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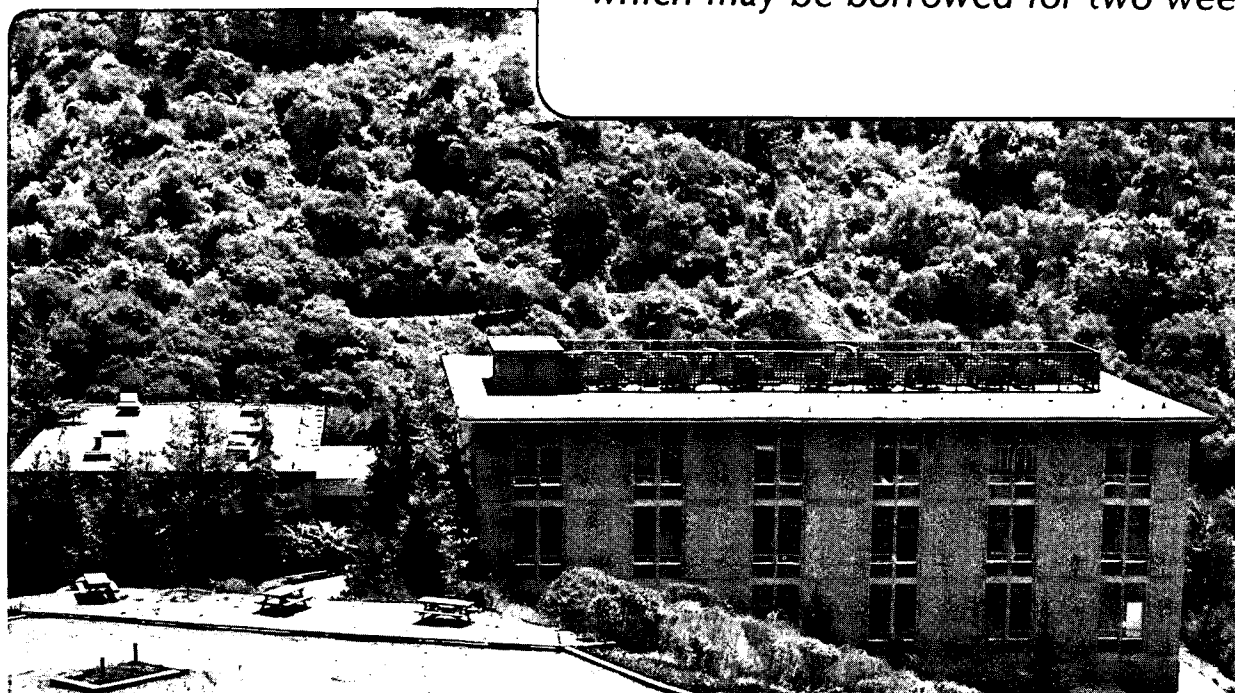
Data Reduction and Analysis of the Dissolution of Copper in Chloride Solutions

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October 1988

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**Data Reduction and Analysis of
the Dissolution of Copper in Chloride Solutions**

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Data Reduction and Analysis of the Dissolution of Copper in Chloride Solutions

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Abstract

A mathematical model is presented that calculates the frequency response of a copper rotating disk in chloride solutions accounting for multicomponent diffusion, migration, and convection. The working algorithm uses concentrated-solution theory, incorporating the Stefan-Maxwell transport equations, and accounts for any number of homogeneous and heterogeneous reactions. The electrochemical impedance is analyzed by examining each contribution of the total cell potential and total current. This gives rise to impedance terms typically neglected in other ac-impedance treatments. Additionally, the faradaic impedance of the copper dissolution system is investigated using a perturbation analysis to split the diffusion layer into inner and outer regions so that the salient features of the problem can be examined separately. Specifically, the effect of finite rates of the homogeneous complexing reaction that follows the electrochemical dissolution reaction is explored. Finally, the perturbation analysis provides a basis for enabling the chemical reaction rate constant to be determined from frequency-response data.

