0 0 0 0 3 9 0 7 5 4 3

Submitted to
Journal of the Electrochemical Soc.

LBL-1881
Preprint

c. 1

TRANSIENT CONVECTIVE DIFFUSION TO A DISK ELECTRODE

Kemal Nisancioglu and John Newman

RECEIVED
LAWRENCE
RADIATION LABORATORY

OCT 22 1973

LIBRARY AND
DOCUMENTS SECTION

July 1973

Prepared for the U.S. Atomic Energy Commission
under Contract W-7405-ENG-48

For Reference

Not to be taken from this room

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY

LBL-1881

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

0 0 0 0 3 9 0 7 0 4 4

Transient Convective Diffusion to a Disk Electrode

Kemal Nisancioğlu and John Newman

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

July 1973

ABSTRACT

Mass transfer to a rotating disk electrode is calculated at large times after a concentration step or a flux step at the surface. Radial dependence of concentration is ignored. Further application of results to treat more complex boundary conditions is discussed.

Key Words: Concentration step, flux step, boundary-value problem, time constant

0 0 0 0 3 9 0 7 0 4 5

Introduction

Nonsteady-state methods are commonly employed in electrochemistry for the study of electrode kinetics and mass transfer in electrolytic solutions. The transient behavior of an electrochemical system is determined by a number of processes of varying complexity, which may occur concurrently at the electrode surface and the bulk solution. To name a few, these processes include convective diffusion[1] and the capacitive discharge of the electric double layer due to a faradaic reaction and/or transfer of charge through the bulk solution in the presence of a nonuniform electric field.[2,3]

The fundamental treatment of transient diffusion at electrode surfaces has been of interest since the classical study of the problem early in the century by Roseburgh and Lash-Miller.[4] The rotating disk electrode has become popular for convective diffusion problems because previous applications of this geometry have been quite fruitful in the assessment of its hydrodynamic conditions,[5,6] mass transfer characteristics,[7,8] and the current distribution in presence of an electric field and complex electrode kinetics.[9,10] Levich[8,11] has solved for the first time the transient diffusion equation for the disk geometry. Since convection is ignored in that treatment, the results are valid only for very short times. Subsequent analytic efforts[12,13] with the consideration of axial convection are also limited to small time intervals due to approximate methods of analysis. Fairly accurate numerical solutions are available for response to

flux step[1] and concentration step[14,15] at the surface. However, analytic results are always more desirable for design calculations, determination of relaxation times, and investigation of complex boundary conditions involving electrode kinetics and capacitive effects.

Krylov and Babak[16] have recently attempted an exact solution of the axial convective-diffusion equation by a classical perturbation expansion technique. They have reported results for the concentration step and flux step conditions. Selman[15] derived independently the same solution for the concentration step. These results provide considerable improvements over the previous analytic work but are still confined to relatively short times if a reasonable number of terms are to be retained in the series expansion. The purpose of this paper is to contribute to the past effort by presenting an alternative treatment for large times, so that the results can be employed interchangeably with the short-time series of Krylov and Babak within their ranges of applicability.

In treating problems of this kind, it is commonly assumed that the concentration variations in the solution are confined to a thin region near the electrode surface (high Péclet numbers). Consequently, the axial velocity component can be approximated by[5-9]

$$v_y = -ay^2\Omega\sqrt{\Omega/\nu} \quad , \tag{1}$$

where a = 0.51023, y is the axial distance from the electrode surface, Ω is the angular rotation speed, and ν is the kinematic viscosity. It is further assumed that the disk is uniformly accessible, and thus

radial convection can be ignored. One should realize, however, that the latter assumption is introduced merely as a mathematical convenience. It is well accepted by now that radial convection becomes significant below the limiting current.[9] The experimental data of Nanis and Klein[17] seem to indicate that this assumption may lead to appreciable error especially during the transient build-up of overpotential after a step increase in the current.

