

MASS TRANSFER IN TURBULENT PIPE FLOW MEASURED BY THE ELECTROCHEMICAL METHOD

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(Received 27 August 1976 and in revised form 14 January 1977)

Abstract—Various factors affecting mass transfer measurements in electrochemical systems are discussed. Ways are indicated for increasing the values of “critical” flow rates and Reynolds numbers up to which meaningful results can be obtained.

Mass-transfer coefficients were measured in fully developed flow in smooth pipes over the range $8 \times 10^3 < Re < 2 \times 10^5$ at Schmidt numbers varying between 1000–6000. When the concentration boundary layer was fully developed the results could be represented by the expression

$$St_d = 0.0165 Re^{-0.14} Sc^{-0.67}.$$

Using the current results together with published data an empirical relation has been developed in the form

$$Nu = 2 + c Re^a Pr^{1/3}$$

$$\text{where } c = 0.0165 + 0.011 Pr e^{-Pr}$$

$$a = 0.86 - \frac{10}{(4.7 + Pr)^3}$$

which can be recommended for predicting heat- and mass-transfer rates over the range $0.6 < Pr$ or $Sc < 10^4$ and $10^4 < Re < 10^6$.

The mean Stanton numbers measured in the entrance section (developing concentration boundary layer) agree well with the integrated turbulent Leveque equation

$$St_d = 0.276 Re^{-0.417} Sc^{-2/3} \left(\frac{L}{d}\right)^{-1/3}.$$

NOMENCLATURE

A , surface area of studied electrode (cathode);
 C , concentration of reacting species;
 C_p , specific heat at constant pressure;
 d , tube diameter;
 d_2/d_1 , ratio of outer to inner diameter in annulus;
 D , diffusion coefficient;
 f , Fanning friction factor;
 F , Faraday constant;
 h , heat-transfer coefficient;
 I_L , limiting current;
 k , thermal conductivity;
 k_d , mass-transfer coefficient;
 K^+ , dimensionless mass-transfer coefficient, k_d/u^* ;
 K_∞^+ , limiting value of K^+ attained in fully developed region;
 L , length of the mass-transfer section;
 n_e , valence charge of ion species;
 Nu , Nusselt number, hd/k ;
 Pr , Prandtl number, $\mu C_p/k$;
 Re , Reynolds number, $\rho U d/\mu$;
 St_d , Stanton number for mass transfer, k_d/U ;
 Sc , Schmidt number, ν/D ;
 Sh , Sherwood number, $k_d d/D$;

U , mean flow velocity;
 u^* , friction velocity $(\tau_w/\rho)^{1/2}$;
 x , distance in the flow direction;
 y , distance perpendicular to the wall.

Greek symbols

μ , viscosity;
 ν , kinematic viscosity;
 ξ , Moody friction factor;
 ρ , density;
 τ , shear stress.

Subscripts

b , bulk;
 w , wall.

INTRODUCTION

THE ELECTROCHEMICAL method of modelling mass transfer between a liquid and a solid surface by measuring the transfer rate of certain ions in aqueous solutions to an electrode has been developed during the past twenty five years. It has also been applied in a variety of convective heat transfer and wall shear stress studies making use of well known analogies between the various transport phenomena. A comprehensive review of most applications has been published by Mizushima [1]. However, some important questions still remain to be answered.

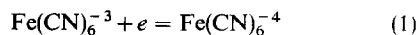
Thus various investigators have correctly stated that the transfer process in an electrochemical system can be studied only within a certain range of Reynolds numbers since above a certain value of Re the limiting current, which is a precondition of reliable measurements, will not be observed. Although some of them have given the maximum Re which could be achieved in their particular experiments, it has not to our knowledge been shown on which parameters the attainable Reynolds number depends and how it can be increased. Another important question is whether and in what way the mutual position of the electrodes can affect the results. Although this effect must have been observed by many investigators, the only meaningful discussion we could find was in [2]. The effect has also been studied by Mackley [12] on a heat exchanger model but due to the very different geometry his results are not directly applicable to the present problem. We believe that clarification of these points should save later workers unnecessary bother and may even have some implications for studies of turbulent mixing; they are therefore discussed in the first part of the present paper.

The second part is concerned with measurements of ion transfer rates in turbulent flow through a circular smooth pipe. Experiments on turbulent heat and mass transfer in conventional gases and liquids (i.e. those with moderate Prandtl or Schmidt numbers) have been performed for many years and their results are usually expressed as power functions of the Colburn or Dittus-Boelter type. As the range of tested fluids was extended it became first apparent that these equations were inadequate for very low Prandtl numbers (liquid metals) and later that the same was true of very high Prandtl or Schmidt numbers. It was concluded that a simple equation with constant exponents and a constant multiplier could not give a satisfactory description of transfer processes over the whole range of fluids. In recent years Petukhov [3] and Notter and Sleicher [4, 5] have suggested more complex semi-empirical equations which are claimed to represent heat- and mass-transfer rates in fully developed turbulent flow for a very wide range of fluid properties. It will be shown that the accuracy of these equations in the high Schmidt number region is open to doubt because of the doubtful value of the experimental data used in their derivation. Conventional heat- and mass-transfer experiments in this region are notoriously difficult, whereas electrochemical systems have high Schmidt numbers due to the low diffusion coefficients and experiments with them are relatively easy. However, Notter and Sleicher [6] have expressed doubts about the reliability of electrochemical measurements. It is hoped that the present paper will help to disperse those doubts. Results are also given on the mass-transfer rates in the entrance section where the concentration boundary layer is developing.

METHOD AND EXPERIMENTAL APPARATUS

The electrochemical system used in the experiments was the well known aqueous solution of potassium

ferri- and ferrocyanide with an addition of sodium hydroxide as the inert electrolyte. The studied surface was always represented by the cathode where the reaction



takes place, with the reverse reaction occurring on the much larger anode. When the potential on the electrode is gradually increased the current first increases until a stable value is reached. This value is called the limiting current and corresponds to the condition when the concentration of the reacting species of ions on the surface of the electrode equals zero. It can be easily shown that under these conditions the ion transfer rate on the electrode is determined by their diffusion (molecular and turbulent) through the boundary layer and the mass-transfer coefficient can be determined from the simple equation

$$k_d = \frac{I_L}{n_e F A C_b} \quad (2)$$

where

I_L = limiting current

n_e = valence charge of ion species

F = Faraday constant

A = surface area of studied electrode (cathode)

C_b = bulk concentration of reacting species.