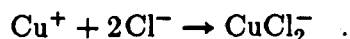
Introduction

Ac impedance is recognized as a most useful method for studying the electrochemical nature of many systems. An advantage of this spectroscopic technique is that the impedance, as a function of frequency, often displays the constituting characteristics of the system separately. Therefore, the electrode frequency response is helpful for elucidating the rate-determining processes of an electrochemical system. However, due to intricate coupling of charge-transfer reactions at the surface and mass transfer in the presence of a nonuniform electric field in the solution, the quantitative interpretation of experimental data is not always easy. Equivalent circuits labeled as "theoretical models" still are frequently used, even though Grahame (1) pointed out the shortcomings of that approach over thirty years ago: "The objection to this procedure is that one has no way of knowing whether or not a given equivalent circuit is, in fact, equivalent to the interface under consideration except by carrying out an independent analysis of the problem which is the objective of those who use this method to avoid." Consequently, the inability to understand frequency-response data quantitatively is probably the biggest problem with using the ac-impedance technique. Controversy in the interpretation of impedance measurements is common and will continue until better methods for data reduction and analysis are available.

The specific objectives of this paper are as follows. First, a generalized theoretical framework (2) for the calculation of the total impedance is to be presented as a function of thermodynamic and kinetic parameters, as well as multicomponent mass-transport properties. Second, a perturbation analysis (3) will be used as a diagnostic technique to determine the desired homogeneous-reaction rate constant and also will aid in estimating the order of magnitude of numerical errors in the Stefan-Maxwell program that can arise for certain values of the input parameters. Additionally, other data reduction schemes (4) based on analytic solutions for the faradaic impedance will be briefly reviewed. The simplifying expressions are derived from dilute-solution theory with no migrational effects and are helpful for verifying ones intuition and for testing the more general, complex Stefan-Maxwell model, which requires a numerical solution.

Copper Dissolution

The largely mass-transfer controlled anodic dissolution of copper in chloride solutions (5) is investigated, where the following mechanism is applicable:



Here, the product of the nearly reversible electrode reaction, the cuprous ion, reacts homogeneously with the added ion of the supporting electrolyte to produce the copper complexed species CuCl_2^- .

A steady-state perturbation analysis (6) has been carried out to characterize the effects of finite rates of the homogeneous reaction that follows the electrode reaction. In that problem, the diffusion-boundary layer was split into two regions: an inner region where convection to the disk is neglected and an outer region where the homogeneous reaction is assumed to be equilibrated. A similar approach is used here to solve the frequency-dependent problem for a wide range of rate constants of the homogeneous reaction.

Model Description

A macroscopic[†] impedance model (2) has been developed that calculates the frequency response of a rotating disk accounting for multicomponent diffusion, migration, and homogeneous and heterogeneous reactions. The working algorithm uses concentrated-solution theory, incorporating the Stefan-Maxwell transport equations, and accounts for a finite Schmidt number and interfacial velocity. The governing equations within the disk boundary layer along with the electrode boundary conditions are solved using a finite-difference procedure, first for the

[†] Macroscopic refers to the rotating-disk boundary layer, as opposed to a microscopic double-layer model (7).

steady-state problem, and then as a function of frequency.

The electrochemical impedance of the disk electrode, defined as the total alternating potential over the total alternating current

$$Z_{tot} = \frac{\tilde{V}_{tot}}{\tilde{i}} = \frac{\tilde{V} + (\tilde{\Phi}_0 - \hat{\Phi}_0)}{\sum_l \tilde{i}_{f,l} + j\omega\tilde{q}} + R_\Omega ,$$

is analyzed theoretically. The potential V_{tot} of the metal electrode relative to a reference electrode placed in the bulk consists of three components: V is the kinetic driving force across the interface, $\Phi_0 - \hat{\Phi}_0$ is the potential difference across the diffusion layer (and includes the diffusion potential and the ohmic drop due to variations in the conductivity), and the last term in the equation above, the primary solution resistance R_Ω , gives rise to the ohmic potential drop. It should be noted that Φ_0 is the potential just outside the diffuse part of the double layer, and $\hat{\Phi}_0$ is the potential of the solution adjacent to the working electrode which would be determined by a reference electrode of a given kind if there were no concentration gradients across the boundary layer. The total alternating current is the sum of the alternating current $\tilde{i}_f$ due to faradaic reactions and the double-layer charging current, $\tilde{i}_c = j\omega\tilde{q}$.