Theoretical Formulation

Without the radial terms, the transient equation for convective diffusion reads

$$\frac{\partial c}{\partial t} + v_y \frac{\partial c}{\partial y} = D \frac{\partial c^2}{\partial y^2} \quad . \tag{2}$$

We introduce the dimensionless variables

$$\theta = \Omega \left(\frac{D}{\nu}\right)^{1/3} \left(\frac{a}{3}\right)^{2/3} t \quad , \tag{3}$$

$$\zeta = y \left(\frac{a\nu}{3D}\right)^{1/3} \sqrt{\frac{\Omega}{\nu}} \quad , \tag{4}$$

$$\Theta = \frac{c_\infty - c}{c_\infty} \qquad \text{(concentration step)} \ , \tag{5}$$

or

$$\Theta = \frac{c_\infty - c}{(\partial c/\partial \zeta)_{\zeta=0}} \qquad \text{(flux step)} \quad . \tag{6}$$

Equation 2 thus becomes

$$\frac{\partial\Theta}{\partial\theta} = 3\zeta^2 \frac{\partial\Theta}{\partial\zeta} + \frac{\partial^2\Theta}{\partial\zeta^2} \quad . \tag{7}$$

Consider the build-up case after a step increase in the concentration or flux. The boundary conditions are

$$\left.\begin{array}{lll} \Theta = 0 & \text{as} & \zeta \to \infty \\ \Theta = 0 & \text{at} & \theta = 0 \end{array}\right\} \quad , \tag{8}$$

$$\Theta = 1 \quad \text{at} \quad \zeta = 0,\ \theta > 0 \quad \text{(concentration step)}, \tag{9}$$

or

$$\partial\Theta/\partial\zeta = -1 \quad \text{at} \quad \zeta = 0,\ \theta > 0 \quad \text{(flux step)} \quad . \tag{10}$$

It is possible to express Θ in terms of a steady-state and a transient part,

$$\Theta = \Theta^{ss} - \Theta^{t} \quad \text{(build-up)} \quad , \tag{11}$$

so that each part satisfies equation 7 separately. The boundary conditions for Θ^{ss} are

$$\Theta^{ss} = 0 \quad \text{as} \quad \zeta \to \infty \quad , \tag{12}$$

$$\left.\begin{array}{l} \Theta^{ss} = 1 \quad \text{at} \quad \zeta = 0 \quad \text{(concentration step)}, \\ \text{or} \\ \partial\Theta^{ss}/\partial\zeta = -1 \quad \text{at} \quad \zeta = 0 \quad \text{(flux step)} \quad . \end{array}\right\} \tag{13}$$

These yield the solutions

$$\Theta^{ss} = \frac{1}{\Gamma(\frac{4}{3})} \int_{\zeta}^{\infty} e^{-x^3} dx \quad \text{(concentration step)}, \tag{14}$$

or

$$\Theta^{ss} = \int_{\zeta}^{\infty} e^{-x^3} dx \quad \text{(flux step)} \quad , \tag{15}$$

where the integral can be found as a tabulated function of ζ.[18] The transient part of concentration satisfies the conditions

$$\left.\begin{array}{lll} \Theta^t = 0 & \text{as} & \zeta \to \infty \\ \Theta^t = \Theta^{ss} & \text{at} & \theta = 0 \end{array}\right\} \quad , \tag{16}$$

$$\Theta^t = 0 \quad \text{at} \quad \zeta = 0,\ \theta > 0 \quad \text{(concentration step)}, \tag{17}$$

$$\partial\Theta^t/\partial\zeta = 0 \quad \text{at} \quad \zeta = 0,\ \theta > 0 \quad \text{(flux step)} \quad . \tag{18}$$

The calculation of transient overpotential decay after a step decrease in the surface concentration or flux may also be of interest.[17] However, it is straightforward to show that

$$\Theta = \Theta^t \quad \text{(decay)} \quad , \tag{19}$$

and therefore a separate formulation is not necessary contrary to the analysis given by Nanis and Klein.[17]

The solution to Θ^t can be derived conveniently in terms of a boundary-value problem since equation 7 is separable, and the conditions 16 to 18 are homogeneous in the ζ-coordinate. Let us express Θ^t in the form

$$\Theta^t = \sum_{n=0}^{\infty} B_n Z_n(\zeta)\, e^{-\lambda_n \theta} \quad , \tag{20}$$

where Z_n is an eigenfunction, and λ_n is the eigenvalue associated with it. Substitution into equation 7 and conditions 16 to 18 yields the Sturm-Liouville system

$$\left.\begin{aligned} & Z_n'' + 3\zeta^2 Z_n' + \lambda_n Z_n = 0 , \\ & Z_n(\infty) = 0 , \\ & Z_n(0) = 0 , \quad Z_n'(0) = 1 \qquad \text{(concentration step)}, \\ \text{or} \quad & Z_n'(0) = 0 , \quad Z_n(0) = 1 \qquad \text{(flux step)} . \end{aligned}\right\} \tag{21}$$

This system has been solved here numerically by a method commonly employed in this laboratory.[19-21] The coefficients B_n are given by

$$B_n = \frac{\int_0^\infty \theta^{ss} e^{\zeta^3} Z_n(\zeta) d\zeta}{\int_0^\infty e^{\zeta^3} Z_n^2(\zeta) d\zeta} , \tag{22}$$

and were evaluated by numerical integration.