All our experiments were carried out under these conditions.

The rig used is shown diagrammatically in Fig. 1 and has been described in detail elsewhere [7-9]. The test

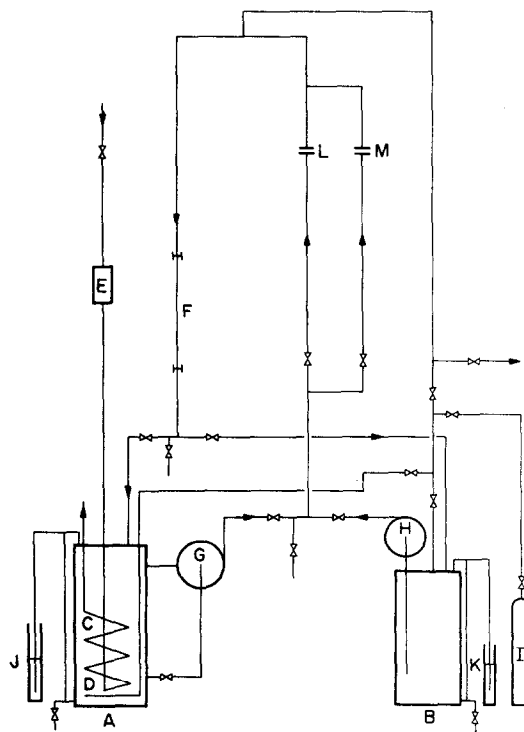


FIG. 1. Flow circuit. A: main tank (working solution); B: activation tank (1 M NaOH); C: cooling coil; D: nitrogen bubbler; E: temperature controller; F: test section; G, H: pump; I: nitrogen cylinder; J, K: water gauge; L, M: orifice plate.

section was made from 9 pieces of nickel tube with an inner diameter of 54.8 mm and varying lengths, i.e. 0.44, 1.38, 3.05, 6.46, 12.98, 26.06, 52.13, 293.1, 500 mm. They were manufactured to a tolerance of 0.02 mm with a polished inner surface ensuring a roughness of about 1 μm , i.e. much smaller than the calculated concentration boundary-layer thickness (10–100 μm). The longest tube served as the anode, all the other ones as cathodes, except in some special cases where a second anode was required. The tubes were insulated from each other by U PVC rings with Araldite as the bonding agent and were all inter-changeable. The U PVC pipe in front of the test section was about 4 m long and its inner diameter was again 54.8 mm; great care was taken to avoid any steps or discontinuities in the whole test section. Since the L/d ratio of the plastic pipe was 73 it could be assumed that the velocity profile in the cathode region was fully developed for all Reynolds numbers. The chosen arrangement made it possible to study the effect of the development of the concentration boundary layer and also the effect of the mutual position of and distance between the electrodes.

The flow rate through the rig was controlled by valves and measured with two different orifice plates. The range of Reynolds numbers covered in the experiments was 6×10^3 – 2×10^5 . The Schmidt number was controlled by changing the concentration of NaOH in the solution from 1 to 4 M and the temperature of the solution from 293 to 308 K; the range of Schmidt numbers covered was then 1×10^3 – 6×10^3 . The initial concentration of both $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{K}_4\text{Fe}(\text{CN})_6$ was 0.005 M; the concentrations were checked for each daily run of experiments by simple titration methods with an accuracy of 1.0%.

Prior to each set of experiments the test section was rinsed with dilute sulphuric acid, washed with CCl_4 and then subjected to 20 min of cathodic activation treatment using a solution without cyanides and a current density of 20 mA/cm². A nitrogen atmosphere was maintained above the free surface of the working solution in the tank and nitrogen was permanently bubbled through the solution in order to prevent oxygen from affecting the solution and electrodes.

FACTORS INFLUENCING THE MAXIMUM ATTAINABLE REYNOLDS NUMBER

It is well known that when the flow rate of a given solution is increased the limiting current is obtained at higher voltages and the potential interval over which the current is constant (i.e. the plateau) becomes shorter. At a certain velocity the plateau disappears completely and no limiting current is observed. The accepted explanation [1] of this phenomenon says that when the flow rate increases the diffusion rate is increased as well, until the chemical reaction rate on the surface becomes too slow to remove all ions reaching the electrode surface and thus reduce the surface concentration to zero. The reaction rate can, of course, be increased by increasing the potential but this does not help since above a certain electrode

potential secondary reactions, mainly hydrogen evolution on the cathode, will lead to a steep increase in current. The upper limit at which a limiting current is still observed is often called "critical flow rate". This explanation is basically correct but it is not the whole story.

In our experiments we found that the critical flow rate was higher for shorter cathodes; similar observations were reported by Schütz [10] and others. We further observed that for a given length of the cathode the critical flow rate can be increased by increasing the concentration of the non-reacting electrolyte or by reducing the concentration of the reacting cyanide ions, and also by using two anodes—one upstream and one downstream of the cathode. Gosman [2] also used two anodes and offered the correct explanation for their effect, namely the reduction in ohmic potential drop.

Indeed, the ohmic potential needed to overcome the electrical resistance between the electrodes can be seen as the explanation of all the aforementioned factors determining the critical flow rate. When the cathode is long the ohmic potential drop in the column of fluid facing the cathode may be greater than the width of the diffusion controlled plateau that would be established if the ohmic potential were negligible (this width might be 1 V say). Consequently it will not be possible to obtain diffusion controlled conditions over the whole surface since the potential difference at that end of the cathode which is near to the anode will have exceeded the hydrogen overvoltage before the ion concentration on the other end of the surface has fallen to zero. Under those conditions a limiting current cannot be obtained.

It follows that the critical flow rate and Reynolds number depend on the ohmic potential drop and can be increased in several ways, each of which has its limitations.

