; feed and outlet streams were interrupted to avoid stray currents. The temperature of the system was kept at 25° ± 0.05°C.

The limiting current curves were obtained by increasing the potential of the working electrode stepwise with respect to the reference electrode, starting at the equilibrium potential. At each increment, the current was measured after steady state had been reached.

For each run, samples of the inlet and outlet streams were taken; subsequently, the composition, the density, the viscosity, and the conductivity were determined. The measurements of the last three quantities can be summarized by three numbers: 1.058 ± 0.001 g/cm^3 for the density, 0.868 ± 0.007 $\text{mN} \cdot \text{s/m}^2$ for the viscosity, and 0.0884 ± 0.0003 $\Omega^{-1} \cdot \text{cm}^{-1}$ for the conductivity. The effective conductivity κ within the pores can then be estimated (Newman and Tiedemann, 1975) to be 0.02 $\Omega^{-1} \cdot \text{cm}^{-1}$.

The accuracy of the current measurements was ±0.5 mA; the concentrations of the ferrocyanide and the ferricyanide (determined by titration) are estimated to be accurate within 5×10^{-8} mole/cm³. Measured values are given in Table 1.

Diffusivities were not measured but were calculated from Smyrl's data (1973):

$$\frac{\mu D_{\text{ferri}}}{T} = 1.68 \times 10^{-11}\frac{N}{{}^\circ K} \qquad (13)$$

RESULTS

In Figure 1 the current is plotted as a function of $U - U_{\text{equil}}$ for different Reynolds numbers. At low flow rates, a long limiting current plateau is obtained, which becomes shorter as the flow rate is increased. As

TABLE 1. MEASURED VARIABLES IN THE PACKED BED EXPERIMENTS. THE pH OF THE SOLUTION WAS 5.9, AND THE PARTICLE DIAMETER WAS 0.397 CM

	Concentrations, 10^{-6} mole/cm^3					
	Ferricyanide		Ferrocyanide			Flow rate
Run #	Inlet	Outlet	Inlet	Outlet	i_{lim} mA	cm^3/s
8	9.92	3.34	9.50	16.18	66.9	0.104
10	9.78	1.60	9.54	17.82	34.4	0.0432
11	9.48	2.43	9.42	16.69	47.9	0.0700
12	9.59	3.71	9.48	15.31	80.3	0.143
13	9.98	1.04	9.17	18.22	23.5	0.0265
15	10.06	4.19	10.11	15.81	80.0	0.142
16	10.06	4.69	10.11	15.44	94.6	0.183
17	10.06	4.98	10.11	15.25	110.1	0.224
19	9.97	0.53	9.98	19.47	9.54	0.0103

TABLE 2. CALCULATED VARIABLES IN THE PACKED BED EXPERIMENTS

Run #	D_{ferri} $\times 10^5$ cm^2/s	k_m $\times 10^5$ cm/s	Nu	Re	Pe
8	0.584	18.4	1.24	0.0218	30.4
10	0.583	12.8	0.860	0.0090	12.6
11	0.583	15.7	1.05	0.0147	20.5
12	0.572	21.5	1.47	0.0294	42.6
13	0.574	10.0	0.69	0.0055	7.88
15	0.576	19.6	1.34	0.0294	42.0
16	0.575	22.3	1.52	0.0378	54.2
17	0.574	25.5	1.74	0.0462	66.5
19	0.575	5.1	0.35	0.00212	3.05

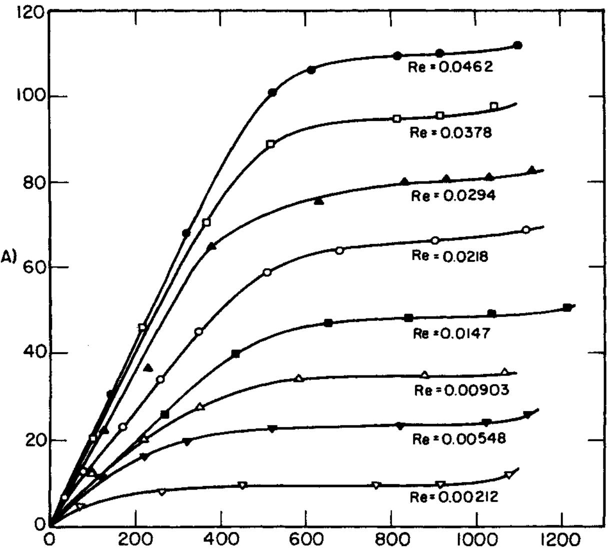

Fig. 1. Limiting current curves.

