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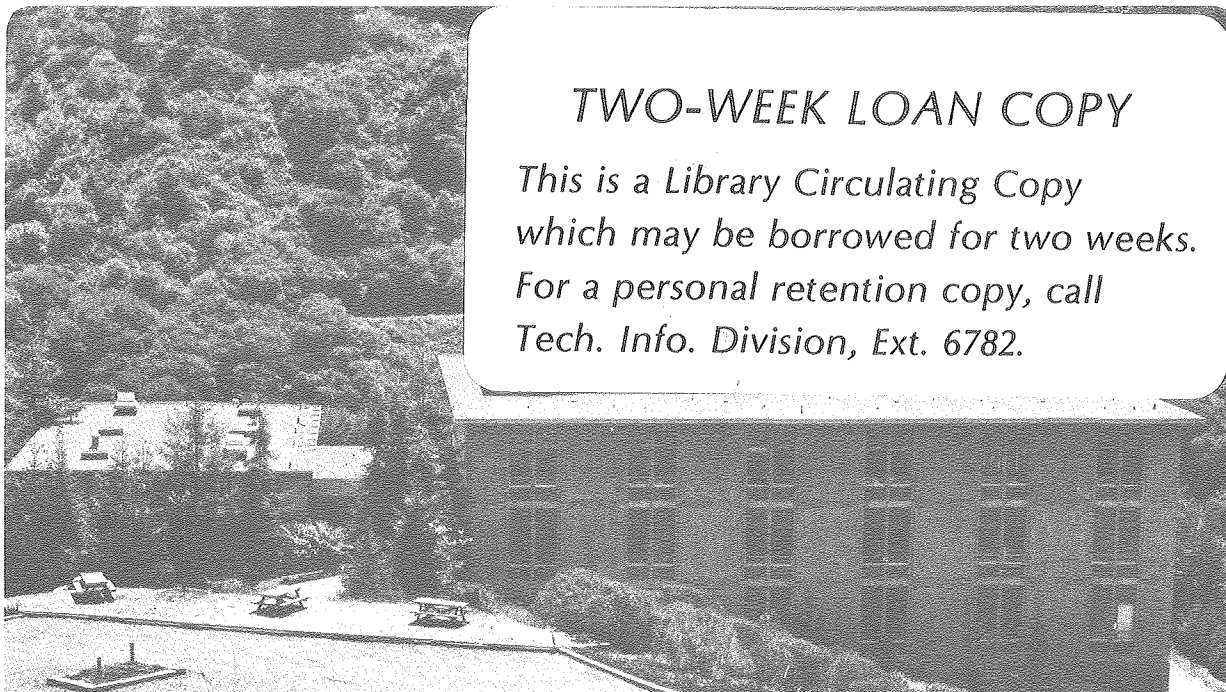## UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

THEORY OF TRANSITION TIMES: CATALYSIS AT ROTATING
DISK ELECTRODES

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DISCLAIMER

"Theory of transition times: Catalysis at rotating disk electrodes"

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Introduction

The Sand equation[1] has been applied to the study of anodic passivation of metals and mass-transfer processes of electrochemically active species in oxidation-reduction reactions at electrode surfaces. It has been observed experimentally[2-5], however, that in some cases a constant must be subtracted from the classical current density-transition time relationship for the lines to intercept the origin. Recently, Littauer and Tsai[4] have reported a model that successfully accounts for this anomalous behavior. Their treatment involves solving Fick's law with initial conditions representing an already developed concentration profile brought about by a heterogeneous process at the surface. Based on this simplified model, and assuming an exponential form for the initial profile, these authors[6] were able to determine rates of catalytic decomposition of hydrogen peroxide using rotating disk electrodes of different materials. This particular forced convection system has been widely utilized in the field of electro-chemistry, because the characteristics of its hydrodynamic flow are well understood.

This communication analyzes in detail the problem of convective diffusion to a rotating disk with specific application given for an electro-active species undergoing a catalytic reaction at the electrode surface. As a result, rate constants for this catalytic step can be determined by chronopotentiometric techniques, without making any assumptions as to the form of the rate law or the relative magnitude of the kinetics. A rigorous mathematical derivation will establish the range of validity of the model proposed by Littauer and Tsai[4], and allows for a precise interpretation of transition times.