1. Reduce the ferricyanide concentration thus reducing the current density and hence the ohmic potential drop.

2. Increase the sodium hydroxide concentration in the solution. This will lead to an increase in critical flow rate even for short cathodes, since the diffusion coefficient will be lower and the ion transfer to the cathode will be reduced. The critical Reynolds number will be increased to a lesser extent (increased viscosity). For a long electrode the additional effect of the increased electrical conductivity of the solution comes into play and leads to a lower ohmic potential drop along the cathode; hence the relative increase in the critical Reynolds number will be significantly greater for long cathodes. However, using this method one has to accept a considerable increase in the Schmidt number.

3. Use two anodes, one upstream and one downstream of the electrode, thus reducing the variation in potential difference along the cathode by about 50% and increasing the Reynolds number at which a well defined plateau can still be obtained. It will be seen in the next paragraph that an upstream anode can cause erroneously high current readings; fortunately this

effect becomes very small at high Re whereas at low Re limiting currents can be obtained with a single anode. The effect of the upstream anode can be further reduced by placing it further ahead of the cathode. Note that the increase in the total ohmic potential drop due to the increased distance between the electrodes does not affect the critical flow rate; it is only the potential drop along the cathode that matters.

By a suitable application of these principles we were able to obtain in our experiments limiting currents at Reynolds numbers as high as 2×10^5 ; this value is 2.5 times higher than the highest Reynolds number which to our knowledge has been used in similar pipe flow experiments by other investigators.

OTHER FACTORS AFFECTING THE RESULTS

In his experiments Gosman [2] observed that the limiting current was higher when the anode was placed immediately in front of the cathode against the case when it was placed downstream. Nevertheless other authors maintain that the position of the electrodes is immaterial and both modes of arrangement have been widely used. Therefore, we carried out tests with a single anode at different distances upstream of the cathode, with a single anode downstream, and with two anodes (one upstream and one downstream). The cathode was divided into two parts, one 26 mm and the other 52 mm long. The results may be summarised as follows:

Under equal conditions the current with the upstream anode was by up to 15% higher than that with the downstream one, the current with the 2 anodes lying in between those values. The difference decreased with increasing distance between the upstream anode and the cathode and with increasing Reynolds number. When the upstream anode was used the current increase on the first cathode (that nearer to the anode) was by a few percent higher when the second cathode was connected in the circuit. However, with the downstream cathode the current on the first cathode was the same whether the second cathode was connected or not.

All these findings are consistent with the explanation that the reaction on the anode leads to an increase in the concentration of ferricyanide ions in the vicinity of the surface thus augmenting the current on a downstream cathode. When both cathodes were connected the production of ferricyanide ions on the anode was higher and one would expect the current on the first cathode to be higher, as indeed it was. When the Reynolds number is increased turbulent mixing is more vigorous and apparently causes the surplus ferricyanide ions to be diluted more rapidly in the main stream and this mixing effect obviously predominates over the higher rate of ion production on the anode. The mixing process also explains the effect of the distance between the electrodes.

It follows that the anode position can significantly affect the results and that data obtained with an upstream anode must be suspect, especially when the Reynolds number was low.

The choice of values of the physical properties (ν and D) determining the Schmidt number poses some problems. There is a shortage of experimental data covering the whole range of concentrations of the components, and the molecular diffusivity D of the reacting ions is not easily measurable with high accuracy. In our evaluation we used for the viscosity the data given by Landolt and Bornstein [11] for NaOH solutions and assumed that the effect of the cyanides was negligible in view of their very low concentration. We further assumed the validity of the Stokes-Einstein equation $D\mu/T = \text{const}$, and calculated D by taking the value of the constant as recommended by Mackley [12]: $\text{const} = 2.50 \times 10^{-15} (\text{m}^2/\text{s}^2)(\text{kg}/\text{K})$. The accuracy of the viscosity is estimated to be within 2% and that of D within 5%, this being the product of possible errors in Stokes' constant, temperature and viscosity. Thus the maximum error in Sc should not exceed 7%. The values are tabulated in Table 1 for various concentrations and temperatures and it may be seen how strongly the Schmidt number is influenced by the temperature of the solution. Accurate temperature measurements are therefore of the utmost importance.

In Table 2 our data for 2M NaOH at 25°C are compared with measured values quoted in the literature. Excluding [24] which exhibits very high ν and low D (perhaps due to high cyanide concentrations) it may be seen that our data on viscosity agree well with [10, 22, 27] and are about 4% lower than in [25] and [26]. The scatter in the diffusion coefficients given by different authors exceeds 10%, probably due to the low accuracy of measurement; our data agree well with those given in [25] and [27] and lie between the values given in [10] and [26]. The quoted Schmidt numbers for the given conditions appear to be on average somewhat higher than our value (although [10] quotes a value by 6% lower), but in view of the variations in the exact concentration of the components and lack of data on other NaOH concentrations there did not seem to be any point in further adjustment and we considered the adopted way of determining Sc as sufficiently accurate.

MASS TRANSFER IN THE FULLY DEVELOPED REGION

The mass-transfer coefficients k_a in fully developed flow were determined from the limiting currents measured on the 293 mm long cathode for Reynolds numbers ranging from 1×10^4 to 2×10^5 and Schmidt numbers from 1160 to 5900. As mentioned earlier the flow was hydrodynamically fully developed before entry into the test section; it will be shown in the next section that since the L/d ratio of the cathode was about 6 the concentration boundary layer was fully developed over a considerable part of its length and the effect of the entrance section on k_a was less than 5% and could be neglected.

In Fig. 2 the Stanton number $St_d = k_a/U$ (where U is the mean flow velocity) is plotted as a function of Re with Sc as parameter; Fig. 3 shows the cross plot St_d vs

Table 1.

NaOH (M)	Temp. (°C)	$\mu \times 10^3$ (kg/ms)	$\nu \times 10^6$ (m ² /s)	$D \times 10^{10}$ (m ² /s)	Sc	$\rho \times 10^{-3}$ (kg/m ³)
1.0	20.5	1.22	1.173	6.014	1950	1.04
1.0	30.5	0.97	0.9327	7.822	1192	1.04
2.0	25.5	1.345	1.245	5.548	2244	1.08
2.0	28.0	1.27	1.176	5.925	1985	1.08
2.0	40.0	0.995	0.9123	7.864	1160	1.08
4.0	24.5	2.26	1.948	3.291	5919	1.16
4.0	29.5	1.995	1.72	3.791	4837	1.16
4.0	35.0	1.73	1.491	4.451	3350	1.16

Table 2.