discussed before, this effect can be attributed to the increasing contribution of the ohmic potential drop at increasing flow rates and indicates an upper limit for the allowable flow rates. At very high voltages, the slope of the curve increases. This indicates that a side reaction has occurred, probably the evolution of hydrogen. No bubbles have been detected in the cathode, however. The values of $\Delta\Phi_2$ calculated from Equation (11) range from 2 to 42 mV.

The mass transfer coefficients were calculated from Equation (5). The inlet concentration of the ferricyanide ion was obtained analytically; the exit concentration of the ferricyanide ion was obtained in three different ways:

1. Analytically.
2. By subtracting the difference between inlet and outlet concentrations of the ferrocyanide ion (also determined analytically) from the inlet concentration of the ferricyanide ion.
3. Same as 2, but the difference between the ferricyanide concentrations was obtained from the limiting current value, according to Equation (8). If, for any run, the mass transfer coefficient calculated by any of these methods deviated more than 10% from the mean, that run was discarded. Calculated quantities are shown in Table 2, where k_m is the mean of the three determinations.

Application of the Graetz analysis through the concept of straight cylindrical pores in the bed suggests that the appropriate Nusselt number to use is

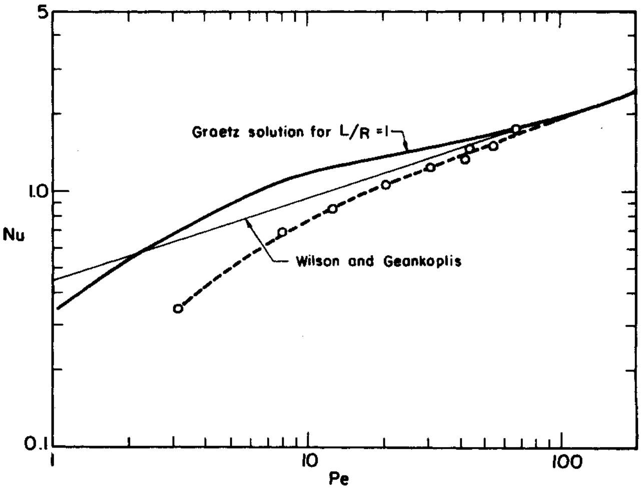

Fig. 2. Nusselt number as a function of Péclet number for packed beds.

$$Nu = \frac{\epsilon k_m}{a D_R} \tag{14}$$

Similarly, the Péclet number is defined as

$$Pe = \frac{v}{a D_R} \tag{15}$$

The Nusselt number has been plotted as a function of the Péclet number in Figure 2. It shows that our experimental values start to deviate from correlation 1 below $Pe = 100$. For comparison, we have plotted the Graetz solution of Sörensen and Stewart (1974*a*) for a ratio of tube length to tube radius of 1. This is an appropriate value for packed beds, and, although our values are also below their predicted values, they also show a deviation from the one third exponent of the Péclet number as the Péclet number is decreased. A similar trend is predicted by the regularly packed sphere model of the same authors (1974*c*).

In the light of these findings and because of the mentioned need for accurate mass transfer correlations in packed beds at very low flow rates, further investigations into the effect of varying the bed thickness on mass transfer coefficients are needed. Furthermore, the limiting current technique is very suitable for investigating the influence of natural convection and migration by varying the concentrations of reactants and supporting electrolyte.

ACKNOWLEDGMENT

This work was supported by the United States Energy Research and Development Administration.