Table 1 lists the eigenvalues and the coefficients B_n after they have been extrapolated to zero mesh size. The first three eigenfunctions are plotted in figures 1 and 2 for concentration step and flux step, respectively. The results are compared with the short time series of Krylov and Babak in figures 3 and 4. The two series match quite well over a certain range of θ for each case even though only three terms were used of each series to plot these figures. Agreement with previous numerical calculations[1,14,15] is also quite satisfactory.

Table 1. The first ten eigenvalues and the related coefficients B_n of the eigenfunctions.

	concentration step		flux step	
n	λ_n	B_n	λ_n	B_n
0	7.21644439	1.12818046	2.58078493	0.663516066
1	18.1596045	0.90505798	12.3099728	0.081564022
2	31.1962389	0.7907692	24.4331401	0.034457046
3	45.7926549	0.718387	38.3054830	0.01962199
4	61.6691473	0.666834	53.5740271	0.0128965
5	78.6461928	0.627481	70.0220380	0.0092267
6	96.5966836	0.596032	87.5010784	0.0069829
7	115.424957	0.570071	105.902059	0.0055048
8	135.05591	0.548117	125.140833	0.0044645
9	155.42872	0.52920	145.15016	0.0037089

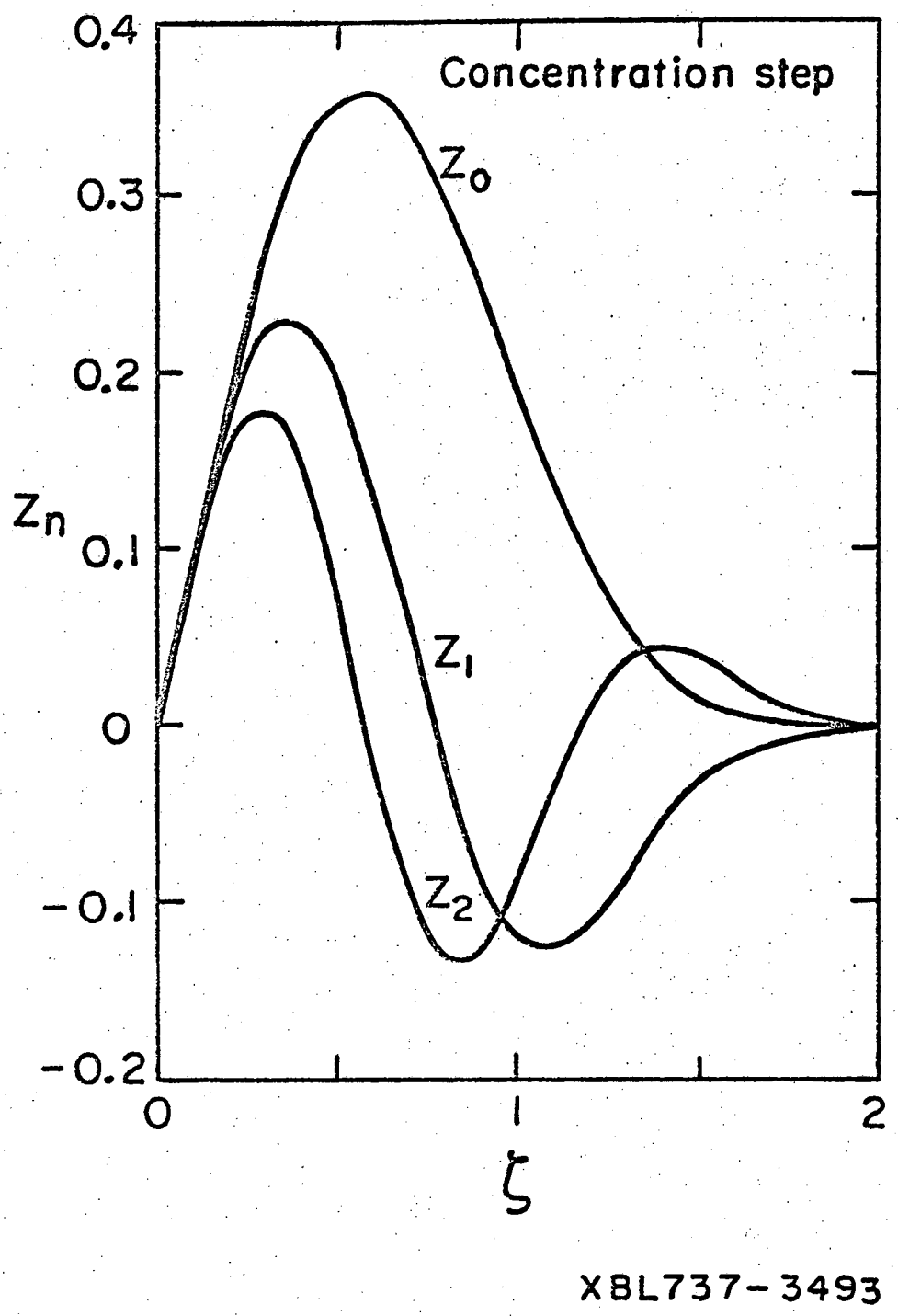

Figure 1. The first three eigenfunctions for the concentration-step case.