The Stefan-Maxwell model is capable of predicting each of these terms and the resulting total impedance simulations should be compared to the following "equivalent-circuit-model" approach:

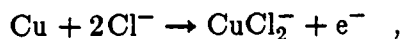
$$Z'_{tot} = \left[\frac{1}{Z_F} + j\omega C_{dl} \right]^{-1} + R_s ,$$

where the double-layer capacitance C_{dl} is assumed to be independent of concentration and potential.[†] R_s is the solution resistance, and the faradaic impedance Z_F , defined as $\tilde{V}$ over $\tilde{i}_f$, is taken to be in parallel with the double-layer capacity. Such an equivalent circuit can be used if the solution potential is negligible and if $\tilde{i}_f$ and $\tilde{i}_c$ can be *a priori* separated. Finally, examining the impedance due to each contribution of the cell potential and total current gives rise to impedance terms typically neglected in other ac-impedance treatments. This approach makes it possible to see where certain assumptions have been made in the electrochemical impedance literature, although they are not always clearly stated.

[†] Details of how to relax the constant double-layer-capacitance assumption are described elsewhere (8).

Results

The electrochemical impedance of a copper rotating disk ($\Omega = 2000$ rpm) in 0.1 N HCl at 298.15 K is calculated by the Stefan-Maxwell macroscopic model based on the following overall dissolution reaction



where an infinitely fast homogeneous reaction has been assumed. The resulting electrode frequency response (at $\bar{V} = -0.205$ V) is plotted in the complex plane in figure 1. Because the overall electrochemical reaction is fast, the charge-transfer resistance is negligible on the scale of the figure, and therefore an additional inner heterogeneous-reaction loop is not observed next to the low-frequency convective-Warburg impedance. Instead, the impedance of the double-layer capacity, with $C_d = 10 \mu\text{F}/\text{cm}^2$, simply shifts the frequency dependence of the dominate mass-transfer impedance. Also shown in the figure are the faradaic (or convective-Warburg impedance) and solution impedances. Although the solution impedance is negligible for the conditions reported here, the inductive loopdy-loop that appears near the origin is interesting and therefore is illustrated in the expanded view in figure 1. This feature in the solution impedance arises from the maximum that occurs in the steady-state potential profile (9), which results from the diffusion potential balancing the potential as given by Ohm's law. This behavior, where the electric field in the solution is reversed, has been shown (10) to occur for a number of different electrochemical systems.

In order to examine the effect of finite rates of the homogeneous complexing reaction, a perturbation analysis is applied, so that the faradaic impedance as a function of frequency is determined. A schematic of the diffusion layer adjacent to the electrode is shown in figure 2. This diagram illustrates the two regions of importance — the inner homogeneous reaction zone, where finite rates of the complexing reaction must be accounted for and the outer region where convection is important and the reaction can be assumed to be equilibrated. The perturbation parameter Δ is a dimensionless homogeneous reaction zone thickness and is used to characterize the effect of finite rates of the complexing reaction ($\Delta \rightarrow 0$ as $\hat{k}_b \rightarrow \infty$ and $\Delta \rightarrow \infty$ as $\hat{k}_b \rightarrow 0$).

Dimensional impedance results from the perturbation analysis for two values of the homogeneous rate constant $\hat{k}_b = 10^2 \text{ s}^{-1}$ and 10^4 s^{-1} are presented on the complex plane plot in figure 3. Two distinct loops with impedance maxima at different characteristic frequencies result because convective-diffusion is important at low frequencies, whereas effects of finite rates of the homogeneous reaction appear at high frequencies. The low-frequency limit of each curve corresponds to the polarization resistance R_p . On the scale of this graph, the magnitude of the convective-diffusion (moderate-frequency) loop is independent of Δ (or $\hat{k}_b$), while the high-frequency loop decreases in magnitude as the rate constant $\hat{k}_b$ of the homogeneous reaction increases. The homogeneous reaction time constant τ and the resistance R' characterize the magnitude of the inner loop. The characteristic dimensionless frequency, K'_{max} , at the impedance maximum of the inner loop is proportional to $\hat{k}_b$ or Δ^{-2} ; whereas, the maximum in the convective-diffusion loop

occurs at $K_{\max} = 3$. The magnitude and the characteristic frequency $K_{\max}$ of the convective-diffusion (outer) loop remain constant because the mass-transfer resistance, $R_0 = R_p - R'$, and the convective-diffusion time constant, $\tau_{MT} \propto Sc^{1/3}/\Omega$, are independent of the homogeneous rate constant. The Schmidt number, $Sc = \nu/D$, is based on the effective diffusion coefficient D .