Mathematical Formalism

Within the framework of approximations specified elsewhere[7], the equation of convective diffusion to a rotating disk electrode is given by,

$$\frac{\partial^2 c}{\partial \zeta^2} + 3\zeta^2 \frac{\partial c}{\partial \zeta} = \frac{\partial c}{\partial \theta} \tag{1}$$

where c is the concentration of the electrochemically active species. The dimensionless variables ζ and θ, are related to y, the axial distance from the disk, and the time t, by

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

Initial and boundary conditions corresponding to a current step at the surface of the electrode can be expressed as,

$$c(\zeta,0) = c_o(\zeta) \qquad\qquad -\left.\frac{\partial c}{\partial \zeta}\right|_{\zeta=0} = \phi \quad , \quad \theta > 0 \tag{3}$$

$$\lim_{\zeta \to \infty} c(\zeta, \theta) = c_\infty$$

where $c_o(\zeta)$ is any prescribed initial profile, c_∞ the bulk concentration, and

$$\phi = \frac{i}{nFD}\left(\frac{3D}{a\nu}\right)^{1/3} \left(\frac{\nu}{D}\right)^{1/3} \quad , \tag{4}$$

the reduced flux at the surface.

The solution to this problem can be formally written as a sum of two functions which independently satisfy the differential equation

$$c = c_1 + c_2 \tag{5}$$

where c_1 and c_2 are subject to initial and boundary conditions specified in EQ(6) and EQ(7) respectively.

$$c_1(\zeta,0) = c_\infty \qquad\qquad -\frac{\partial c_1}{\partial \zeta}\bigg|_{\zeta=0} = \phi \qquad \theta > 0$$

$$\lim_{\zeta \to \infty} c_1(\zeta,\theta) = c_\infty \tag{6}$$

$$c_2(\zeta,0) = c_0(\zeta) \qquad\qquad -\frac{\partial c_2}{\partial \zeta}\bigg|_{\zeta=0} = 0 \qquad \theta > 0$$

$$\lim_{\zeta \to \infty} c_2(\zeta,\theta) = 0 \tag{7}$$

If the electroactive species is undergoing a catalytic (chemical) reaction at the surface of the electrode, a steady state concentration profile will be established prior to the current step. Consequently, $c_0(\zeta)$ assumes an explicit functional form[8]

$$c_2(\zeta,0) = -c_\infty \frac{(1 - c_0/c_\infty)}{\Gamma(4/3)} \int_\zeta^\infty e^{-x^3} dx \tag{8}$$

where c_0 corresponds to the unknown concentration of the species at the surface at time zero.

Nisancioglu and Newman[9] have reported a solution for $c_1(\zeta, \theta)$, valid for long times, in terms of numerically evaluated coefficients, eigenfunctions and eigenvalues of the resulting Sturm-Liouville system, that is

$$c_1(\zeta, \theta) = c_\infty - \phi \left\{ \int_\zeta^\infty e^{-x^3} dx - \sum_{n=0}^\infty B_n Z_n(\zeta) e^{-\lambda_n \theta} \right\} \tag{9}$$

It is interesting to note that due to the unique form of $c_o(\zeta)$ a solution for $c_2(\zeta, \theta)$ can be obtained from the same eigenfunction expansion, yielding

$$c_2(\zeta, \theta) = \frac{c_\infty (c_o/c_\infty - 1)}{\Gamma(4/3)} \sum_{n=0}^{\infty} B_n Z_n(\zeta) \, e^{-\lambda_n \theta} \tag{10}$$

Based on EQ(9), EQ(10), and EQ(4), the solution for the time dependent concentration at the electrode surface, $c(0, \theta)$, can be shown to be given by

$$\frac{c_\infty - c(0,\theta)}{\phi} = \Gamma(4/3) - \left\{ 1 - \frac{c_\infty - c_o}{\phi \Gamma(4/3)} \right\} \sum_{n=0}^{\infty} B_n e^{-\lambda_n \theta} \tag{11}$$

Given that measurements of transition times will require applying currents in excess of the limiting current it is convenient to express ϕ in those terms. For the particular dimensionless variables chosen the reduced flux at the surface at the limiting current, is

$$\left. \frac{\partial c}{\partial \zeta} \right|_{\zeta=0} = \frac{c_\infty}{\Gamma(4/3)} \tag{12}$$