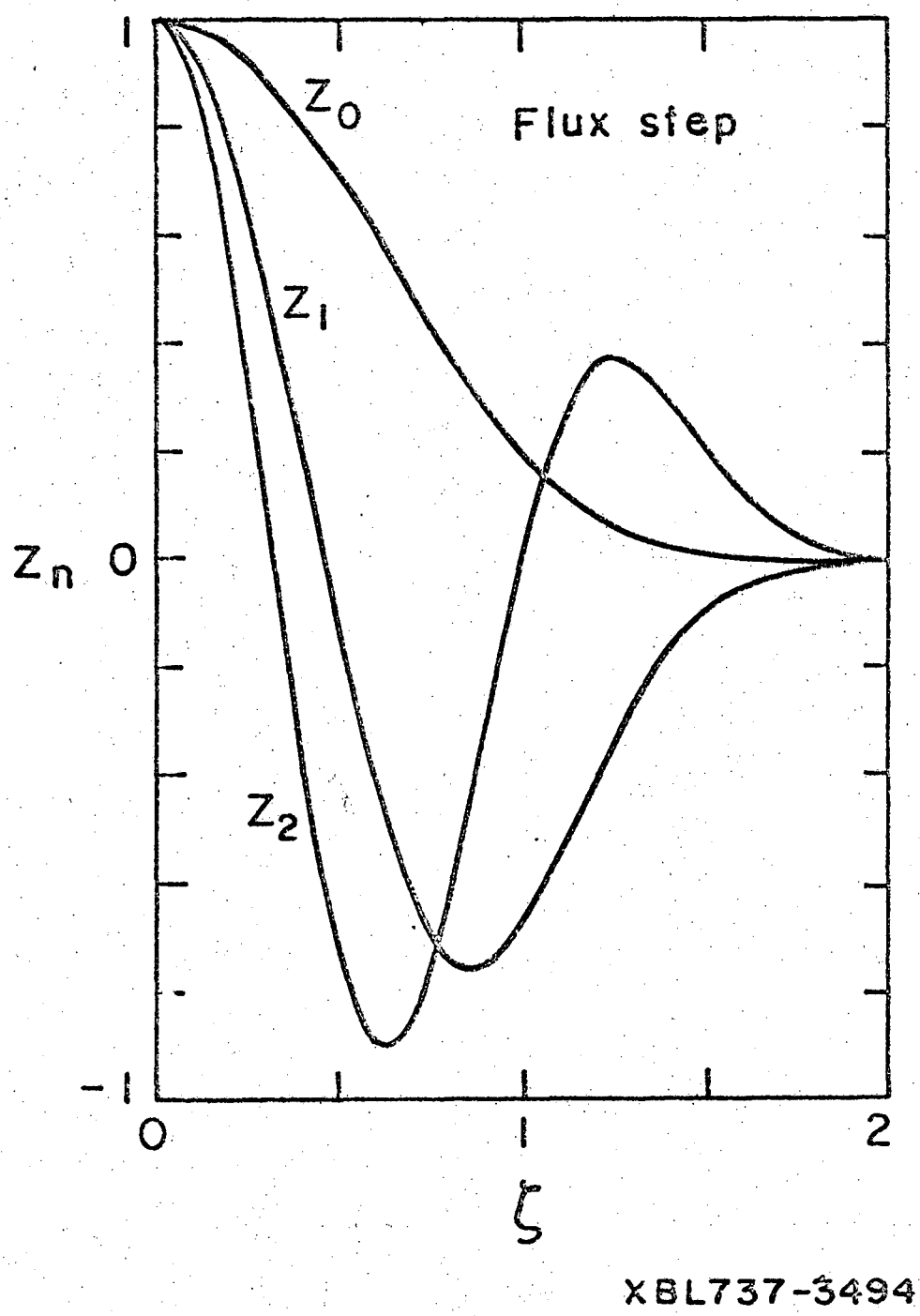

Figure 2. The first three eigenfunctions for the flux-step case.

