Turbulent Flow and Mass Transfer on a Rotating Hemispherical Electrode

Using the Karman-Pohlhausen integral method, an analysis has been made for turbulent flow on a rotating hemispherical electrode mounted on an inert support rod of equal radius. The resulting friction coefficient is then substituted into the Chilton-Colburn relation to give a rate equation for mass transfer at high Schmidt numbers. Experiments with a diffusion-controlled electrolytic system over a range of Sc from 910 to 6,300 confirm the validity of the theory for $Re > 40{,}000$. A comparison with the results of previous heat and mass transfer measurements reveals that the turbulent flow on the present geometry is different from that on a rotating sphere and on a hemispherical electrode mounted on a support rod of larger radius.

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SCOPE

The flow induced by a sphere rotating in an otherwise undisturbed fluid is characterized by an inflow of the fluid toward each hemisphere along the axis of rotation and an axial symmetrical motion of the fluid along the surface toward the equator. The two identical flow boundary layers developed on the opposite hemispheres then interact at the equator where they form a thin, swirling, radial jet to the bulk of the fluid (Bowden and Lord, 1963; Kreith et al., 1963). Mathematical analysis of the boundary layer in laminar flow has been made by Howarth (1951), Banks (1965), and Manohar (1967). The theory agrees with the measured turning moment coefficient in spite of the fact that none of the authors was able to predict the outflow at the equator. No theory has been reported in the literature concerning turbulent flow on hemispheres.

Recently, the electrochemical application of a hemispherical electrode mounted on a rotating support rod has been discussed in a number of papers. A theory was formulated for the rate of ionic transfer in laminar flow (Chin, 1971a, 1972a; Newman, 1972), and the experimental set up for the use of such an electrode was described (Chin, 1971b, 1973). This geometry has been shown to have certain advantages over the rotating disk in studying metal dissolution reactions.

In this study, the application of the rotating hemispherical electrode has been extended into the turbulent flow regime. Karman-Pohlhausen's integral method and the 1/7th power velocity distributions (Schlichting, 1960) were used in the analysis of the turbulent boundary layer on the hemisphere. The resulting differential equations describing the boundary layer thickness and the direction of local flow relative to the surface were solved numerically on a digital computer. The results for the shear stress on the spherical surface were then substituted into the Chilton-Colburn relation (1934) to give a rate equation for mass transfer at high Schmidt numbers.

To test the validity of the theory, a mass transfer experiment was made on a platinum-plated rotating hemispherical electrode. The diffusion-limited reduction reaction of tri-iodide ions in the presence of excess potassium iodide was used for the measurement. This paper describes the details of these studies.

CONCLUSIONS AND SIGNIFICANCE

Analytical results are presented for turbulent flow on a rotating hemispherical electrode mounted on a cylindrical support rod of equal radius. The flow boundary layer is shown to originate at the pole of rotation and develop meridionally toward the equator. On the present geometry, there is no interaction of the opposite boundary layers at the equator as in the case of a rotating sphere; however, the calculation reveals that flow separation would occur naturally at latitude 74.05°. This results in a rapid increase in the boundary layer thickness in the equatorial region. It is shown that the turning moment coefficient for the hemisphere varies with $0.174/Re^{0.2}$.

The use of the Chilton-Colburn analogy leads to the following relation:

$$Sh = 0.0198\, Re^{4/5}\, Sc^{1/3}$$

for mass transfer at high Schmidt numbers. Experiments over a range of Schmidt numbers between 910 and 6,300 confirm the validity of the theory for Reynolds number greater than 40,000. A comparison with the results of previous publications indicates that the turbulent flow induced by the present geometry is different from that on a rotating sphere and on a hemisphere mounted on a support rod of larger radius where the transition Reynolds number was found to occur at 15,000 and the rate of turbulent mass transfer varied with $Re^{0.67}$. Consequently, the present theory does not apply to these two geometries.