The dimensionless faradaic impedance as calculated by the perturbation analysis for different values of $\hat{k}_b = 10^x$, where x ranges from 0 to 10, is given in figure 4. The complex plane plot is somewhat busy, but it clearly summarizes the point that significant differences in the frequency response occur for different values of $\hat{k}_b$. As $\hat{k}_b$ increases, the homogeneous reaction resistance decreases, and the relative sizes of the two loops are shifted: the high-frequency, complexing-reaction impedance decreases, and the low-frequency convective-diffusion loop increases (because of the different scale for the dimensionless complex-plane plot). Finally, these results imply that the faradaic impedance of a rotating disk is a useful means for determining the homogeneous rate constant $\hat{k}_b$. Both the frequency $K_{\max} = 2\Delta^{-2}$ and the magnitude of the impedance R' can be used for this purpose.

We examine next results of the theoretical treatments of the EC reaction mechanism by employing the "zone diagram" given in figure 5, a log-log plot of the reciprocal of the dimensionless perturbation parameter squared, Δ^{-2} , versus the dimensionless frequency K . The reaction diagram defines the regions of applicability of the different-limiting-case zones for both high and low values of K and Δ^{-2} . The perturbation analysis is valid for $\Delta \rightarrow 0$ or large $\hat{k}_b$; therefore, the region where it is valid covers the top half of the figure. At low to moderate frequencies ($K < K_{\min}$) and $\log \Delta^{-2} \gg 2$ ($\hat{k}_b \gg 10^0$), there is a clear separation of the outer and the thin inner (homogeneous reaction zone) regions. For this limiting case, the homogeneous reaction behaves like a boundary condition to the outer region, where convection is important and the homogeneous reaction is equilibrated. At high frequencies ($K \gg K_{\max}$), the boundary-layer thickness is governed by a Warburg diffusion line, and the impedance is dictated by diffusion and the rate of the homogeneous reaction. Additionally, the high-frequency analysis becomes valid for all $\hat{k}_b$ (right side of the diagram) because convection becomes completely unimportant. The overlapping region of the high and moderate-frequency solutions for $\Delta \rightarrow 0$ is enclosed by the $K_{\min} = 1.5\Delta^{-2}$ line and a line parallel and to the right of the $K_{\max}$ line.

As $\hat{k}_b$ decreases (or $\Delta > 0.1$), the perturbation analysis breaks down. Although the emphasis of this paper has been on small Δ , impedance results that are generally applicable over a wider range of the perturbation parameter have also been presented (3). A stagnant Nernst-layer approximation is applied such that the resulting impedance equation is valid for any $\hat{k}_b$. The impedance calculated using this expression is reliable in the region on the right side of figure 5 and is approximately valid over the entire frequency range, although not in a rigorous manner.

Conclusions

The general Stefan-Maxwell program (2) is a very powerful algorithm for studying the frequency response of a rotating disk, and the macroscopic model enabled the electrochemical impedance to be predicted yielding the components of the total impedance that are typically neglected in other theoretical treatments. However, when utilizing computer implemented techniques, one must be cautious of numerical inaccuracies that can arise for certain values of the system parameters. In this paper investigating the dissolution of copper, we have shown that a perturbation analysis can be used to elucidate numerical errors that did occur for the case of large, but finite, rate constants of the homogeneous complexing reaction. Additionally, introduction of the dimensionless impedance proved to be very helpful for generalization and elimination of strong and otherwise overriding steady-state factors (like $\bar{V}$ or $\bar{i}_n$).

The perturbation analysis has been most useful for characterizing the effect of finite rates of the homogeneous reaction on the faradaic impedance spectrum. The theoretical results have helped verify that an additional impedance loop is possible due to the homogeneous complexing reaction. Limiting behavior for asymptotic values of the homogeneous rate constant were presented and provided a window for studying the finite rate cases. The analysis also indicates that the characteristic frequency, $K'_{\max}$, at the maximum in the imaginary part of the high-frequency homogeneous-reaction impedance loop is equal to $2\Delta^{-2}$. Thus, the measured frequency response of an *EC* reaction mechanism taking place at a rotating disk enables the homogeneous reaction rate constant $\hat{k}_s$ to be determined, independent of the steady-state method previously discussed (6). The magnitude of the impedance R' or $K_{\min}$ at the break between the loops can be used in a similar manner. These separate techniques for parameter determination provide an internal check of the proposed reaction mechanism.