Therefore, it is natural to define $\phi = \mu c_\infty / \Gamma(4/3)$, where $\mu > 1$ and EQ(11) can then be rearranged to yield,

$$\Lambda_0 = \mu \left\{ 1 - 1/\Gamma(4/3) \left\{ 1 - \frac{\Lambda_0^o}{\mu} \right\} \sum_{n=0}^{\infty} B_n e^{-\lambda_n \theta_o} \right\} \tag{13}$$

where

$$\Lambda_0 = \frac{c_\infty - c(0,\theta)}{c_\infty} \quad , \quad \Lambda_0^o = \frac{c_\infty - c_o}{c_\infty} \quad \text{and} \quad \theta_o = \frac{\theta}{(\Gamma\{4/3\})^2} \tag{14}$$

Although EQ(13) represents the solution for any arbitrary time θ_o, it would be necessary to include an increasing number of eigenfunctions and eigenvalues in order to generate acceptable values for short times, i.e. $\theta_0 < .1$. However, a rapidly convergent series valid for short times can be obtained by using Siver's approximation[10]. As it has been shown by Hale[11], this approximation yields excellent results in this regime and is only up to 4% different from the exact numerical solution in the whole domain.

Introducing Siver's variable,

$$\psi = \int_0^\zeta e^{-x^3} dx \qquad (15)$$

into EQ(1), and assuming a value of unity for the slowly varying function, $e^{-2\zeta^3}$, the governing differential equation is transformed into the heat equation

$$\frac{\partial c}{\partial \theta} = \frac{\partial^2 c}{\partial \psi^2} \qquad (16)$$

Defining initial and boundary conditions corresponding to those specified in EQ(5) and EQ(6), and making use of Rosebrugh and Lash-Miller[12] solution in terms of Fourier series, an expression analogous to EQ(13) is obtained.

$$\Lambda_o = \mu \left\{ 1 - \left(1 - \frac{\Lambda_o^O}{\mu}\right) \sum_{n=1}^\infty \frac{8}{\pi^2 (2n-1)^2} \exp\left(-\frac{1}{4}(2n-1)^2 \pi^2 \theta_o\right) \right\} \qquad (17)$$

The predicted values of Λ_o arising from the two different approximations i.e., EQ(13) and EQ(17), are compared with Hale's numerical solution in Table I, for the specific case $\mu = 1$ and $\Lambda_o^O = 0$.

Based on this analysis, a dimensionless transition time, τ_o, corresponding to $\Lambda_o = 1$ can be defined, and a generalized expression relating the current density to the transition time is obtained.

$$\mu = \frac{1 - \Lambda_o^o \sum_{n=0,1}^{\infty} \chi_{1,2}(\tau_o)}{1 - \sum_{n=0,1}^{\infty} \chi_{1,2}(\tau_o)} \tag{18}$$

where

$$\chi_1(\tau_o) = \frac{B_n}{\Gamma(4/3)} e^{-\lambda_n \tau_o} \quad \text{and,} \quad \chi_2(\tau_o) = \frac{8}{\pi^2 (2n-1)^2} \exp\left(-\frac{1}{4}(2n-1)^2 \pi^2 \tau_o\right) \tag{19}$$

Discussion

The exact treatment presented here enables a proper interpretation of diagrams in a regime where transition times are more accessible to measurement. As a means of illustration, selected values of Λ_o^o have been chosen to generate $\tau_o^{-\frac{1}{2}}$ vs μ curves through the combined use of $\chi_1(\tau_o)$ and $\chi_2(\tau_o)$ in EQ(18) (see Figure 1). A more detailed graph of the region in which departures from the linear behavior are observed is given in Figure 2. The curves for $\Lambda_o^o = 1$ correspond to the simpler case of chronopotentiometry in the absence of catalysis[9].

By plotting experimental results in the format of Figures 1 and 2 a unique value of Λ_0^0 is prescribed and, thus, the catalytic rate. The functional relationship between catalytic rate and surface concentration can be easily established either by changing the rotation speed of the disk, or by varying the bulk concentration. Standard analysis of this relationship determines the rate law and

relevant kinetic parameters.