BOUNDARY LAYER EQUATIONS

In this analysis we shall consider a hemispherical electrode mounted on a cylindrical support rod of an equal radius a as shown in Figure 1. The advantage of this geometry is that there is no collision of opposite boundary layers at the equator (Bowden and Lord, 1963). Thus, one does not have to take into account the problem associated with a radial swirling jet as in the case of a rotating sphere. The domain around the electrode may be specified by a set of spherical polar coordinates, r, θ, and ϕ. The coordinate r is measured radially outward from the center of curvature of the spherical surface, θ is an angle measured from the axis of rotation, and ϕ is the azimuth. The electrode is rotating with an angular velocity ω in a stationary, infinitely large, incompressible fluid of constant properties. Neglecting the effect of external forces, the turbulent boundary layer equations describing the time-averaged, axial-symmetrical flow components are given as

continuity

$$\frac{\partial V_r}{\partial r} + \frac{1}{a}\frac{\partial V_\theta}{\partial \theta} + \frac{V_\theta}{a}\cot\theta = 0 \qquad (1)$$

r-momentum

$$\frac{V_\theta^2 + V_\phi^2}{a} = \frac{1}{\rho}\frac{\partial P}{\partial r} \qquad (2)$$

θ-momentum

$$V_r\frac{\partial V_\theta}{\partial r} + \frac{V_\theta}{a}\frac{\partial V_\theta}{\partial \theta} - \frac{V_\phi^2}{a}\cot\theta = -\frac{1}{\rho}\frac{\partial \tau_{r\theta}}{\partial r} \qquad (3)$$

ϕ-momentum

$$V_r\frac{\partial V_\phi}{\partial r} + \frac{V_\theta}{a}\frac{\partial V_\phi}{\partial \theta} + \frac{V_\theta V_\phi}{a}\cot\theta = -\frac{1}{\rho}\frac{\partial \tau_{r\phi}}{\partial r} \qquad (4)$$

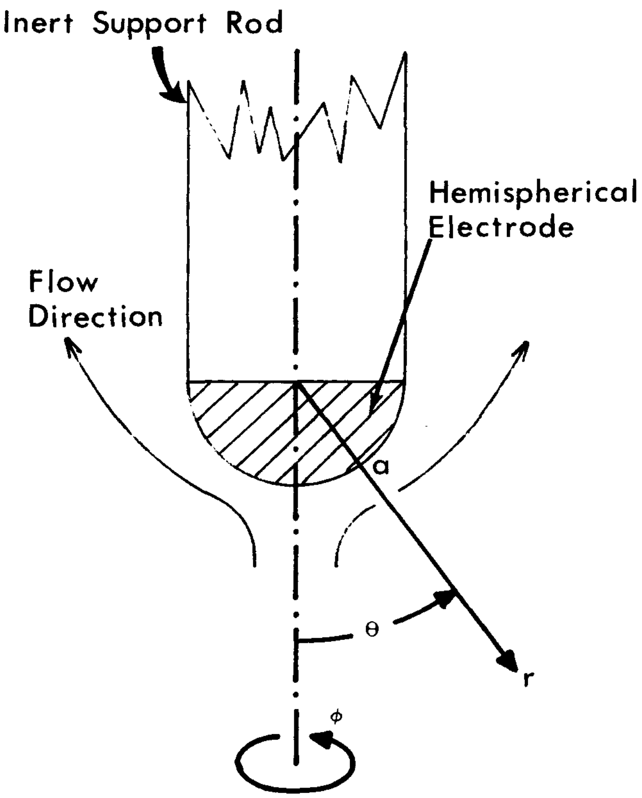

Fig. 1. Rotating hemispherical electrode and spherical polar coordinates.

boundary conditions

$$\text{at} \quad r = a, \quad V_r = V_\theta = 0, \quad V_\phi = a\omega\sin\theta$$
$$\text{at} \quad r = \delta, \quad V_\theta = V_\phi = 0 \qquad (5)$$

Here δ is the thickness of the turbulent boundary layer, and is a function of θ.

ONE-SEVENTH POWER LAW ANALYSIS

To provide a rapid solution, we integrate Equations (3) and (4) with respect to r through the boundary layer, $\int_a^\delta$ [Equation (3) or (4)] $\cdot\, dr$. Making use of Equations (1) and (5) and introducing a dimensionless radial distance

$$\xi = \frac{r - a}{\delta} \qquad (6)$$

the integrations are simplified to

θ-momentum

$$\frac{d}{d\theta}\left(\delta\int_0^1 V_\theta^2\, d\xi\right) + \delta\cot\theta\cdot\int_0^1 (V_\theta^2 - V_\phi^2)d\xi = \frac{a}{\rho}T_{r\theta} \qquad (7)$$

ϕ-momentum

$$\frac{d}{d\theta}\left(\delta\int_0^1 V_\theta V_\phi\, d\xi\right) + 2\delta\cot\theta\cdot\int_0^1 V_\theta V_\phi\, d\xi = \frac{a}{\rho}T_{r\phi} \qquad (8)$$

Here $T_{r\theta}$ and $T_{r\phi}$ are the components of the shear stress on the hemisphere surface along the θ- and the ϕ-directions, respectively.