Finally, other analytic expressions have been developed (4) that are useful for analyzing experimental impedance results. These simplifying expressions yield new ways of plotting the frequency-response data for determining important kinetic and transport parameters of an electrochemical system. For example, a plot of the real and imaginary parts of the faradaic impedance *versus* the angular frequency $\omega^{-1/2}$ provides a method for determining the kinetic and thermodynamic parameters. Additionally, a new way of plotting the dimensionless convective-diffusion impedance reduces the Schmidt number dependence of the frequency response nearly to one curve by stretching the abscissa using $(\omega/\Omega)Sc^{1/3}$. It is hoped that by applying these simple and straightforward procedures for analyzing frequency-response data the impedance method will become an even more powerful diagnostic tool in the study of electrochemical systems.

Acknowledgments

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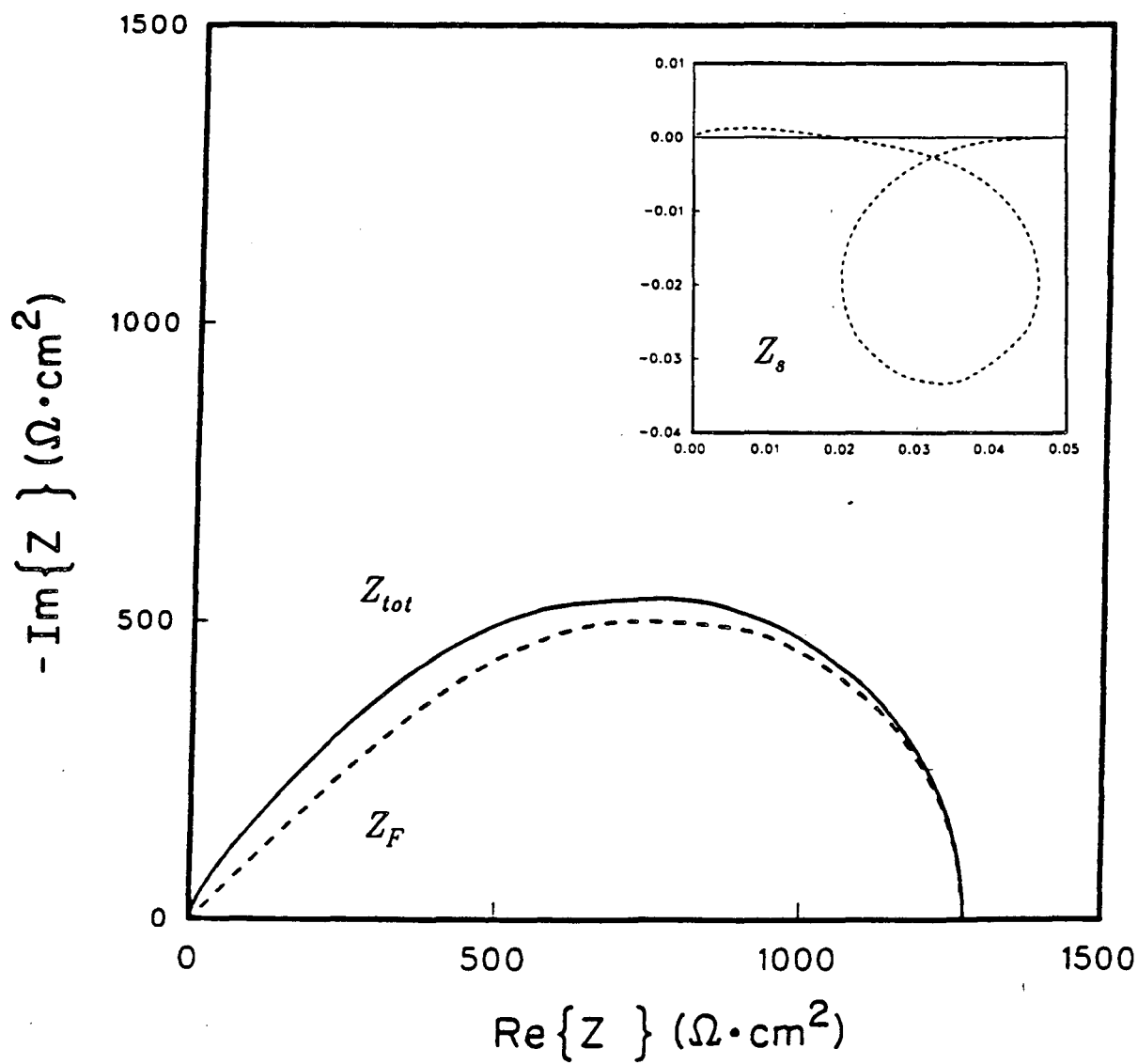


Figure 1. Complex-plane plot of the total, faradaic, and solution impedances for the overall one step copper dissolution mechanism.