NaOH (M)	K ₃ Fe(CN) ₆ (M)	K ₄ Fe(CN) ₆ (M)	$\mu \times 10^3$ (kg/ms)	$\nu \times 10^6$ (m ² /s)	$D \times 10^{10}$ (m ² /s)	Const. $\times 10^{15}$ ($\frac{m \text{ kg}}{s^2 \text{ K}}$)	Sc	Temp. (°C)	Ref.
2.0	0.005–0.002	0.01–0.005	1.36	1.289	5.478	2.50	2298	25	*
2.0	0.025	0.025	1.385	1.26	5.80	2.70	2170	25	[10]
2.004	0.2	0.2	1.64	1.423	4.54	2.50	3134	25	[24]
2.2028	0.0245	0.0255	1.433	1.303	5.33	2.56	2445	25	[25]
2.2028	0.0049	0.0051	1.416	1.311	5.56	2.64	2455	25	[25]
1.9	0.01–0.001	0.01–0.001	1.33	1.236	5.155	2.30	2400	25	[22]
2.015	0.001	0.001	1.419	1.314	5.103	2.43	2575	25	[26]
2.011	0.01224	0.01228	1.382	1.276	5.39	2.50	2367	25	[27]

* Present data.

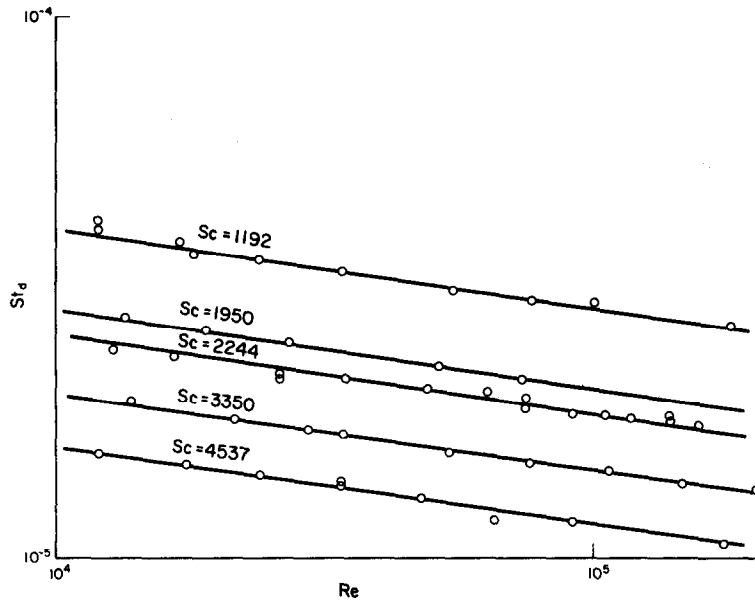


FIG. 2. Stanton number vs Reynolds number in fully developed flow (Schmidt number as parameter).

Sc with Re as parameter. It is seen that parallel straight lines are obtained in both graphs, their slope in graph 2 being -0.14 and in graph 3: -0.67 . The results can then be represented by the expression

$$St_d = 0.0165 Re^{-0.14} Sc^{-0.67} \quad (3)$$

In the investigated range of Re and Sc the Stanton numbers obtained from equation (3) are by 20–30% higher than those calculated from the well known

Colburn relation

$$St_d = 0.023 Re^{-0.2} Sc^{-0.67} \quad (4)$$

This is not surprising since it is now known that the Colburn equation underestimates St_d at high Schmidt numbers; it can also be shown from theoretical considerations [3, 6] that the absolute value of the exponent of Re should be smaller than 0.2.

Notter and Sleicher [4, 5] recognising the shortcom-

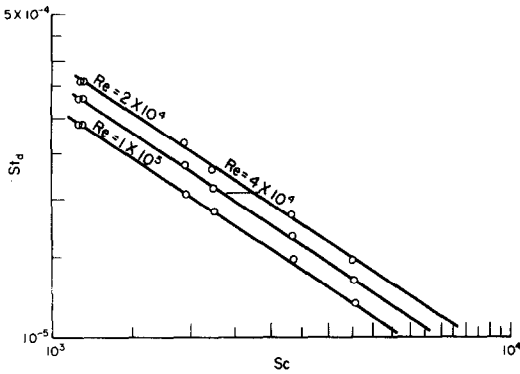


FIG. 3. Stanton number vs Schmidt number (Reynolds number as parameter).

ings of the Colburn equation, suggested in a recent paper a new formula for heat and mass transfer in smooth pipes which is supposed to be valid for $0.1 < Pr < 10^5$ and $10^4 < Re < 10^6$. For isothermal conditions they suggest:

$$Nu = 5 + 0.015 Re^a Pr^b \quad (5)$$

$$\text{where } a = 0.88 - 0.24/(4 + Pr)$$

$$b = \frac{1}{3} + 0.5 e^{-0.6Pr}$$

For mass transfer Nu is simply replaced by the Sherwood number Sh and Pr by Sc . This equation was a fit to numerical solutions of the turbulent Graetz problem, where eddy diffusivities had been determined from selected experimental heat- and mass-transfer data.

There exists a number of theoretical studies aiming at the prediction of Nusselt numbers which will not be discussed here. The basic problem is always the behaviour of the eddy diffusivities in the close vicinity of the wall which is not known with sufficient accuracy for fluids with high Pr or Sc . The dependence of the eddy diffusivities on the distance from the wall is in fact often deduced from heat- and mass-transfer measurements. The procedure chosen by Notter and Sleicher is, therefore, quite acceptable in principle.

For high Schmidt numbers ($Sc > 50$) the asymptotic form of equation (5) for mass transfer is

$$St_d = 0.015 Re^{-0.12} Sc^{-0.67} \quad (6)$$

yielding Stanton numbers by 10–18% higher than the results of the present study.