To evaluate the integrals in Equations (7) and (8), one needs information regarding the velocity distribution within the boundary layer. For this reason, we shall follow Karman's 1/7th power assumption (1921) for turbulent flow on the rotating disk and assume that

$$V_\theta = \alpha a\omega\sin\theta\cdot\xi^{1/7}(1-\xi) \qquad (9)$$

$$V_\phi = a\omega\sin\theta\cdot(1-\xi^{1/7}) \qquad (10)$$

In his analysis of an infinite rotating disk, Karman considered α as a constant. In the case of a rotating hemisphere, α is a function of θ because of the effect of surface curvature. However, the flow characteristic near the pole of the hemisphere should be similar to that on the rotating disk. This implies that α is a constant near the pole of rotation; mathematically it may be expressed as

$$\frac{d\alpha}{d\theta} = 0 \quad \text{for} \quad \theta \to 0 \qquad (11)$$

To find the velocity component normal to the spherical surface V_r, we substitute Equation (9) into Equation (1) and carry out the integration with respect to the radial coordinate. The result is

$$V_r = -7\delta\omega\left(\sin\theta\cdot\frac{d\alpha}{d\theta} + 2\alpha\cos\theta\right)\xi^{8/7}\left(\frac{1}{8} - \frac{\xi}{15}\right) \qquad (12)$$

The local velocity relative to the electrode surface can then be calculated from

$$|V| = \sqrt{V_r^2 + V_\theta^2 + (V_\phi - a\omega\sin\theta)^2}$$
$$\simeq U\xi^{1/7} \quad \text{for} \quad \xi \to 0 \qquad (13)$$

with

$$U = (1 + \alpha^2)^{1/2} a\omega\sin\theta \qquad (14)$$

Thus, near the electrode surface, the local velocity relative to the surface is at an angle of $\tan^{-1}(1/\alpha)$ from the θ-vector, and at an angle of $\cot^{-1}(1/\alpha)$ from the negative of the ϕ-vector (opposite to the direction of rotation).

Using the results for turbulent flow over a flat plate (Schlichting, 1960), the local shear stress on the spherical surface can be calculated from the following formula

$$|T| = 0.0225\, \rho U^2 \left(\frac{\nu}{U\delta}\right)^{1/4} \qquad (15)$$

The component of T along the θ-direction is related to $|T|$ by

$$T_{r\theta} = -\,|T| \cos\left(\tan^{-1}\frac{1}{\alpha}\right)$$

$$= -\,0.0225\, \rho\alpha(1 + \alpha^2)^{3/8}\, (a\omega\sin\theta)^{7/4}\nu^{1/4}\delta^{-1/4} \qquad (16)$$

Also

$$T_{r\phi} = -\left[-\,|T| \sin\left(\tan^{-1}\frac{1}{\alpha}\right)\right]$$

$$= 0.0225\, \rho(1 + \alpha^2)^{3/8}\, (a\omega\sin\theta)^{7/4}\nu^{1/4}\delta^{-1/4} \qquad (17)$$

Notice that $T_{r\theta}$ is negative; this implies that in the immediate neighborhood of the hemispherical electrode, the flux of θ-momentum is toward the surface. On the other hand, the positive $T_{r\theta}$ implies that ϕ-momentum is transferred toward the bulk of the fluid.