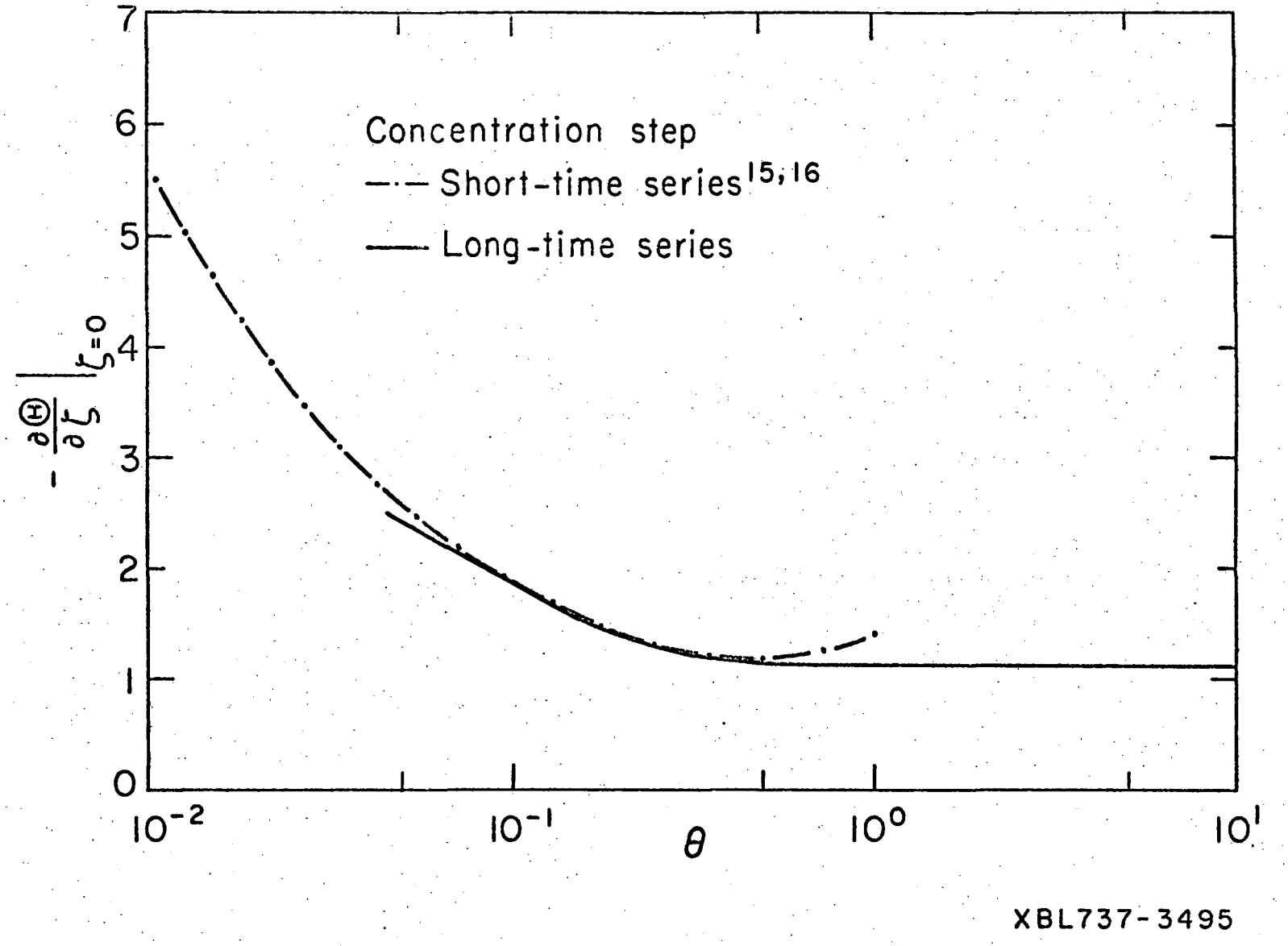

Figure 3. Comparison of the short-time and the long-time series for a concentration step.

