

AN A. C. POLAROGRAPHIC STUDY OF AQUEOUS Cd (II).
EFFECTS OF LARGE AMPLITUDES AND DOUBLE-LAYER
CORRECTIONS

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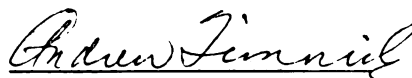
An A.C. Polarographic Study of Aqueous Cd(II).
Effects of Large Amplitudes and Double-Layer Corrections.

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ABSTRACT

AN A.C. POLAROGRAPHIC STUDY OF AQUEOUS Cd(II). EFFECTS OF LARGE AMPLITUDES AND DOUBLE-LAYER CORRECTIONS

by James Dennis McLean

Existing a.c. polarographic equations with which the kinetic parameters, α , $k_{a,h}$, for the electron transfer process can be readily calculated, were derived with the assumption that the amplitude of the applied a.c. potential would not exceed $8/n$ mv. Experiments were performed with aqueous solutions of Cd(II) in various supporting electrolytes at amplitudes from 5 to 50 mv so that the effect of increasing amplitudes on values of $k_{a,h}$ and α , calculated with the aid of the low amplitude equations, could be tested.

Apparent heterogeneous rate constants, $k_{a,h}$, evaluated from $\cot \phi$ versus $\omega^{1/2}$ plots for $5.0 \times 10^{-4}M$ Cd(II) in 1.0M H_2SO_4 at 5, 10, 15, 20, 25, 30, 35, 40, 45, and 50 mv were 0.15, 0.14, 0.13, 0.14, 0.14, 0.15, 0.16, 0.15, 0.16, and 0.18 cm/sec, respectively. Charge-transfer coefficients, α , for the same system at the same respective amplitudes were 0.22, 0.21, 0.20, 0.20, 0.22, 0.20, 0.22, 0.26, 0.26, and 0.24. For an identical Cd(II) concentration in 1.0M Na_2SO_4 , the range in $k_{a,h}$ values was 0.06 to 0.08 cm/sec and the charge-transfer coefficients varied from 0.24 to 0.32 for the stated amplitudes. It is apparent that if $k_{a,h}$ is between 0.05 and 0.20 cm/sec, acceptable values for $k_{a,h}$

and α can be determined with the aid of the low amplitude equations up to the limit of amplitudes tested. Deviations from linearity in the $\cot \phi$ versus $\omega^{1/2}$ plots become apparent above 30 mv and 800 Hz at $E_{1/2}^R$ and above 20 mv and 600 Hz at $E_{1/4}$ and $E_{3/4}$. The deviations increase with increasing amplitudes in all cases. Intercepts of one on the $\cot \phi$ axis as predicted by the low amplitude equations, were obtained in the $\cot \phi$ versus $\omega^{1/2}$ plots at all d.c. potentials and all a.c. amplitudes.

Studies of $5.0 \times 10^{-4} \text{M}$ Cd(II) in 1.0M KNO_3 demonstrated that if $k_{a,h}$ is 0.5 cm/sec or faster, the low amplitude equations do not yield reasonable $k_{a,h}$ and α values for amplitudes greater than 5 mv.

Frumkin double-layer corrections were applied to apparent heterogeneous rate constants for 1.0 mM aqueous Cd(II) in 0.5M Na_2SO_4 , 1.0M Na_2SO_4 , 0.5M H_2SO_4 , 1.0M H_2SO_4 , 1.0M KNO_3 , 1.0M NaClO_4 , 1.0M HClO_4 , 1.0M KCl , 1.0M NaCl , and 1.0M HCl and the following corrected rate constants were obtained respectively: 0.77, 0.41, 1.2, 0.81, 0.96, 1.3, 3.0, 1.6, 1.5, and 1.4 cm/sec. These values have considerably less spread than the uncorrected values, which have a range of 0.063 cm/sec in 1.0M Na_2SO_4 , to 1.2 cm/sec in 1.0M KCl . The only cadmium species in chloride media which yields rate constant values which agree with the remaining corrected rate constants, is CdCl^+ .