Substituting V_θ, V_ϕ, $T_{r\theta}$ and $T_{r\phi}$ into Equations (7) and (8), carrying out integrations, and introducing a dimensionless dependent variable,

$$\Delta = \frac{\delta}{a} Re^{1/5} \qquad (18)$$

we arrive at two simultaneous, linear, first-order differential equations describing the thickness of the turbulent boundary layer and the direction of local flow relative to the hemispherical surface:

$$\frac{d\Delta}{d\theta} + 2\frac{\Delta}{\alpha}\frac{d\alpha}{d\theta} + \left(3 - \frac{0.134111}{\alpha^2}\right)\Delta\cot\theta = -\,0.108630\,\frac{(1 + \alpha^2)^{3/8}}{\alpha\Delta^{1/4}\sin^{1/4}\theta} \qquad (19)$$

$$\frac{d\Delta}{d\theta} + \frac{\Delta}{\alpha}\frac{d\alpha}{d\theta} + 4\Delta\cot\theta = 0.330612\,\frac{(1 + \alpha^2)^{3/8}}{\alpha\Delta^{1/4}\sin^{1/4}\theta} \qquad (20)$$

It is a common practice in the analysis of turbulent flows to assume a zero thickness at the leading edge of the turbulent boundary layer (Karman, 1921; Schlichting, 1960). This, together with Equation (11), leads to the following initial conditions for the differential equations:

$$\text{at} \quad \theta = 0, \quad \Delta = 0, \quad \text{and} \quad \frac{d\alpha}{d\theta} = 0 \qquad (21)$$

Now, the problem is to solve Equations (19) and (20) for α and Δ. Notice that the differential equations have a singular point at $\theta = 0$. In the following paragraph, we shall obtain an analytical expression valid near $\theta = 0$.

SOLUTION FOR SMALL θ

For small values of θ, we have $\cot\theta \sim 1/\theta$, $\sin\theta \sim \theta$, $d\alpha/d\theta \sim 0$, and Equations (19) and (20) are reduced to

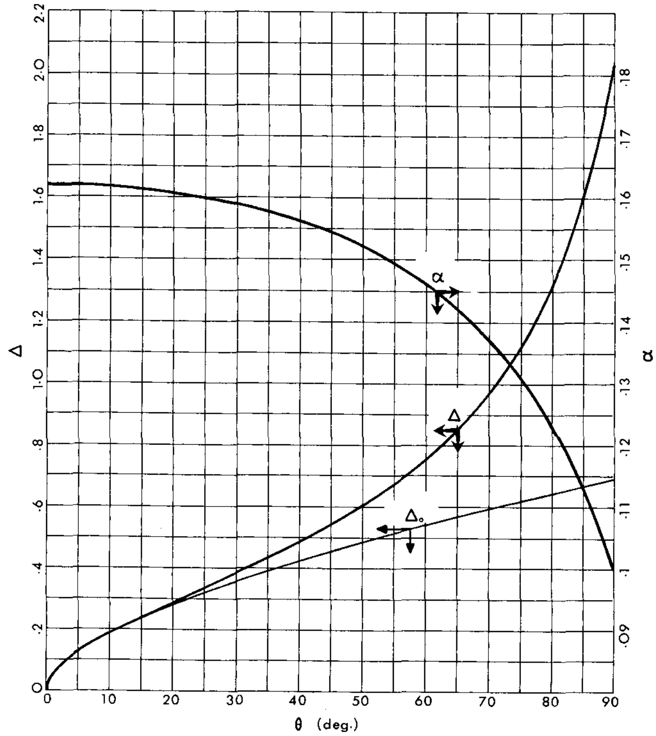

Fig. 2. Numerical solutions of α and Δ. For comparison, values of Δ_0 as calculated from Equation (24) are also plotted in the figure as the thin curve.

$$\frac{d\Delta_0}{d\theta} + \left(3 - \frac{0.134111}{\alpha^2}\right)\frac{\Delta_0}{\theta} = -\,0.108630\,\frac{(1 + \alpha_0^2)^{3/8}}{\alpha_0\Delta_0^{1/4}\theta^{1/4}} \qquad (22)$$

$$\frac{d\Delta_0}{d\theta} + 4\frac{\Delta_0}{\theta} = 0.330612\,\frac{(1 + \alpha_0^2)^{3/8}}{\alpha_0\Delta_0^{1/4}\theta^{1/4}} \qquad (23)$$

Here the subscript 0 denotes the values of α and Δ in the neighborhood of $\theta = 0$. Equations (22) and (23) are of the Bernoulli-type differential equations, and a solution that satisfies the condition, $\Delta_0 = 0$ at $\theta = 0$ can be found as

$$\left.\begin{aligned} \alpha_0 &= 0.161980 \\ \Delta_0 &= 0.526084\theta^{3/5} \end{aligned}\right\} \qquad (24)$$

This solution is identical to that found on a rotating disk (Karman, 1921; Schlichting, 1960), thus conforming the hypothesis that flow near the pole of rotation is the same as that on the rotating disk.