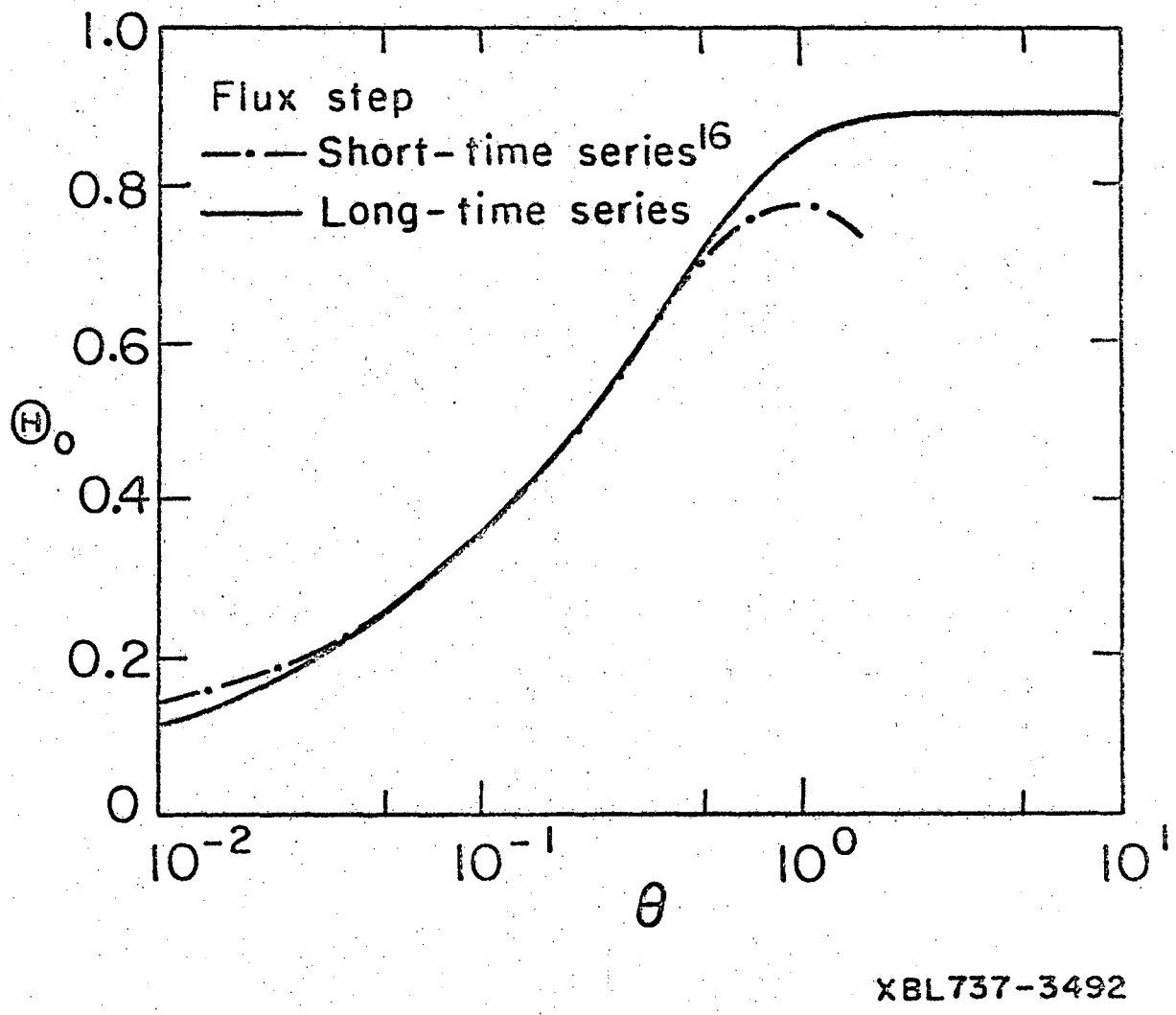

Figure 4. Comparison of the short-time and long-time series for a flux step.