We believe that this discrepancy can be explained by Notter and Sleicher's [6] choice of experimental data in the region of Schmidt (or Prandtl) numbers higher than 10^3 . For this region there is a dearth of data obtained by conventional mass- and heat-transfer methods, and they based their expression exclusively on the results of Harriot and Hamilton [13] who measured mass-transfer rates by determining the weight loss of benzoic acid tubes in flowing glycerine-water solutions. However, their results are in all probability too high for the following reasons: Their tubes were reported to be slightly porous and they did in fact find deposits of glycerine in the walls after the experiments and added the weight of this deposit to the measured weight loss. Thus the size of

the interacting surface was larger than the inner tube surface considered in the evaluation. Moreover the apparent transfer rate might well have been further increased by the particular flow conditions over a porous wall. Most importantly, Harriott and Hamilton themselves state that the roughness of the walls (40–70 μm) was not negligible and could have led to increased transfer rates; they estimate that the deviation might have been up to 10% at $Sc = 1000$ and a good bit more at very high Sc .

The only other data for high Pr (up to $Pr = 600$) giving similarly high (or indeed even somewhat higher) values of Nu come from the heat-transfer measurements of Friend and Metzner [14] with molasses and syrups. However, most of their experiments were done at low Reynolds numbers ($Re < 10^4$) and extrapolated in a somewhat arbitrary manner. They also neglected the effect of property variations due to the temperature gradient in the boundary layer. Notter and Sleicher did not consider these results as sufficiently reliable probably for these reasons.

On the other hand Lin *et al.* [15] and Hubbard and Lightfoot [16] measured mass-transfer rates by an electrochemical method very similar to the one used in this study and obtained lower St_d values. Friend and Metzner fairly criticised Lin's results because he had used an annular geometry and disregarded the effect of the d_2/d_1 parameter. Referring to this criticism Notter and Sleicher rejected not only Lin's but also Hubbard's data (because they agreed well with Lin's) and dismissed the electrochemical method as not sufficiently proven. In view of what has been said about Harriott and Hamilton's data we consider this rejection as unjustified and believe that the electrochemical method yields the more reliable results.

It may be seen that equations (3) and (6) exhibit different exponents of Re . The exponent -0.12 or even -0.10 has been suggested by various authors on the basis that for high Sc the Stanton number should be proportional to $f^{1/2}$. From the present work it appears that the exponent on f , although much lower than 1 as for $Pr = 1$, is somewhat higher than $\frac{1}{2}$ (i.e. 0.56 if $f \propto Re^{-0.25}$). This is supported by Hubbard's [16] findings that in the range $10^3 < Sc < 10^4$ the value of $\partial \ln St / \partial \ln f$ is between $\frac{1}{2}$ and 1.

In Fig. 4 the present results are compared to those of several other authors in the form K_∞^+ vs Sc . The dimensionless mass-transfer coefficient $K_\infty^+ = k_d/u^*$, where $u^* = (\tau_w/\rho)^{1/2}$ is the friction velocity, would be independent of Re if the Stanton number were exactly proportional to $f^{1/2}$. In reality K_∞^+ is very slightly dependent on Re ; mean values of our present results were taken, the deviation in the given range of Re being less than 3%. All other results in the graphs are from electrochemical experiments with the exception of Meyerink and Friedlander's who used a dissolution method. Lin's data was corrected to take account of the annular geometry. It is seen that the present results agree very well with Gosman's [2], and Meyerink's [17], and well with Lin's, Schütz's [10] and Shaw's [18] results obtained for a single Sc are by about 12%

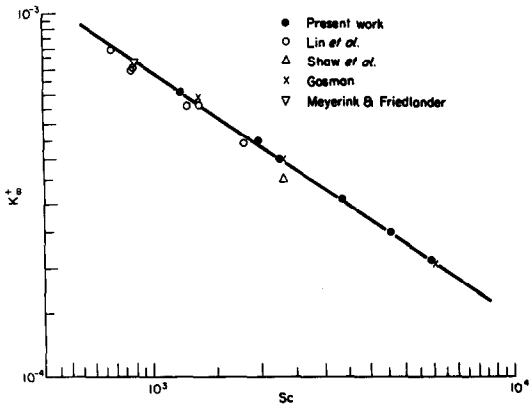


FIG. 4. Comparison of experimental results for high Sc.

lower and the reason for this deviation is not clear; it may be due to their particular techniques.

As a result of this discussion we believe that equation (3) is a better description of the transfer process at high Schmidt and Prandtl numbers than equation (6). On the other hand we have no reason to doubt the reliability of the results used in Notter's analysis of the lower Prandtl number region. Using the same data as Notter-Sleicher for $Pr < 20$ one can suggest again a single empirical equation covering the range $0.6 < Pr < 10^4$; $10^4 < Re < 10^6$ in the form

$$Nu = 2 + cRe^a Pr^{1/3} \tag{7}$$

where $c = 0.0165 + 0.011 Pr e^{-Pr}$

$$a = 0.86 - \frac{10}{(4.7 + Pr)^3}$$

For high Prandtl numbers equation (7) converts into (3) which may be written as

$$Nu = 0.0165 Re^{0.86} Pr^{1/3} \tag{8}$$

For $Pr = 0.8$ one obtains from (7)

$$Nu = 2 + 0.0205 Re^{0.8} Pr^{1/3} \tag{9}$$

It will be noted that the exponents in (9) are the same as in Colburn's equation; however, the values from equation (9) are by up to 11% lower, as one would expect since Colburn's equation is known to overestimate Nu for gases.

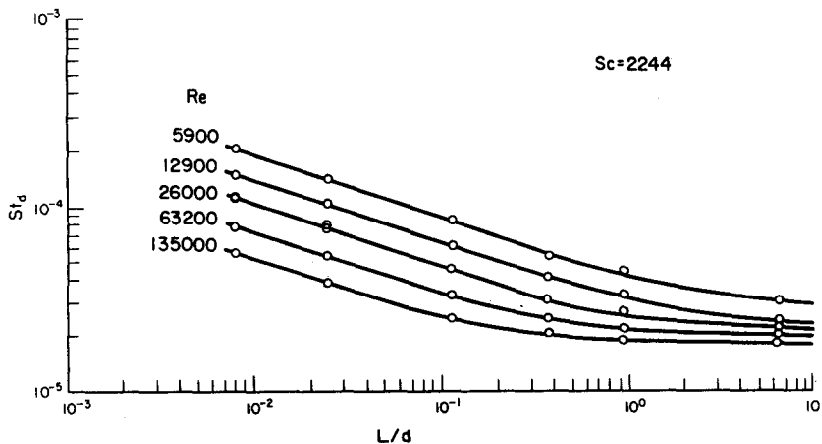


FIG. 6. Stanton number vs L/d (developing concentration boundary layer).