NUMERICAL SOLUTIONS

Equations (19) and (20) have been integrated on a digital computer over a range of θ from 0 to $\pi/2$ with a step of $\pi/180$. To avoid the singularity in the numerical computation, Equation (24) was used to evaluate starting values near $\theta = 0$; the successive numerical integrations were then made with a fourth order Runge-Kutta method. The results are expressed graphically in Figure 2, where the abscissa θ is in degrees. It is seen that α is a decreasing function of θ. The behavior of Δ indicates that the flow boundary layer originates at $\theta = 0$; its thickness increases rapidly with increasing θ, especially near the equatorial region of the hemisphere. For comparison, we also plot Δ_0 in the figure as the thin curve. The results show that the solution for small θ, Equation (24), is valid for $\theta < 20°$; within this region, the accuracy is better than 98%.

The torque required to rotate the hemisphere at a constant speed can be obtained from the following relation

$$M = \int_0^{2\pi} \int_0^{\pi/2} a\sin\theta T_{r\phi} a\sin\theta \cdot d\theta \cdot a d\phi \qquad (25)$$

It is customary to introduce a turning moment coefficient defined as

$$C_M \equiv \frac{M}{\frac{1}{2}\rho a^5 \omega^2} = \frac{0.09}{Re^{1/5}} \int_0^{\pi/2} \frac{(1+\alpha^2)^{3/8}\sin^{15/4}\theta}{\Delta^{1/4}} d\theta \qquad (26)$$

Using the numerical results in Figure 2 and carrying out the integration with Simpson's formula, we have

$$C_M = \frac{0.174}{Re^{1/5}} \qquad (26a)$$

Although the rotating geometry shown in Figure 1 has enabled us to disregard the outflowing radial jets in the equatorial region, there is still a possibility of flow separation on the hemispherical surface. Let us consider the coefficient function of V_r given in Equation (12)

$$f(\theta) = \sin\theta \cdot \frac{d\alpha}{d\theta} + 2\alpha\cos\theta \qquad (27)$$

If $f(\theta)$ is positive, the flow is toward the hemispherical surface; on the other hand, if $f(\theta)$ is negative, the flow is away from the hemispherical surface. The point of separation can be found by setting $f(\theta) = 0$ and solving the equation for θ. The result is

$$\theta(\text{separation}) = 74.05° \qquad (28)$$

independent of the Reynolds number. Thus, for $\theta > 74.05°$, V_r becomes positive, and the fluid starts to flow away from the surface. This results in a rapid increase in the thickness of the turbulent boundary layer near the equator as shown in Figure 2.

MASS TRANSFER PREDICTION

In this section we shall use the Chilton-Colburn correlation (1934)

$$Sh_x = Re_x\, Sc^{1/3} \left(\frac{f_x}{2}\right) \qquad (29)$$

to derive a rate equation for turbulent mass transfer on the rotating hemispherical electrode. Here Sc is the Schmidt number; Sh_x, Re_x, and f_x are the local Sherwood number, the local Reynolds number, and the local friction coefficient, respectively, based upon the surface distance from the leading edge of the flow boundary layer. Although the Chilton-Colburn relation is empirical in nature, it has been found to give a satisfactory estimate of the rate of heat and mass transfer for channel flows (Hubbard and Lightfoot, 1966), on a rotating disk (Dorfman, 1958), and for laminar flow on a rotating sphere (Chin, 1972b).

Following the procedures illustrated in Chin (1972b) for mass transfer on the rotating sphere, we have

$$Sh_x = \frac{ka\theta}{D} \qquad (30)$$

$$Re_x = \frac{a^2\omega\theta\sin\theta}{\nu} \qquad (31)$$

$$f_x = \frac{T_{r\phi}}{\frac{1}{2}\rho a^2\omega^2\sin^2\theta} \qquad (32)$$

Substituting Equations (30) to (32) into Equation (29) and making use of Equation (17), we arrive at an expression for the local Sherwood number based upon the radius of the hemisphere:

$$Sh_{loc} \equiv \left(\frac{ka}{D}\right) = 0.0225\, Re^{4/5}\, Sc^{1/3} \frac{(1+\alpha^2)^{3/8}\sin^{3/4}\theta}{\Delta^{1/4}} \qquad (33)$$