This model is valid for any transition time or current step above the limiting current giving rise to considerable experimental flexibility and minimizing the difficulties associated with high currents (small transition times).

In the limit of very small times, i.e. $\theta_o \ll .1$

$$\frac{1}{\pi^2} \sum_{n=1}^{\infty} \frac{8}{(2n-1)^2} \exp\{ -\frac{1}{4}(2n-1)^2 \pi^2 \theta_o \} \sim 1 - 2\sqrt{\frac{\theta_o}{\pi}} \tag{20}$$

and EQ(17) reduces to

$$\Lambda_o = \mu \{ 1 - (1 - \frac{\Lambda_o^o}{\mu}) (1 - 2\sqrt{\frac{\theta_o}{\pi}})\} \tag{21}$$

In particular, for $\Lambda_o^o = 1$

$$i = \frac{nF\sqrt{\pi D}}{2} c_o \tau_o^{-\frac{1}{2}} + \frac{(c_\infty - c_o) nFD}{\delta} \tag{22}$$

where δ, the thickness of the diffusion layer, is equal to

$$\delta = \Gamma(\frac{4}{3})\left(\frac{\nu}{\Omega}\right)^{\frac{1}{2}}\left(\frac{3D}{a\nu}\right)^{1/3} \tag{23}$$

Consequently, EQ(22) can be rearranged to yield the same expression reported by Littauer and Tsai[4], namely

$$i - i_\tau = k^* \tau_o^{-\frac{1}{2}} \tag{24}$$

where in this case, the critical current density, i_τ, and k^* are given by

$$i_\tau = \frac{c_\infty - c_0}{\delta} nFD \qquad \text{and,} \qquad k^* = \frac{nF\sqrt{\pi D}}{2} c_0 \qquad (25)$$

Therefore, the introduction of adjustable parameters in order to derive EQ(24), as proposed by these authors is unnecessary.

If the initial concentration is constant throughout the solution, i.e. no catalysis, the second term in EQ(22) vanishes, yielding as expected the Sand equation[1]. Finally, it is important to note that EQ(22) could have also been obtained by solving Fick's law in a semi-infinite medium and expanding $c_2(\zeta, 0)$ as defined in EQ(9), in terms of a Taylor series around $\zeta = 0$.

Summary

An exact solution to the problem of convective diffusion to a rotating disk electrode with a prescribed initial profile and current step conditions at the surface is presented. Based on this solution a current density-transition time relationship is established which in the limit reduces to a previously proposed expression that accounts for experimentally observed deviations from the Sand equation. Applications of this theory in connection with the determination of rate parameters for electroactive species undergoing a catalytic reaction at the electrode surface are discussed.

Acknowledgement

TABLE I

Values of the Dimensionless Surface Concentration Λ_o as a Function of the Dimensionless Time θ_0 . ($\Lambda_o^0 = 0$, $\mu = 1$).

θ_0	Λ_o^* EQ.(11)	Λ_0^* EQ.(13)	Exact Solution
.1	0.355	0.357	0.352
.2	0.494	0.504	0.492
.3	0.594	0.613	0.593
.4	0.672	0.697	0.671
.5	0.734	0.764	0.733
.6	0.783	0.815	0.783
.7	0.824	0.855	0.824
.8	0.856	0.887	0.857
.9	0.883	0.912	0.884
1.0	0.905	0.931	0.905

*These values have been calculated using only the first three terms of the sums.