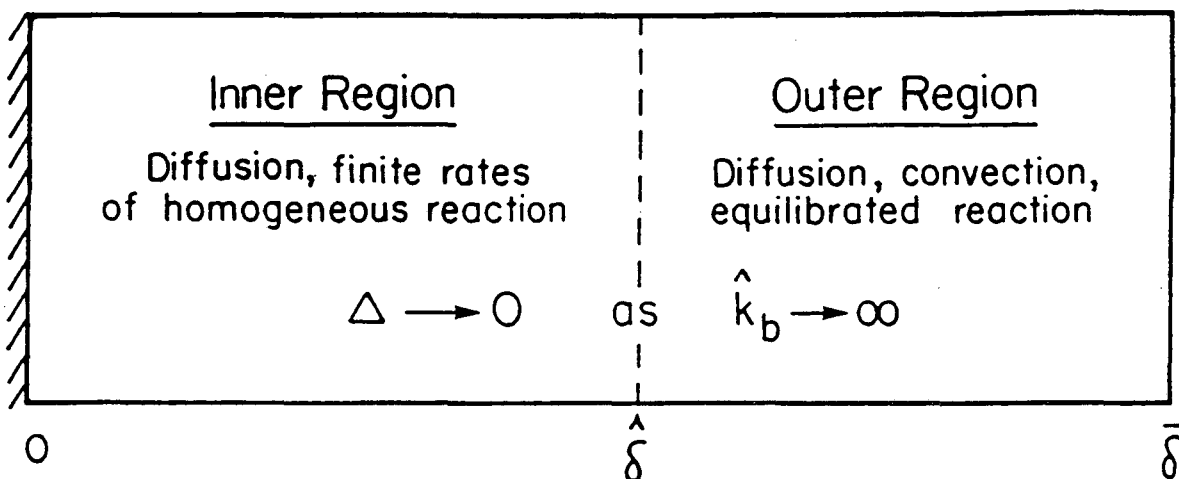


Figure 2. Schematic illustrating the physical basis for the perturbation analysis. The diffusion layer is separated into two regions so that the effects of finite rates of the homogeneous complexing reaction on copper dissolution can be studied.