NOTATION

a = specific interfacial area, cm^{-1}
$c_{R,O}$ = feed concentration, mole/cm^3
$c_{R,L}$ = exit concentration, mole/cm^3
c_R = reactant concentration per unit volume of solution, mole/cm^3
d_p = sphere diameter, cm
D_R = diffusion coefficient of reactant in feed solution, cm^2/s
E = axial mixing coefficient, cm^2/s
F = Faraday's constant, 96 487 C/equiv
i_2 = superficial current density in pore phase, A/cm^2
$I_{\lim}$ = limiting cell current density, A/cm^2
k_m = coefficient of mass transfer between flowing solution and electrode surface, cm/s
L = thickness of bed, cm
Nu = $\epsilon k_m/aD_R$, modified Nusselt number
Nu' = $k_m d_p/D_R$, Nusselt number
Pe = $ReSc$, modified Péclet number
Pe' = $Re'Sc$, Péclet number
R = equivalent tube radius, cm
Re = $v/a\nu$, modified Reynolds number
Re' = vd_p/ν, Reynolds number
Sc = ν/D_R, Schmidt number
T = absolute temperature, °K
U = cathode potential, V
v = superficial fluid velocity, cm/s
x = distance from bed entrance, cm

Greek Letters

α = ak_m/v, cm^{-1}
ϵ = porosity
κ = conductivity of solution within the electrode, mho/cm
μ = dynamic viscosity of solution, $N \cdot s$/cm^2
ν = kinematic viscosity of solution, cm^2/s
τ = tortuosity factor
Φ_2 = electric potential in the solution, V
$\Delta\Phi_2$ = electric potential difference in the solution between bed inlet and bed outlet

LITERATURE CITED

Appel, Peter, "Electrochemical Systems: Impedance of a Rotating Disk and Mass Transfer in Packed Beds," Dissertation, LBL-2280, Univ. Calif., Berkeley (1976).

Bennion, Douglas N., and John Newman, "Electrochemical removal of copper ions from very dilute solutions," *J. Appl. Electrochem.*, **2**, 113 (1972).

Davis, John C., "New Spark Comes to Electroorganic Synthesis," *Chem. Eng.*, **82**, 44 (1975).

Dunning, John Stephen, "Analysis of Porous Electrodes with Sparingly Soluble Reactants," Dissertation, Univ. Calif., Los Angeles (1971).

El-Kaissy, Mohammed, M., and George M. Homsy, "A Theoretical Study of Pressure Drop and Transport in Packed Beds at Intermediate Reynolds Numbers," *Ind. Eng. Chem. Fundamentals*, **12**, 82 (1973).

Fleischmann, M., J. W. Oldfield, and L. Tennakoon, "Fluidized Bed Electrodes Part IV. Electrodeposition of copper in a fluidized bed of copper-coated spheres," *J. Appl. Electrochem.*, **1**, 103 (1971).

Gracon, Brian Eugene, "Experimental Studies of Flow-through Porous Electrodes," M.S. thesis, Univ. Ill., Urbana (1974).

Happel, John, "Viscous Flow in Multiparticle Systems: Slow Motion of Fluids Relative to Beds of Spherical Particles," *AIChE J.*, 4, 197 (1958).

Johnson, A. M., and John Newman, "Desalting by Means of Porous Carbon Electrodes," *J. Electrochem. Soc.*, **118**, 510 (1971).

Karabelas, Anastasius J., Theodore H. Wegner, and Thomas J. Hanratty, "Use of asymptotic relations to correlate mass transfer data in packed beds," *Chem. Eng. Sci.*, **26**, 1581 (1971).

Kunni, Daizo, and J. M. Smith, "Heat Transfer Characteristics of Porous Rocks: II. Thermal Conductivities of Unconsolidated Particles with Flowing Fluids," *AIChE J.*, **7**, 29 (1961).

Kusik, C. Lembit, and John Happel, "Boundary Layer Mass Transport with Heterogeneous Catalysis," *Ind. Eng. Chem. Fundamentals*, **1**, 163 (1962).

Le Goff, P., F. Vergnes, F. Coeuret, and J. Bordet, "Applications of Fluidized Beds in Electrochemistry," *Ind. Eng. Chem.*, **61**, No. 10, 8 (1969).