Maximum and minimum probable values of $\Delta\Phi_E$, the potential difference necessary for the Frumkin double-layer corrections on the apparent heterogeneous rate constant were calculated by assuming reasonable error levels of ± 6 per cent for the integral double-layer capacitance, ± 3 per cent for the bulk concentration of each ionic species present in the solution, and ± 3 mv for the applied d.c. potential and the same level for the potential at the point of zero charge. Assuming also an error of ± 0.03 units in the charge-transfer coefficient and ± 20 per cent in $k_{a,h}$, the probable ranges of the corrected rate constants were calculated. These ranges overlapped for all supporting electrolytes with the exception of 1M Na_2SO_4 and 1M HClO_4 .

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INTRODUCTION

Many electrochemical techniques currently in use are based at least in part on d.c. polarography. Heyrovsky (1) developed this technique in 1922 after studying the behavior of dropping mercury electrodes. Using the ideas and methods of Heyrovsky, electrochemists began to examine the total electrode process by determining the effects of mass transfer to and from the electrode, and electron transfer. Up to the early 1950's, d.c. polarography was developed for both qualitative and quantitative analytical applications, for determining whether an electrode process was reversible, for evaluating the number of electrons involved in a reduction or oxidation step, for determining whether step-wise reduction occurred, for complexation studies, and for evaluating diffusion coefficients.

Since many electrode processes were found to be irreversible, electrochemists began to study kinetic effects to determine causes of irreversibility. Eyring and Koutecky were leading pioneers in this field.

Eyring (2) applied the absolute rate theory to electrode processes, and developed the general current-potential relationship for electrochemical studies in terms of the kinetic parameters $k_{a,h}$ and α . The heterogeneous rate constant, $k_{a,h}$, in cm/sec, is the apparent rate constant for charge-transfer at the standard electrode potential. The charge-transfer coefficient, α , represents the fraction of the potential that favors the forward reaction, and $(1 - \alpha)$ represents the fraction which favors the backward reaction.

Koutecky (3) derived equations for irreversible processes which indicated that α and $k_{a,h}$ could be evaluated by d.c. polarography. In practice, however, applications were limited and difficult. To extend the evaluation to faster electron transfer reactions, newer electrochemical techniques such as the galvanostatic, potentiostatic, faradaic rectification, and faradaic impedance methods, cyclic voltammetry, and various forms of a.c. polarography were developed.

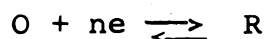
A.c. polarography was first used in 1938 by Müller et. al. (4) to evaluate d.c. half-wave potentials by noting the d.c. potential at which the alternating current had minimum distortion.

The first correct interpretation of the electrode process in the presence of an applied a.c. potential was reported in 1941 by Grahame (5). He concluded that the large apparent change in double-layer capacity in the potential range between the start of the reduction of Cd(II) and the peak of the wave, was due to the electro-reduction of Cd(II) and re-dissolution of Cd in phase with the applied a.c. potential.

The earliest equations reported for the evaluation of rate constants from faradaic impedance measurements were derived independently in 1947 by Randles (6) and Ershler (7).

A more complete discussion of the developments in a.c. polarography up to 1962 is recorded in a monograph by Breyer and Bauer (8). Smith (9), in 1966, presented a very complete theoretical discussion of the field.

Alternating current polarography is an electrochemical technique in which the a.c. and d.c. potentials applied to the polarographic cell are controlled and the resulting alternating current and its phase-angle are measured at a selected d.c. potential, with the amplitude of the alternating potential held constant. With this technique, only reversible and quasi-reversible electrode processes for the reaction



can be examined, since irreversible processes yield no measurable a.c. waves.

From the theoretical expressions, it becomes apparent that α and $k_{a,h}$ can be evaluated for small amplitudes of the applied a.c. potential by a.c. polarography from alternating current measurements. Such currents can be measured accurately, but the final evaluation of the kinetic parameters is difficult. The parameters can be more directly evaluated by measuring the phase-angle between the applied a.c. potential and the faradaic alternating current.

An experimental instrument was constructed in this laboratory by Frischmann (10), with which exactly known constant amplitude a.c. potentials of selected values could be impressed between the electrodes, and with which phase-angles could be precisely and accurately measured.