Application of the superposition integral makes possible the treatment of more complex boundary conditions:

$$c-c_\infty = [c_o(0)-c_\infty]\ \Theta_c(\theta,\zeta) + \int_0^\theta \left.\frac{dc_o}{d\theta}\right|_{\theta=\theta'} \Theta_c(\theta-\theta',\ \zeta)d\theta' , \tag{23}$$

or equivalently,

$$c-c_\infty = -\int_0^\theta \left.\frac{\partial c}{\partial \zeta}\right|_{\substack{\zeta=0\\ \theta=\theta'}} \frac{\partial}{\partial\theta'}\ [\Theta_f(\theta-\theta',\ \zeta)]d\theta' , \tag{24}$$

where the subscript o denotes conditions at the electrode surface, and Θ_c and Θ_f represent the concentration-step and the flux-step solutions, respectively. Differentiation of equation 23 yields an explicit expression for the flux at the surface,

$$\left.\frac{\partial c}{\partial \zeta}\right|_{\zeta=0} = [c_o(0)-c_\infty] \left.\frac{\partial \Theta_c}{\partial \zeta}\right|_{\zeta=0} + \int_0^\theta \left.\frac{\partial c_o}{\partial \theta}\right|_{\theta=\theta-\theta'} \left.\frac{\partial \Theta_c}{\partial \zeta}\right|_{\substack{\zeta=0\\ \theta=\theta-\theta'}} d\theta' , \tag{25}$$

which may prove more useful for certain calculations.

Discussion and Conclusions

The results enable the assessment of time constants,

$$\tau = K\, Sc^{1/3}/\Omega \quad , \tag{26}$$

for build-up or decay of a concentration gradient after a step change in the surface concentration or flux. For a concentration step, $K = 0.45142$, and for a flux step, $K = 1.2623$. These results are accurate insofar as the radial dependence of concentration can be ignored, such as in heat-transfer studies[14] and mass transfer in nonelectrolytes. In electrolytic mass transfer, equation 26 is sufficient for making estimates, but correction for nonuniform current distribution is probably necessary for more accurate calculations. A complete analysis of the convective diffusion equation with radial dependence appears to be very complicated and rather demanding in numerical effort. However, an asymptotic calculation for large times may be tractable to determine the necessary time constants.[22]

Double-layer effects may become important in transient electrode processes.[2,3] Delahay and coworkers[23,24] have discussed how to treat the conditions at an electrode surface in the presence of mass transfer, faradaic reaction, and double-layer charging. Equations 23 to 25 can be applied conveniently to treat these effects. In many cases, one can express the flux as a function of the surface concentration, so that a numerical solution of the integral equation 24 or 25 is necessary.[22] The capacitive effect of the double layer has been

investigated in a solution with single reactant and excess supporting electrolyte[22] and was found to be negligible in situations where the transient process is mass transfer controlled.[17] These integral equations can also be used in a straightforward manner to calculate the potential in current-controlled applications, or, *vice versa*, the current in potentiostatic cases.

Acknowledgment

This work was supported by the United States Atomic Energy Commission.

Nomenclature

a	0.51023
B_n	coefficients in series for Θ^t
c	concentration, mole/cm^3
D	diffusion coefficient, cm^2/sec
K	$(1/\lambda_o)(3/a)^{2/3}$, constant defined in equation 26
Sc	ν/D, Schmidt number
t	time, sec
v_y	axial velocity, cm/sec
y	axial distance from disk, cm
Z_n	eigenfunctions in series for Θ^t
λ_n	eigenvalues in series for Θ^t
ν	kinematic viscosity, cm^2/sec
Ω	angular rotation speed, radians/sec
τ	characteristic time constant, sec
θ	dimensionless time
Θ	dimensionless concentration
ζ	dimensionless axial distance from disk

Suffixes:

c	concentration step
f	flux step
o	evaluated at the electrode surface
ss	steady state part
t	transient part
∞	evaluated far away from the disk

References

1. J. M. Hale, "Transients in Convective Systems. I. Theory of Galvanostatic and Galvanostatic with Current Reversal Transients at a Rotating Disk Electrode," Journal of Electroanalytical Chemistry, 6, 187-197 (1963).