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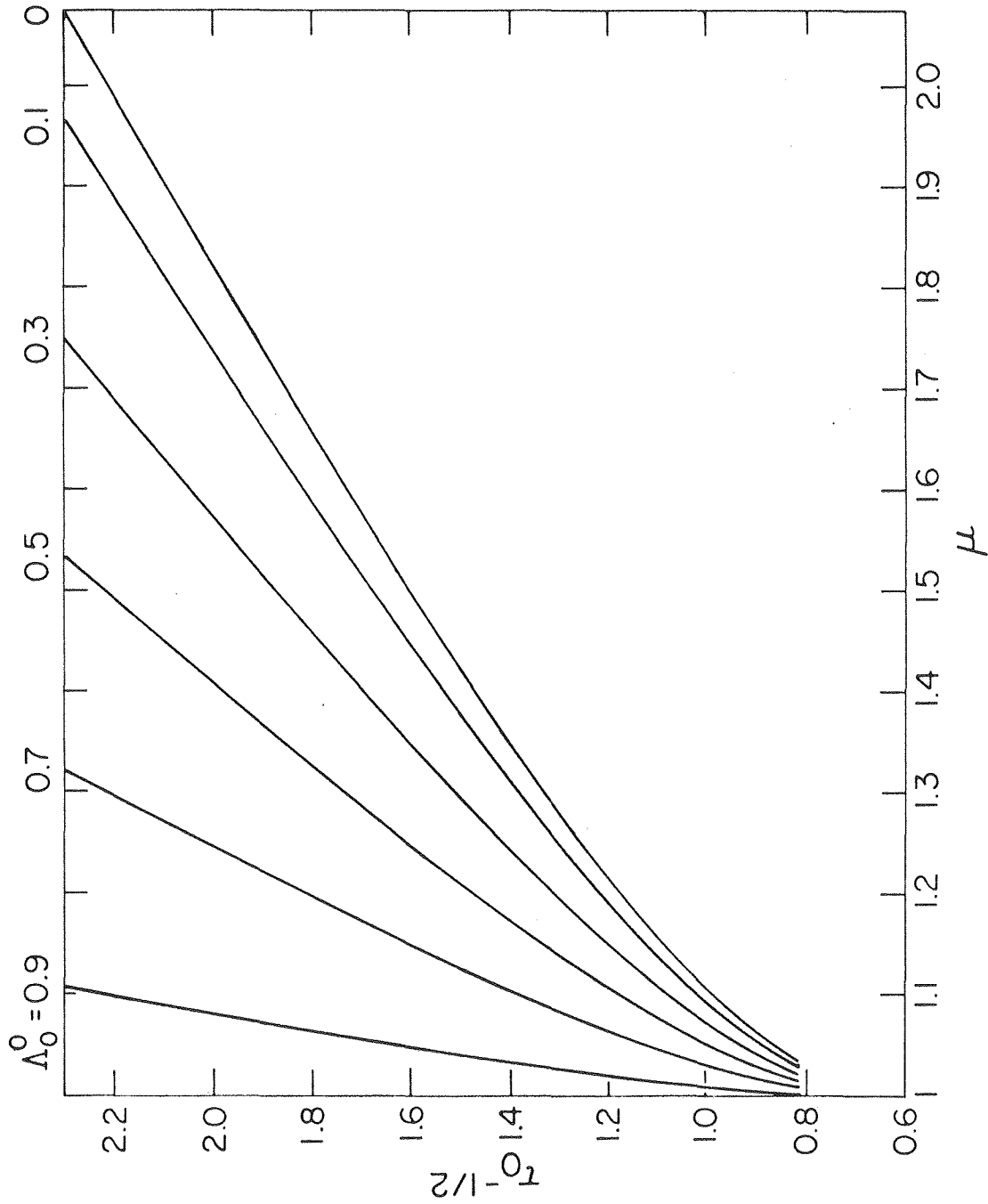12. T. R. Rosebrugh and W. Lash-Miller, J. Phys. Chem., 14, 816 (1910).

Nomenclature

a 0.51023

B_n Coefficients of Sturm-Liouville system

c Concentration/mol cm^{-3}

D Diffusion coefficient/$cm^2 s^{-1}$

F Faraday's constant/cb mol^{-1}

i Current density/amp $cm^{-2} s^{-1}$

k^* $\dfrac{nF\sqrt{\pi D}}{2}\, c_o$, constant defined in EQ.(19)

n Number of electrons transferred

t Time/s

y Axial distance from disk/cm

Z_n Eigenfunction of Sturm-Liouville system

Λ Dimensionless concentration

λ_n Eigenvalues of Sturm-Liouville system

ν Kinematic viscosity/$cm^2 s^{-1}$

Ω Angular rotation speed/radian s^{-1}

τ Transition time/s

θ Dimensionless time, see EQ.(2)

ψ Siver's variable, see EQ.(12)

χ Terms in sum, see EQ.(14)

μ i/i_{lim}

δ Diffusion layer thickness/cm, see EQ.(18)

ζ Dimensionless distance normal to the disk, see EQ.(2)