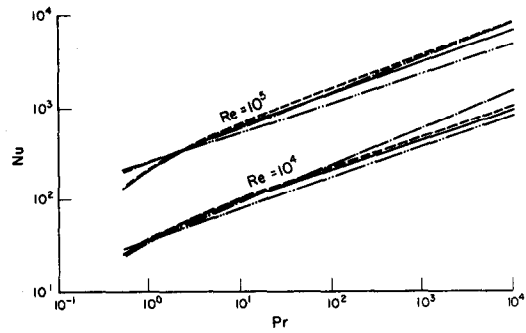


FIG. 5. Comparison of semiempirical equations for heat and mass transfer. —, present correlation; ---, Notter-Sleicher; - · - ·, Dittus-Boelter; · · · ·, Colburn.

In Fig. 5 equation (7) is compared for $Re = 10^4$ and $Re = 10^5$ with Notter-Sleicher's equation (5). At $Pr < 10$ the difference between the two equations does not exceed 6%, at $Pr > 100$ the difference is 10–18% at $Re = 10^4 - 10^5$ and is up to 23% at $Re = 10^6$.

Petukhov [3] performed computer calculations of Nu from an analytical model, compared the results to experimental results and approximated them by the equation

$$Nu = \frac{Re Pr \frac{\xi}{8}}{1.07 + 12.7(Pr^{2/3} - 1)(\xi/8)^{1/2}} \tag{10}$$

where the friction factor $\xi = (1.82 \log Re - 1.64)^{-2}$. For $Pr > 1000$ equation (10) simplifies to

$$Nu = 0.0855 \left(\frac{\xi}{8}\right)^{1/2} Re Pr^{1/3} \tag{11}$$

Petukhov again checked his results at high Pr only against Harriott-Hamilton's experimental data. Hence it is not surprising that equation (8) gives lower values of Nu than equation (11) although the deviation is somewhat smaller than from (5).

Petukhov's equation is not shown in Fig. 5 since the results are fairly similar to Notter-Sleicher's. Shown however are Colburn's equation and the Dittus-Boelter equation

$$Nu = 0.023 Re^{0.8} Pr^{0.4} \tag{12}$$

which are both seen to deviate substantially from the experimental curve at high Pr . This only confirms that an equation with constant exponents and multiplier is unsuitable for the wide range of Pr .

The present findings that Nu varies with $Pr^{1/3}$ implies that the eddy diffusivity near the wall ($y^+ < 10$) is proportional to y^{+3} as proposed by Reichardt [19] rather than to y^{+4} as proposed by Deissler [20]. The same conclusion was reached by both Petukhov and Notter.

Since the proposed equation (7) is believed to be based on more reliable data than equations (5) and (10) in the high Pr region, and similar data were used for all equations at lower Pr , the accuracy of equation (7) over the whole range should be at least as good as that quoted by Notter and Sleicher, i.e. $\pm 10\%$.

MASS TRANSFER IN THE REGION OF THE DEVELOPING CONCENTRATION BOUNDARY LAYER

Using the aforementioned short cathodes the mean mass-transfer coefficient was measured as a function of the dimensionless distance from the inlet L/d . The results for one Schmidt number and varying Reynolds numbers are plotted in Fig. 6. It will be remembered that the velocity profile at the entrance to the cathode was fully developed and the increase in St_d in the entrance region is, therefore, due only to the developing concentration boundary layer. As one would expect the Stanton number approaches the fully developed value the faster the higher the Reynolds number. The distance from the entrance where St_d reaches a value by 5% higher than the asymptotic one was found to vary from $L/d \doteq 5$ for $Re = 10^4$ to $L/d \doteq 1$ for $Re = 10^5$.

Linton and Sherwood [21] suggested that the mass-transfer process for very short pipes at high Sc could be expressed by the equation

$$\frac{u^*}{\nu} y \frac{\partial C}{\partial x} = \frac{\partial^2 C}{\partial y^2} \quad (13)$$

where u^* is friction velocity.

Using the Blasius friction relation for the solution of equation (13) one obtains:

$$St_d = 0.276 Re^{-0.417} Sc^{-2/3} \left(\frac{L}{d}\right)^{-1/3} \quad (14)$$

Figure 7 shows a plot of measured $St_d(L/d)^{1/3}$ against Re for various Sc together with the lines calculated from equation (14). Only the linear part of the lines in Fig. 6 was used for the experimental points, since equation (13) can only be applied to this initial part of the inlet section. The range of validity of equation (14) is seen to depend on the Reynolds number and changes from $0 < L/d < 0.5$ for $Re \leq 1 \times 10^4$ to $0 < L/d < 0.1$ for $Re > 1 \times 10^5$. The agreement is excellent and the average deviation does not exceed 5%. Shaw *et al.* [22] found similar agreement with the slope of the calculated lines but lower numerical values. However, Son and Hanratty [23] later stated that an error was found in Shaw's experiments which led to deflated values of St_d . They

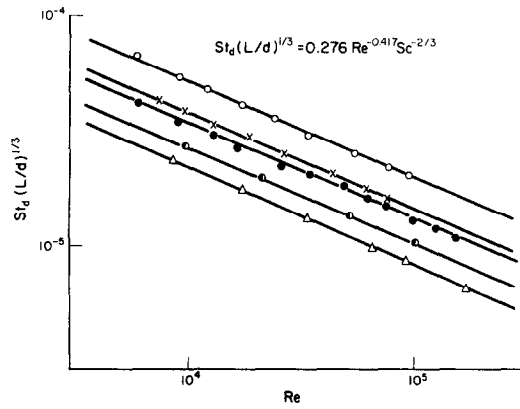


FIG. 7. $St_d(L/d)^{1/3}$ vs Reynolds number. Symbols denote the following values: \circ , 1190; \times , 1950; \bullet , 2244; \bullet , 3350; Δ , 4537.

repeated Shaw's measurements and their results agree very well with those of the present study. On the other hand Schütz [10] measured local values of St_d with little probes fitted into the cathode. His data have been converted into mean values and these are by 20–35% higher than the present results. No doubt this deviation is at least in part caused by Schütz's use of an upstream anode.