The average Sherwood number can be obtained by numerically integrating Equation (33) over the surface; the result for a hemisphere may be given as

$$Sh = 0.0198\, Re^{4/5}\, Sc^{1/3} \qquad (34)$$

EXPERIMENT

To verify the validity of Equation (34), a mass transfer experiment has been made on a 5.09-cm diam. platinum-plated hemispherical electrode. The electrode was mounted on a Teflon support rod of an equal radius, thus giving a rotating geometry as illustrated in Figure 1. The rate of mass transfer to the electrode was determined by measuring the limiting current for the reduction of tri-iodide ions in an excess supporting electrolyte. The solution used was composed of 0.1M KI, 0.001M I_2, and 0-1M sucrose. The addition of sucrose to the electrolyte increased the solution viscosity and decreased the diffusion coefficient of tri-iodide ion. This allowed a variation of Schmidt numbers ranging from 910 to 6,300 at a constant temperature of 24°C. The details of the experimental setup and procedures have been described previously (Chin, 1971b) and will not be repeated here.

RESULTS AND DISCUSSION

Figure 3 shows the experimental results over a range of Reynolds numbers between 5,000 and 100,000. The limiting current data as represented by the open symbols ▽, △, □, ○ are presented in the form of a log-log plot of $Sh/Sc^{1/3}$ versus Re for four different Schmidt numbers. The thick solid lines are the theoretical predictions given by Equation (34) for turbulent flow and by

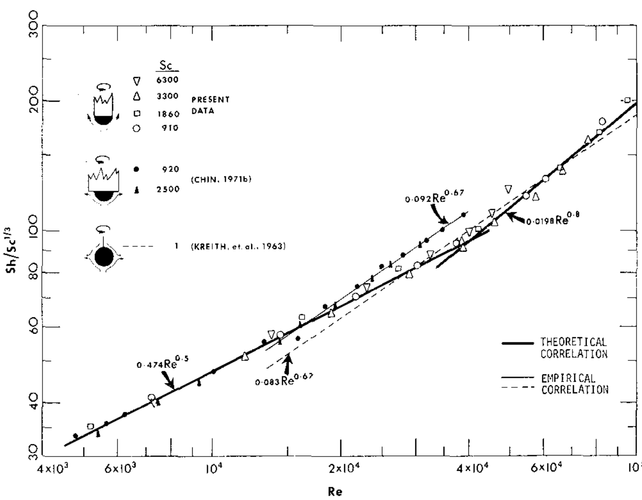

Fig. 3. Comparison of experimental results with mass transfer predictions.

$$Sh = 0.474\, Re^{1/2}\, Sc^{1/3} \quad (35)$$

for laminar flow (Chin, 1971a). It is seen that the present results agree reasonably well with both theories. The point of transition for the present geometry occurs at $Re = 40{,}000$. A regressional analysis of the turbulent data located between $Re = 40{,}000$ and $Re = 100{,}000$ gives a $(0.020 \pm 0.001)Re^{4/5}$ dependence for $Sh/Sc^{1/3}$. Thus, the experimental coefficient agrees with the theoretical value of 0.0198 to within ± 5%.

For comparison, some of the transfer data reported in a previous study (Chin, 1971b) are also plotted in Figure 3 as the filled symbols ▲, ●. These data were obtained with a rotating hemispherical electrode mounted on an inert support of a larger diameter as shown in the figure. The close agreement of the laminar data with Equation (35) indicates that the shape of the support rod has no effect on the average rate of mass transfer in laminar flow. However, the use of a larger diameter rod arbitrarily introduces a radial outflowing stream at the equator. Apparently, the radial stream reduces the stability of the boundary layer on the hemispherical surface, and the transition to turbulent flow occurs earlier at $Re = 15{,}000$. Thus, the turbulent data for the larger diameter support rod are seen to deviate considerably from the theoretical prediction of Equation (34); a regressional analysis of the data results in a $(0.092 \pm 0.005)Re^{0.67}$ dependence for $Sh/Sc^{1/3}$ as indicated by the thin solid line passing through the data points. The 0.67 power of Re agrees with the result of a turbulent heat transfer measurement on a rotating sphere (Kreith et al., 1963) as represented by the thin dashed line in the figure ($(0.082 \pm 0.012)Re^{0.67}$). Since the flow induced by a rotating sphere is also characterized by a radial outflowing jet caused by a collision of the opposite boundary layers at the equator, the 0.67 power dependence on Re is clearly related to the radial stream in the equatorial region. Probably, the turbulent flow on both geometries (rotating hemisphere with a larger diameter support rod and rotating sphere) is caused by the spreading inward of the turbulences from the radial jet at the equator and is different from the turbulent flow on the present geometry shown in Figure 1. Any attempt to analyze theoretically the turbulences on the rotating sphere must take into account the boundary layer collision in the equatorial region.