ϕ Reduced flux at the surface/mol cm^{-3}
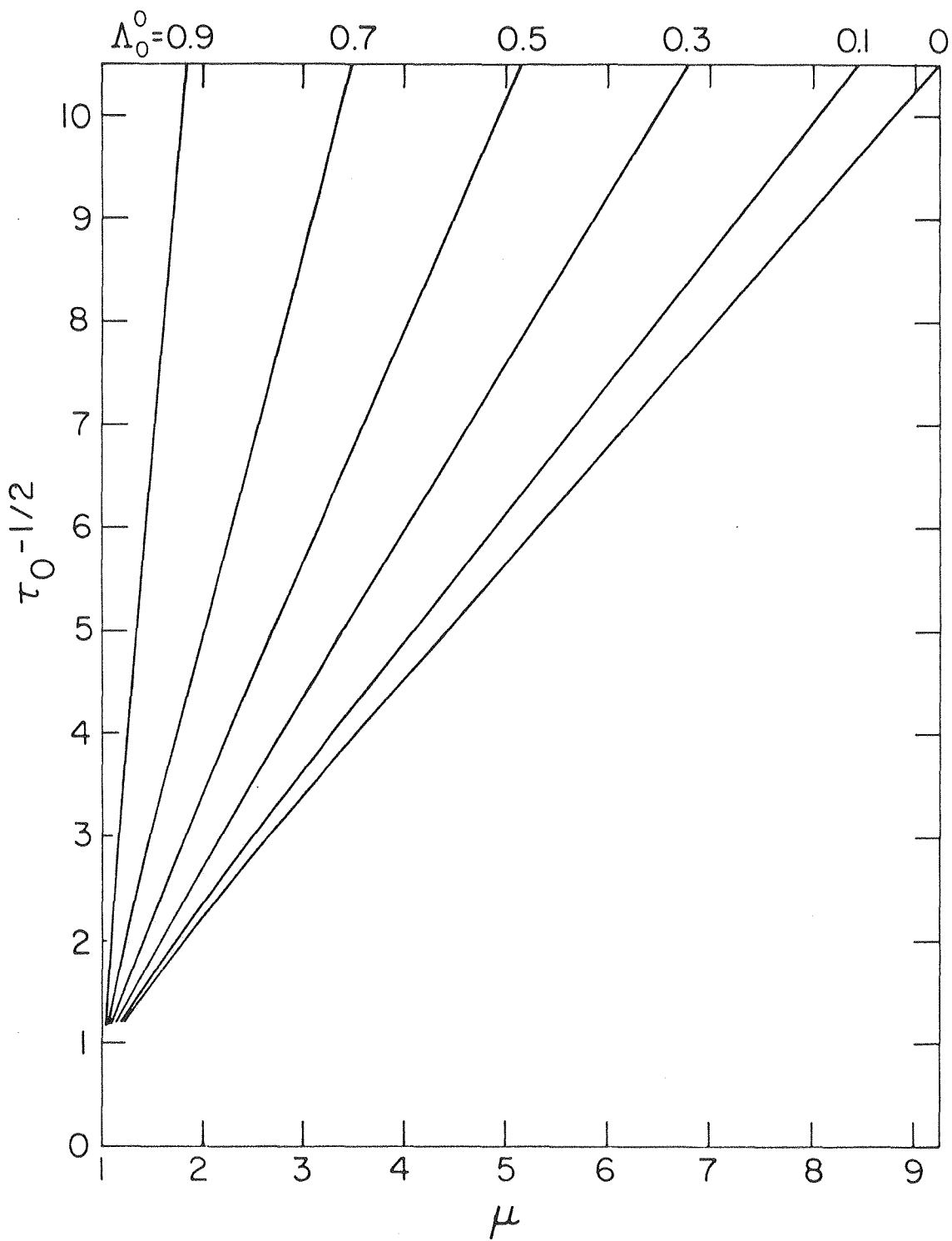
FIGURE CAPTIONS:

Figure 1:   Square root of inverse transition time vs. number of
            limiting currents plotted for selected values of Λ_o^o as
            calculated through the combined use of $\chi_1(\tau_o)$ and $\chi_2(\tau_o)$
            in EQ.(18).

Figure 2:   Expanded form of Figure 1 in the region closer to the
            limiting current as evaluated from $\chi_1(\tau_o)$ in EQ.(18).

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