GENERAL CONCLUSIONS

From the results of this study it may be concluded that there is no reason to doubt that the electrochemical method provides representative results on mass transfer in the range of Schmidt numbers which can be obtained with the given electrolyte. In the studied case of turbulent transfer in smooth pipes at very high Sc it appears that the electrochemical method is actually superior to others. It avoids changes in surface roughness and pipe diameter inherent in mass-transfer measurements based on dissolution. It also avoids the difficulties of heat-transfer measurements with high Pr , where one has to work with uncommon highly viscous fluids which may be even non-Newtonian, and where one always has to deal with the problem of varying properties in the boundary layer.

On the other hand great care must be exercised in the prediction of mass- and heat-transfer rates at moderate Sc or Pr from results obtained by the electrochemical method. In practice it is often assumed that a power function (such as the Colburn equation) obtained for a certain limited range of Pr or Sc can be directly extrapolated to very different values of these criteria. This study confirms previous findings that this is not so, the power function itself depends on the value of Sc or Pr , and predictions for low Pr solely from the results of electrochemical measurements may be unreliable. In the given case of turbulent transfer in smooth pipes there is, of course, no need to do so as there is an abundance of data for low Pr . But if, as an example, we assumed equation (3) to be valid over the whole range of Pr the predicted Nu for say $Pr = 1$ and $Re = 5 \times 10^4$ would be 42% higher than that from the more correct equation (7). (Note, however, that for $Pr = 10$ the difference in the results of the two equations is only

1%.) Similar behaviour may be expected in other geometries and flow regimes. Thus if data is required for low Prandtl number fluids the electrochemical method may provide qualitative information on general trends, relative distributions of local transfer coefficients etc., but if reliable quantitative answers are sought it must be accompanied by a thorough theoretical analysis or preferably by at least a limited amount of confirmatory experiments at the actual Pr .

Acknowledgements—This project was carried out under contract with the Atomic Energy Establishment, Winfrith and the authors wish to express their gratitude to AEE for material support and permission to publish the results. Thanks also are due to Professor D. C. Leslie, Head of Department of Nuclear Engineering, QMC, for his support of the project, and to all technicians engaged in the construction and running of the rig.

REFERENCES

1. T. Mizushima, The electrochemical method in transport phenomena, *Adv. Heat Transfer* **7**, 87 (1971).
2. A. D. Gosman, Diffusion controlled electrolysis in two phase flow, Ph.D. Thesis, Imperial College, University of London (1969).
3. B. S. Petukhov, Heat transfer and friction in turbulent pipe flow with variable physical properties, *Adv. Heat Transfer* **6**, 504 (1970).
4. R. H. Nottter and C. A. Sleicher, A solution to the turbulent Graetz problem—III. Fully developed and entry region heat transfer ratio, *Chem. Engng Sci.* **27**, 2073–2093 (1972).
5. C. A. Sleicher and M. W. Rouse, A convenient correlation for heat transfer to constant and variable property fluid in turbulent pipe flow, *Int. J. Heat Mass Transfer* **18**, 677–683 (1975).
6. R. H. Nottter and C. A. Sleicher, The eddy diffusivity in the turbulent boundary layer near a wall, *Chem. Engng Sci.* **26**, 161–171 (1971).
7. F. P. Berger, An electrochemical analogy rig for heat transfer and fluid flow studies, QMC EP 6009 (1974).
8. K. F. Hau, An electrochemical analogy rig for heat transfer studies, M.Sc. Thesis, QMC, University of London (1974).
9. F. P. Berger and K. F. Hau, The electrochemical mass heat transfer analogy in forced convection pipe flow, QMC EP 6021 (1976).
10. G. Schültz, Untersuchung des Stoffaustauschanlaufsgebietes in einem Rohr bei vollaugsgebildeter hydrodynamischer Strömung mit einer elektrochemischen Methode, *Int. J. Heat Mass Transfer* **7**, 1077–1087 (1964).
11. Landolt-Börnstein, *Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik, Technik*, Vol. 2, part 5, p. 316. Springer, Berlin (1969).
12. N. V. Mackley, Local shell-side coefficients, Ph.D. Thesis, University of Aston (1973).
13. P. Harriott and R. M. Hamilton, Solid liquid mass transfer in turbulent pipe flow, *Chem. Engng Sci.* **20**, 1073–1078 (1965).
14. W. L. Friend and A. B. Metzner, Turbulent heat transfer inside tubes and analogy heat, mass and momentum transfer, *A.I.Ch.E. Jl* **4**, 393–402 (1958).
15. C. S. Lin, E. B. Denton, H. S. Gaskill and G. L. Putnam, Diffusion-controlled electrode reactions, *Ind. Engng Chem.* **43**, 2136–2143 (1951).
16. D. W. Hubbard and E. N. Lightfoot, Correlation of heat and mass transfer data for high Schmidt and Reynolds numbers, *I/EC Fundamentals* **5**, 370–379 (1966).
17. E. S. C. Meyerink and S. K. Friedlander, Diffusion and diffusion controlled reactions in fully developed turbulent pipe flow, *Chem. Engng Sci.* **17**, 121 (1962).
18. P. Van Shaw and T. J. Hanratty, Fluctuations in the local rate of turbulent mass transfer to a pipe wall, *A.I.Ch.E. Jl* **10**, 475–482 (1964).
19. H. Reichardt, Die Grundlagen des turbulenten Wärmeübergangs, *Arch. Ges. Wärmetech.* **2**, 129–142 (1951).
20. R. G. Deissler, Analysis of turbulent heat transfer, mass transfer and friction in smooth tubes at high Pr and Sc , NACA, TN 3145 (1954).
21. W. H. Linton and T. K. Sherwood, Mass transfer from solid shapes to water in streamline and turbulent flow, *Chem. Engng Progr.* **46**, 288 (1950).
22. P. Van Shaw, L. P. Reiss and T. J. Hanratty, Rates of turbulent transfer to a pipe wall in the mass transfer entry region, *A.I.Ch.E. Jl* **9**, 362–364 (1963).
23. J. S. Son and T. J. Hanratty, Limiting relation for the eddy diffusivity close to a wall, *A.I.Ch.E. Jl* **13**, 689–696 (1967).
24. M. Eisenberg, C. W. Tobias and C. R. Wilke, Ionic mass transfer and concentration polarisation on rotating electrodes, *J. Electrochem. Soc.* **101**, 306 (1954).
25. J. C. Bazan and A. J. Arvia, Diffusion of ferri- and ferrocyanide ions in aqueous solutions of NaOH *Electrochem. Acta* **10**, 1025 (1968).
26. P. L. Duffield, Diffusion controlled electrolysis at a porous electrode with gas injection, Ph.D. Thesis, Imperial College, University of London (1966).
27. M. Eisenberg, C. W. Tobias and C. R. Wilke, Selected physical properties of ternary electrolytes employed in ionic mass transfer, *J. Electrochem. Soc.* **103**, 413 (1956).