The present results suggest that the Chilton-Colburn analogy based upon the local tangential friction coefficient is a simple method to predict the rate of turbulent mass transfer on a rotating geometry where the flow is not complicated by the boundary layer collision. The procedures illustrated in this work may also be used for other rotating axisymmetric surfaces such as a cone or an elliptic paraboloid.

NOTATION

- a = radius of the hemispherical electrode, cm
- C_M = turning moment coefficient defined as $M/(\frac{1}{2}\rho a^5 \omega^2)$, dimensionless
- D = diffusion coefficient of the diffusing species, cm²/s
- f_x = local friction coefficient based upon the surface distance x from the leading edge of the flow boundary layer, dimensionless
- k = local mass transfer coefficient, cm/s
- K = average mass transfer coefficient, cm/s
- M = moment required to maintain a constant speed of rotation for the hemispherical electrode, dyne · cm
- P = time-averaged pressure exerted on the fluid, dyne/cm²
- r = radial coordinate, cm
- Re = Reynolds number defined as $a^2\omega/\nu$, dimensionless
- Re_x = local Reynolds number based upon the surface distance x from the leading edge of the flow boundary layer, dimensionless
- Sc = Schmidt number defined as ν/D, dimensionless
- Sh = average Sherwood number defined as Ka/D, dimensionless
- Sh_{loc} = local Sherwood number defined as ka/D, dimensionless
- Sh_x = local Sherwood number based upon the surface distance x from the leading edge of the flow boundary layer, dimensionless
- T = local shear stress on the hemispherical surface, dyne/cm²
- $T_{r\theta}$ = component of local shear stress on the surface along the θ-direction, dyne/cm²
- $T_{r\phi}$ = component of local shear stress on the surface along the ϕ-direction, dyne/cm²
- V_r = time-averaged radial velocity component, cm/s
- V_θ = time-averaged meridional velocity component, cm/s
- V_ϕ = time-averaged azimuthal (or tangential) velocity component, cm/s

Greek Letters

- α = a dimensionless function of θ defined in Equation (9); it is related to the direction of local flow relative to the surface
- α_0 = values of α calculated from Equation (24) and valid only in the neighborhood of $\theta = 0$
- δ = thickness of the flow boundary layer, cm
- Δ = dimensionless thickness of the boundary layer defined as $(\delta/a)Re^{1/5}$
- Δ_0 = values of Δ calculated from Equation (24) and valid only in the neighborhood of $\theta = 0$
- θ = latitude coordinate, rad
- ν = kinematic viscosity of the fluid, cm²/s
- ξ = dimensionless radial coordinate defined as $(r - a)/\delta$
- ρ = density of the fluid, g/cm³
- $\tau_{r\theta}$ = time-averaged shear stress exerted in the θ direction on a fluid surface of constant r by the fluid in the region of lesser r, dyne/cm²
- $\tau_{r\phi}$ = time-averaged shear stress exerted in the ϕ direction on a fluid surface of constant r by the fluid in the region of lesser r, dyne/cm²
- ϕ = azimuthal coordinate, rad
- ω = angular velocity of the hemispherical electrode, rad/s

LITERATURE CITED

Banks, W. H. H., "The Boundary Layer on a Rotating Sphere," *Quart. J. Mech. Applied Math.*, **18**, 443 (1965).

Bowden, F. P., and R. G. Lord, "The Aerodynamic Resistance to a Sphere Rotating at High Speed," *Proc. Roy. Soc.*, **A271**, 143 (1963).

Chilton, T. H., and A. P. Colburn, "Mass Transfer (Absorption) Coefficients. Prediction from Data on Heat Transfer and Fluid Friction," *Ind. Eng. Chem.*, **26**, 1183 (1934).