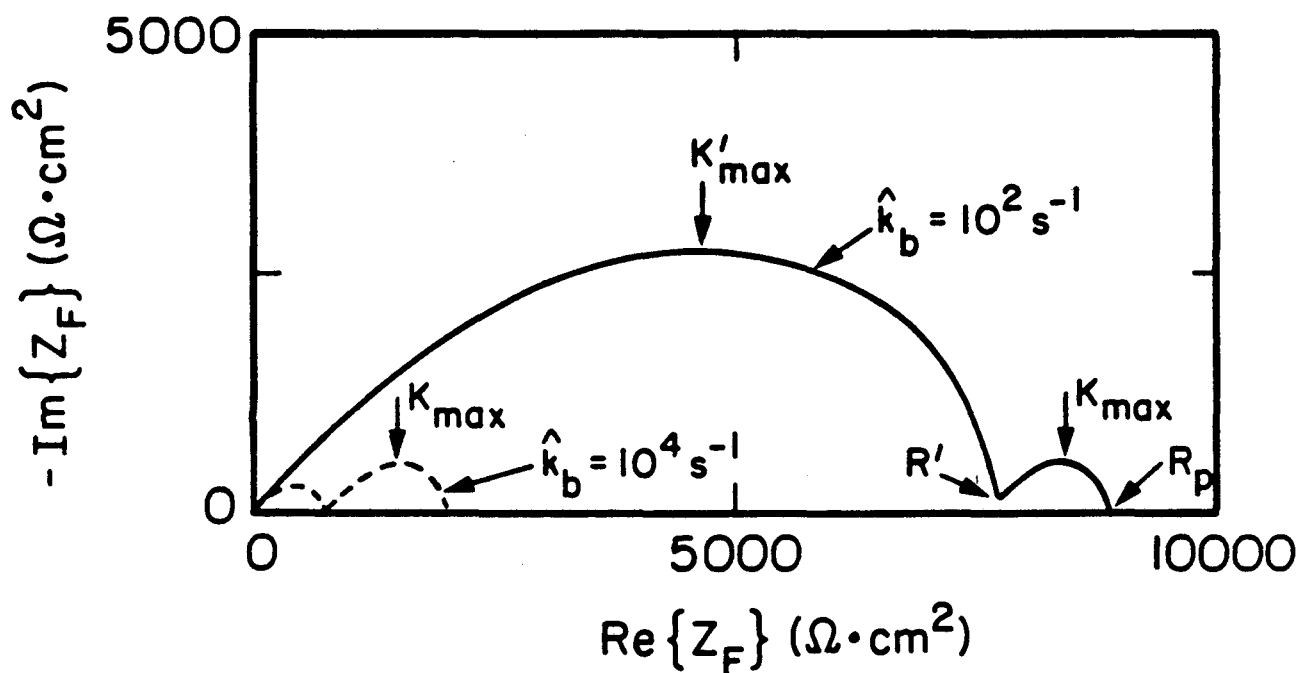


Figure 3. Complex-plane plot of the dimensional faradaic impedance as calculated from the perturbation analysis for $\hat{k}_b = 10^2$ and 10^4 s^{-1} .

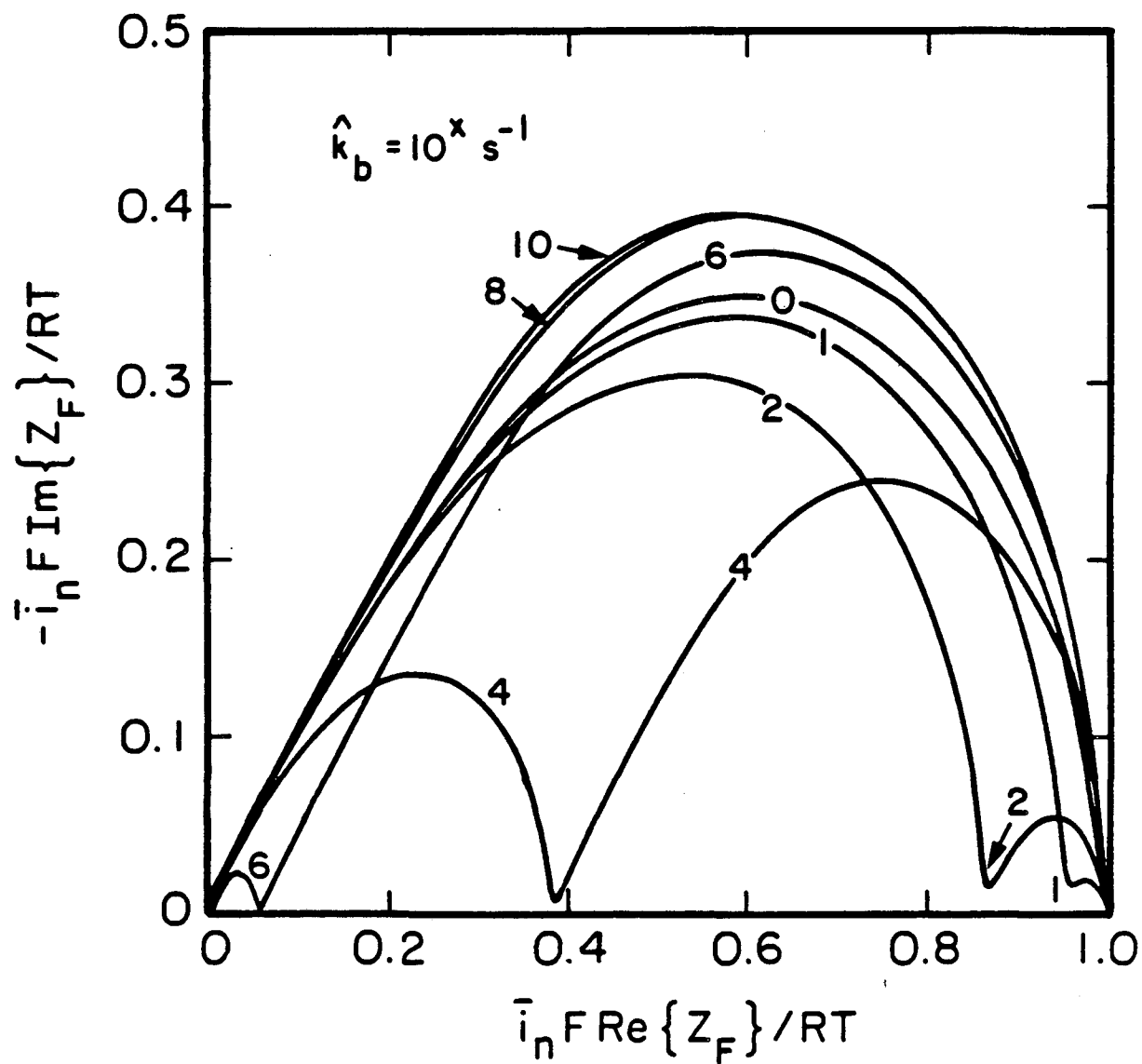


Figure 4. Complex-plane plot of the dimensionless faradaic impedance as calculated from the perturbation analysis for $k_b = 10^x \text{ s}^{-1}$, and $x = 0$ to 10.