TRANSFERT MASSIQUE DANS UN ECOULEMENT TURBULENT EN CONDUITE, MESUREE PAR LA METHODE ELECTROCHIMIQUE

Résumé—On considère les nombreux facteurs qui influent sur les mesures de transfert massique dans les systèmes électrochimiques. On indique des moyens pour accroître les valeurs des débits "critiques" et des nombres de Reynolds auxquels on obtient des résultats intéressants.

Les coefficients de transfert massique sont mesurés en écoulement turbulent établi dans des tubes lisses pour un domaine $8 \times 10^3 < Re < 2 \times 10^5$ et des nombres de Schmidt variant entre 1000 et 6000. Quand la couche limite de concentration est complètement développée, les résultats peuvent être représentés par l'expression

$$St_a = 0,0165 Re^{-0,14} Sc^{-0,67}$$

Utilisant les résultats avec ceux publiés, une relation empirique est donnée sous la forme

$$Nu = 5 + c Re^a Pr^{1/3}$$

où

$$c = 0,0165 + 0,0011 Pe e^{-Pr}$$

$$a = 0,86 - \frac{10}{(4,5 + Pr)^3}$$

qui peut être recommandée pour estimer les flux de transfert massique et thermique dans le domaine $0,5 < Pr$ ou $Sc < 10^4$ et $10^4 < Re < 10^6$.

Les nombre de Stanton moyens mesurés à l'entrée (couche limite de concentration en développement) s'accordent bien avec l'équation de Lévêque pour le régime turbulent

$$St_d = 0,276 Re^{-0,417} Sc^{-2/3} (L/d)^{-1/3}.$$

MESSUNG DES STOFFÜBERGANGS BEI TURBULENTER ROHRSTRÖMUNG MIT HILFE DER ELEKTROCHEMISCHEN METHODE

Zusammenfassung—Es werden verschiedene Faktoren, welche Stoffübergangsmessungen in elektrochemischen Systemen beeinflussen, diskutiert und Wege aufgezeigt, bis zu welchen Werten, bei denen noch aussagekräftige Ergebnisse erzielt werden, die "kritischen" Durchflußraten und die Reynoldszahlen erhöht werden können. Bei voll ausgebildeter Strömung für die Bereiche $8 \cdot 10^3 < Re < 2 \cdot 10^5$ und $1000 < Sc < 6000$ gemessen. Für den Fall der vollständig ausgebildeten Konzentrationsgrenzschicht, können die Ergebnisse mit Hilfe der Gleichung

$$St_d = 0,0165 Re^{-0,14} Sc^{-0,67}$$

wiedergegeben werden. Aus den eigenen Meßwerten und anderen veröffentlichten Daten konnte die empirische Beziehung

$$Nu = 5 + c Re^a Pr^{1/3}$$

hergeleitet werden, wobei

$$c = 0,0165 + 0,011 Pr e^{-Pr}$$

$$a = 0,86 - \frac{10}{(4,5 + Pr)^3}.$$

Diese Beziehung kann zur Berechnung des Wärme- und Stoffübergangs im Bereich $0,5 < Pr(Sc) < 10^4$ und $10^4 < Re < 10^6$ empfohlen werden. Die im Einlaufbereich gemessenen mittleren Stantonzahlen (bei sich ausbildender Konzentrationsgrenzschicht) stimmen gut mit der integrierten Leveque-Beziehung

$$St_d = 0,276 Re^{-0,417} Sc^{-2/3} \left(\frac{L}{d}\right)^{-1/3}$$

für turbulente Grenzschicht überein.

ЭЛЕКТРОХИМИЧЕСКИЕ ИЗМЕРЕНИЯ МАССООБМЕНА ПРИ ТУРБУЛЕНТНОМ ТЕЧЕНИИ В ТРУБЕ

Аннотация—Обсуждается влияние различных факторов на измерения переноса массы в электрохимических системах. Показаны пути повышения «критических» значений расходов и чисел Рейнольдса. Коэффициенты массопереноса измерялись в полностью развитом течении в гладких трубах в диапазоне $8 \times 10^3 < Re < 2 \times 10^5$ при числах Шмидта 1000–6000. Для полностью развитого концентрационного пограничного слоя получено

$$St_d = 0,0165 Re^{-0,14} Sc^{-0,67}.$$

На основе результатов настоящего исследования и опубликованных данных предложено эмпирическое соотношение

$$Nu = 5 + c Re^a Pr^{1/3},$$

где $c = 0,0165 + 0,011 Pr e^{-Pr}$,

$$a = 0,86 - \frac{10}{(4,5 + Pr)^3}.$$

Это соотношение можно рекомендовать для расчета скоростей переноса тепла и массы в диапазонах $0,5 < Pr$ или $Sc < 10^4$ и $10^4 < Re < 10^6$.

Средние числа Стантона, измеренные на входном участке (неразвитый концентрационный пограничный слой), хорошо согласуются с интегральным уравнением Левека для турбулентного режима течения

$$St_d = 0,276 Re^{-0,417} Sc^{-2/3} \left(\frac{L}{d}\right)^{-1/3}.$$