Chin, D-T., "Convective Diffusion on a Rotating Spherical Electrode," *J. Electrochem. Soc.*, **118**, 1434 (1971a).

———., "An Experimental Study of Mass Transfer on a Rotating Spherical Electrode," *ibid.*, **118**, 1764 (1971b).

———., "Rotating Spherical Electrode: A Perturbation Theory for Schmidt Number Corrections," *ibid.*, **119**, 1049 (1972a).

———., "Mass Transfer to a Rotating Sphere at High Schmidt

Numbers," *ibid.*, **1699** (1972b).
———., "A Rotating Ring-Hemispherical Electrode for Electroanalytical Applications," *ibid.*, **120**, 631 (1973).
Dorfman, L. A., "Thermal Boundary Layer on a Rotating Disc," *Soviet Phys. Dokladay*, 3, 248 (1958).
Howarth, L., "Note on the Boundary Layer on a Rotating Sphere, *Phil. Mag., Ser* 7, **42**, 1308 (1951).
Hubbard, D. W., and E. N. Lightfoot, "Correlation of Heat and Mass Transfer Data for High Schmidt and Reynolds Numbers," *Ind. Eng. Chem. Fundamentals*, **5**, 370 (1966).
Kármán, Th. v., "Über laminare and turbulente Reibung," *Z. Angew. Math. Mech.*, **1**, 233 (1921).
Kreith, F., L. G. Roberts, J. A. Sullivan, and S. N. Sinha, "Convection Heat Transfer and Flow Phenomena on Rotating Spheres," *Intern. J. Heat Mass Transfer*, **6**, 881 (1963).
Manohar, R., "The Boundary Layer on a Rotating Sphere," *ZAMP*, **18**, 320 (1967).
Newman, J., "Mass Transfer to a Rotating Sphere at High Schmidt Numbers," *J. Electrochem. Soc.*, **119**, 69 (1972).
Schlichting, H., *Boundary Layer Theory*, McGraw-Hill, New York (1960).

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A New Method for the Estimation of Parameters in Differential Equations

A new objective function for estimating parameters in differential equations, based upon a weighted least squares criterion for the residuals of these equations, is presented. The use of Lobatto quadrature in combination with the collocation technique reduces the original problem to one of minimizing a simple algebraic expression with respect to a series of unknowns. The method can be applied to different types of differential equations as shown by a series of examples and leads to very good estimates. It becomes particularly useful for systems which are linear in the parameters and for which all states are observable since in this case the usual convergence problem is avoided. The gain in computation time when compared with classical methods is significant.

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SCOPE

Most chemical engineering problems are modeled by complex sets of algebraic or differential equations. In the common problem of engineering analysis the outputs of a model are calculated for given values of the parameters. Contrary to this direct problem the inverse situation often occurs, that is, when measurements of the outputs can be performed without knowing values of the parameters. The form of the model itself is usually obtained from a priori knowledge on the nature of the process. In this grey box problem, the unknown parameters are identified or estimated from an analysis of the output data. This is performed by selecting an appropriate objective function based upon deviations of the observation equations. The parameters are calculated by use of an algorithm for minimization of the objective function, which often involves a problem of convergence. Methods derived from the general gradient techniques are most commonly encountered, calling for repetitive and time-consuming solutions of the differential equations.

In this investigation a new criterion based upon the residuals of the differential equations is presented. The application of the Lobatto quadrature formulas with appropriate weighting functions in combination with the collocation technique leads to a simple algebraic expression for the objective function. The parameters can then be estimated in the same way as for systems described by algebraic equations.

CONCLUSIONS AND SIGNIFICANCE

The use of quadrature formulas and the collocation technique for approximating objective functions for parameter estimation reduces significantly the complexity of the problem. An algebraic expression is obtained, which has to be minimized with respect to a series of unknowns. By defining an objective function based upon residuals of the differential equations instead of upon deviations from the observation equations, it is possible to eliminate part of the unknowns, since constraints derived from boundary conditions and from observation equations are usually linear with respect to the unknowns. Repetitive solution of the differential equations, typical for classical methods, is avoided, and the computation time for obtaining estimates of the parameters is drastically reduced. Because of the general validity of the objective criterion and of the two approximation techniques, no a priori restrictions

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