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The Diffusion Layer on a Rotating Disk Electrode

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In a recently published work,[1] the author treated the current distribution on a rotating disk under conditions where ohmic potential drop, surface overpotential, and concentration variations near the electrode must all be taken into account. The diffusion layer, which is then characterized by a nonuniform current density and concentration at the surface, was handled by a power-series expansion in r, the radial distance from the axis of rotation:

$$c = c_\infty \left[1 + \sum_{m=0}^{\infty} A_m (r/r_o)^{2m} \theta_m(\zeta) \right] , \tag{1}$$

where c is the concentration of the reactant, c_∞ is the bulk concentration, r_o is the radius of the electrode, and θ_m represents functions of $\zeta = y\,(a\nu/3D)^{1/3}\sqrt{\Omega/\nu}$, where y is the normal distance from the disk, $a = 0.51023$, ν is the kinematic viscosity, D is the diffusion coefficient, and Ω is the rotation speed of the disk.

The functions θ_m and, in particular, the derivatives $\theta_m'(0)$ at the surface were obtained by a finite-difference solution of the differential equations

$$\theta_m'' + 3\zeta^2\theta_m' - 6m\zeta\theta_m = 0, \tag{2}$$

subject to the boundary conditions

$$\theta_m = 1 \text{ at } \zeta = 0 \text{ and } \theta_m = 0 \text{ at } \zeta = \infty.$$

Subsequent numerical difficulties were encountered which required accurate values of the derivatives $\theta_m'(0)$.

As suggested by the work of Rosner,[2] one can use the equations in section 58 of Levich's book[3] to obtain the concentration at the surface in terms of an integral over the concentration derivative at the surface:

$$c(r,o) = c_o(r) = \frac{1}{\Gamma(2/3)}\int_o^r \frac{J(r')r'\,dr'}{(r^3-r'^3)^{2/3}} , \tag{3}$$

where $J(r) = -\partial c/\partial\zeta$ at $\zeta = 0$. Substitution of a power-series expansion for c into equation (3) yields an expression for $\theta_m(0)$:

$$\theta_m'(0) = -\frac{3\Gamma(\frac{5}{3})\Gamma(\frac{2m+3}{3})}{2\Gamma(\frac{4}{3})\Gamma(\frac{2m+2}{3})} . \tag{4}$$

The gamma functions necessary to evaluate $\theta_m'(0)$ from equation (4) are given[4] to 15 significant figures. The values of $\theta_m'(0)$ are in satisfactory agreement with those tabulated in table 1 of reference 1. At the same time direct use of equation (3) or its inverse[2] provides a possibility of avoiding the numerical difficulties encountered in the earlier work.[1]

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1. John Newman. "Current Distribution on a Rotating Disk below the Limiting Current." Journal of the Electrochemical Society, 113, 1235-1241 (1966).

2. Daniel E. Rosner. "Reaction Rates on Partially Blocked Rotating Disks--Effect of Chemical Kinetic Limitations." Journal of the Electrochemical Society, 113, 624-625 (1966).

3. Veniamin G. Levich. Physicochemical Hydrodynamics. Englewood Cliffs, N. J.: Prentice-Hall, Inc., 1962.

4. Milton Abramowitz and Irene A. Stegun, eds. Handbook of Mathematical Functions. Washington: National Bureau of Standards, 1964. p.3.

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