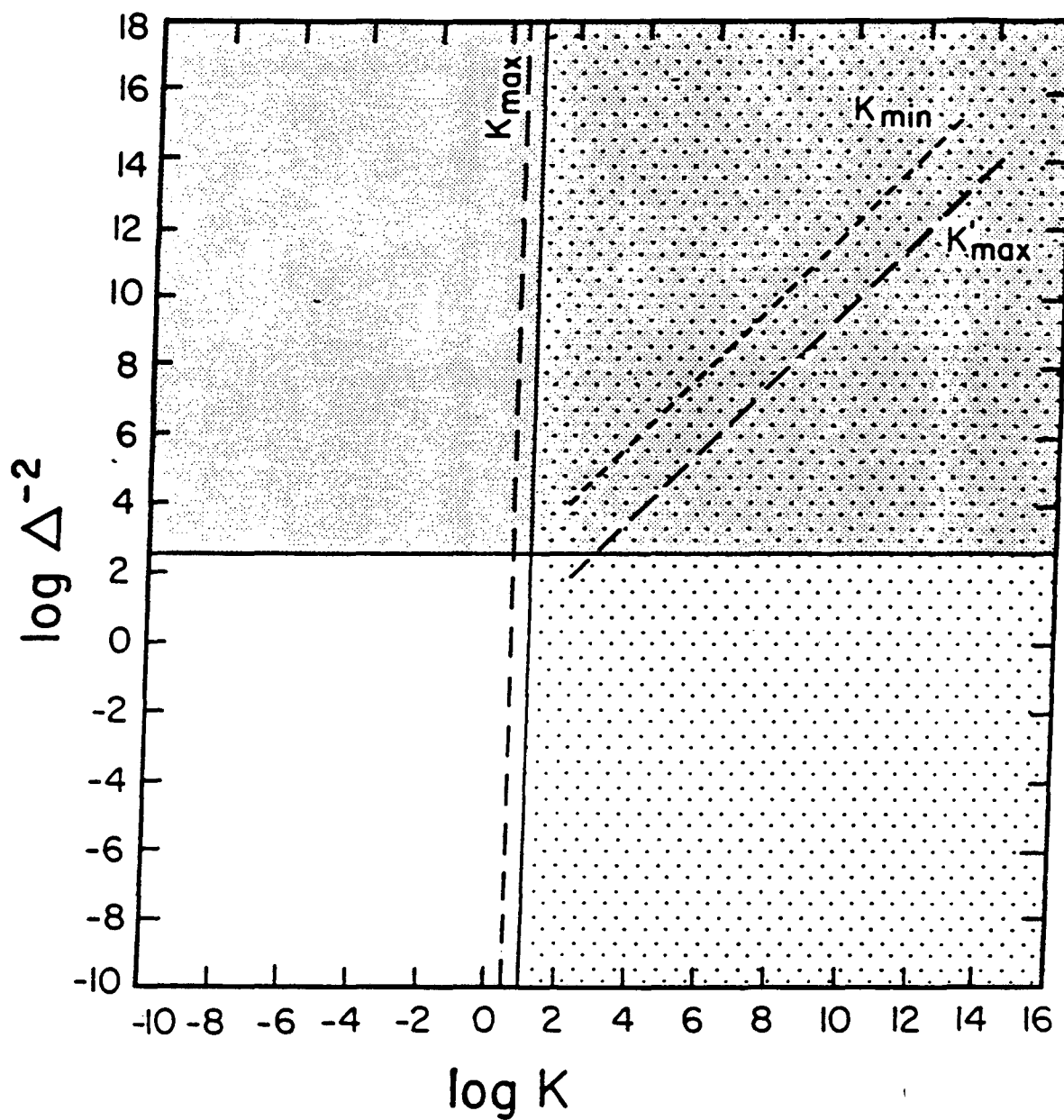


Figure 5. Reaction-zone diagram showing the important behavior of the dimensionless perturbation parameter Δ^{-2} and frequency K .

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