2. Kemal Nişancioğlu and John Newman, "The Transient Response of a Disk Electrode," Journal of the Electrochemical Society, to be published.

3. Kemal Nişancioğlu and John Newman, "The Transient Response of a Disk Electrode under Potentiostatic Control," ibid., to be published.

4. T. R. Roseburgh and W. Lash-Miller, "Mathematical Theory of the Changes of Concentration at the Electrode, Brought about by Diffusion and by Chemical Reaction," Journal of Physical Chemistry, 14, 816-884 (1910).

5. Th. v. Kármán, Über laminare und turbulente Reibung, "Zeitschrift für angewandte Mathematik und Mechanik, 1, 233-252 (1921).

6. W. G. Cochran, "The flow due to a rotating disc," Proceedings of the Cambridge Philosophical Society, 30, 365-375 (1934).

7. B. Levich, "The Theory of Concentration Polarization," Acta Physicochimica U.R.S.S., 17 (5-6), 257-307 (1942).

8. Veniamin G. Levich, Physicochemical Hydrodynamics (Englewood Cliffs: Prentice-Hall, Inc., 1962).

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

10. John Newman, "The Diffusion Layer on a Rotating Disk Electrode," ibid., 114, 239 (1967).

11. B. Levich, "Theory of Concentration Polarization. III," Acta Physicochimica U.R.S.S., 19, (2-3), 133-138 (1944).

12. Yu. G. Siver, "Unsteady Electrode Processes in Stirred Media. II. Voltammetry at Constant Current Density," Zhurnal Fizicheskoi Khimii, 34, 577-584 (1960).

13. V. Yu. Filinovskii and V. A. Kiryanov, "Contribution to the Theory of Nonstationary Convective Diffusion near a Rotating Disc Electrode," Doklady Physical Chemistry, 156, 650-652 (1964)(Doklady Akademii Nauk SSSR, 156, 1412-1415 (1964)).

14. Donald R. Olander, "Unsteady-state Heat and Mass Transfer in the Rotating-Disk-Revolving-Fluid System," International Journal of Heat and Mass Transfer, 5, 825-836 (1962).

15. Jan Robert Selman, Measurement and Interpretation of Limiting Currents, Ph.D. Thesis (UCRL-20557), University of California, Berkeley, June 1971.

16. V. S. Krylov and V. N. Babak, "Nonsteady-State Diffusion to the Surface of a Rotating Disc," Soviet Electrochemistry, 7, 626-632 (1971)(Élektrokhimiya, 7, 649-654 (1971)).

17. Leonard Nanis and Irving Klein, "Transient Mass Transfer at the Rotating Disk Electrode," Journal of the Electrochemical Society, 119, 1683-1687 (1972).

18. Milton Abramowitz and Irene A. Stegun, eds. Handbook of Mathematical Functions (Washington: National Bureau of Standards, 1964), p. 320.

19. John Newman, "Numerical Solution of Coupled, Ordinary Differential Equations," Industrial and Engineering Chemistry Fundamentals, 7, 514-517 (1968).

20. John Newman, "The Fundamental Principles of Current Distribution and Mass Transport in Electrochemical Cells," in Electroanalytical Chemistry, A. J. Bard, ed., 6, 187-352 (New York: Marcel-Dekker, 1973).

21. John Newman, Electrochemical Systems (Englewood Cliffs: Prentice-Hall, Inc., 1973).

22. Kemal Nişancioğlu, Current Distribution and Mass Transfer in Rotating Electrode Systems, (LBL-1880) Ph.D. Thesis, University of California, Berkeley, in preparation.

23. Paul Delahay, "Electrode Processes without a Priori Separation of Double-Layer Charging," Journal of Physical Chemistry, 70, 2373-2379 (1966).

24. Karel Holub, Gino Tessari, and Paul Delahay, "Electrode Impedance without a Priori Separation of Double-Layer Charging and Faradaic Process," ibid., 71, 2612-2618 (1967).

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720