Mandelbaum, J. A., and U. Böhm, "Mass transfer in packed beds at low Reynolds numbers," *Chem. Eng. Sci.*, **28**, 569 (1973).

Miyauchi, Terukatsu, Kozo Matsumoto, and Takashi Yoshida, "Liquid Film Coefficient of Mass Transfer in Low Péclet Number Region for Sphere Packed Beds," *J. Chem. Eng. Japan*, **8**, 228 (1975).

Nelson, Paul E., and Terry R. Galloway, "Particle-to-fluid Heat and Mass Transfer in Dense Systems of Fine Particles," *Chem. Eng. Sci.*, **30**, 1 (1975).

Newman, John, and William Tiedemann, "Porous-Electrode Theory with Battery Applications," *AIChE J.*, **21**, 25 (1975).

Payatakes, Alkiviades C., Chi Tien, and Raffi M. Turian, "A New Model for Granular Porous Media," *ibid.*, **19**, 58 (1973).

Pfeffer, Robert, and John Happel, "An Analytical Study of Heat and Mass Transfer in Multiparticle Systems at Low Reynolds Numbers," *ibid.*, **10**, 605 (1964).

Posey, F. A., "Electrolytic Demonstration Unit for Copper Removal from Distillation Plant Blowdown," *ORNL-TM-4112*, Oak Ridge National Lab., Oak Ridge, Tenn. (1973).

Selman, Jan Robert, and John Newman, "Free-Convection Mass Transfer with a Supporting Electrolyte," *J. Electrochem. Soc.*, **118**, 1070 (1971).

Selman, Jan Robert, "Measurement and Interpretation of Limiting Currents," Dissertation, UCRL-20557, Univ. Calif., Berkeley (1971).

Scheidegger, Adrian E., *The Physics of Flow Through Porous Media*, University of Toronto Press, Canada (1960).

Sherwood, Thomas K., Robert L. Pigford, and Charles R. Wilke, *Mass Transfer*, McGraw-Hill, New York (1975).

Smyrl, W. H., Private Communication (1973).

Sörensen, Jan P., and Warren E. Stewart, "Computation of Forced Convection in Slow Flow through Ducts and Packed Beds—I. Extensions of the Graetz Problem," *Chem. Eng. Sci.*, **29**, 811 (1974*a*).

————, "Computation of Forced Convection in Slow Flow through Ducts and Packed Beds—II. Velocity Profile in a Simple Cubic Array of Spheres," *ibid.*, 819 (1974*b*).

————., "Computation of Forced Convection in Slow Flow through Ducts and Packed Beds—III. Heat and Mass Transfer in a Simple Cubic Array of Spheres," *ibid.*, 827 (1974*c*).

————., "Computation of Forced Convection in Slow Flow through Ducts and Packed Beds—IV. Convective Boundary Layers in Cubic Arrays of Spheres," *ibid.*, 833 (1974*d*).

Van Brocklin, Lester P., and Morton M. David, "Coupled Ionic Migration and Diffusion During Liquid-Phase Controlled Ion Exchange," *Ind. Eng. Chem. Fundamentals*, **11**, 91 (1972).

Van Swaäy, W. P. M., A. A. C. M. Beenakkers, and A. Welmers, "Fluid-bed Electrode Reactor," *K.I.V.I. Symposium*, Holland (May, 1975).

Wehner, J. F., and R. H. Wilhelm, "Boundary conditions of flow reactor," *Chem. Eng. Sci.*, **6**, 89 (1956).

Wilson, E. J., and C. J. Geankoplis, "Liquid Mass Transfer at Very Low Reynolds Numbers in Packed Beds," *Ind. Eng. Chem. Fundamentals*, **5**, 9 (1966).

Yip, Harry Hung-Kwan, "Mass Transfer Coefficient in Packed Beds at Low Reynolds Numbers," M.S. thesis, LBL-1831, Univ. Calif., Berkeley (1973).

Manuscript received December 23, 1975; revision received July 20, and accepted July 21, 1976.