Considerable effort has been expended in the development of theoretical equations for the a.c. polarographic wave which are valid for large amplitudes of the applied

a.c. potential. From the complexity of the equations of Matsuda (11) and Smith (9) it is apparent that it would be time consuming and difficult to treat large amplitude a.c. polarographic data exactly.

During the course of this investigation several papers were published concerning the electrochemical behavior of Cd(II). Various explanations were offered for the wide range of values for the apparent heterogeneous rate constants reported in the literature for aqueous Cd(II) in various supporting electrolytes. Lingane and Christie (12) attributed the differences between perchlorate media and sulfate media to unknown chemical complications or to inadequacies of the potential-step method when applied to fast reactions. Bauer (13) claimed that the potential at the outer Helmholtz plane governed the values of the rate constants in various supporting electrolytes, but he gave no quantitative proof. He discussed chloride, sulfate and nitrate media. Hamelin (14) concluded that the differences were due to complications of the electrochemical reaction by specific adsorption of the supporting electrolyte. He studied chloride, bromide, iodide, sulfate and perchlorate media.

Frischmann and Timnick (15) recently evaluated the apparent heterogeneous rate constants for aqueous Cd(II) in sulfate, nitrate, perchlorate, and chloride media. They found that the variation in rate constants paralleled the variation in double-layer capacity, but they made no double-layer corrections.

Frumkin (16) and his school developed double-layer corrections in 1933 to account for rate constant differences observed while studying the reduction of hydrogen ions in various media. Frumkin's corrections were based on the Stern modification of the classical Gouy-Chapman theory (17). In 1947, Grahame (18), presented an extensive critical review of the existing information on the electrical double-layer and included double-layer capacitance measurements which he made as well as contemporary measurements made by others. In 1953, Gerischer (19) pointed out the necessity of correction for the double-layer in a.c. electrolysis. Gierst (20), in 1958, investigated the influence of the double-layer structure in detailed d.c. polarographic studies of the reduction of chromate ion, and several other related processes. In 1966, Mohilner (21) presented a very complete theoretical discussion of the elements of double-layer theory.

This work was undertaken to test the extent of applicability of existing a.c. polarographic equations developed for low amplitudes by determining the effect of large amplitudes on experimentally determined $k_{a,h}$ and α values for aqueous solutions of Cd(II). Furthermore, it became apparent that Frumkin double-layer corrections should be applied to $k_{a,h}$ values obtained at low amplitudes, to determine whether double-layer effects are significant in explaining the variation of $k_{a,h}$ values for various supporting electrolytes. Therefore such corrections were undertaken.

THEORETICAL

Before proceeding with discussion of the theoretical section which will require the statement of numerous equations, the definitions of symbolism employed are tabulated below for ready reference.

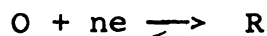
A	=	electrode area
$C_{\text{diff.}}$	=	differential capacity of the electrical double-layer
$C_{\text{d.l.}}$	=	measured capacity of the electrical double-layer
C_f	=	equivalent series capacitive component of faradaic impedance
C_i	=	concentration of species i
$C_i^* = C_i^s$	=	initial concentration of species i
$C_{i_{x=0}}$	=	surface concentration of species i
D_i	=	diffusion coefficient of species i
ΔE	=	amplitude of the applied a.c. potential
$E_{\text{d.c.}} = E$	=	applied d.c. potential
E^0	=	standard electrode potential
$E_{1/2}^R$	=	reversible half-wave potential
$E(t)$	=	instantaneous applied potential
E_z	=	potential at the point of zero charge
f_i	=	activity coefficient of species i
F	=	Faraday's constant
$i(t)$	=	total faradaic current (cathode current positive)
$i_{\text{d.c.}}(t)$	=	d.c. faradaic current

$I(\omega t)$	=	fundamental harmonic faradaic alternating current
$k_{a,h}$	=	apparent heterogeneous rate constant for charge-transfer at E^0
k_h	=	heterogeneous rate constant for charge-transfer at E^0 , corrected for Frumkin double-layer effects
k_h^*	=	heterogeneous rate constant for charge-transfer at E^0 , corrected for Frumkin double-layer effects and for activity effects
K_i	=	integral capacity of the electrical double-layer
n	=	number of electrons transferred in the heterogeneous charge-transfer step
R	=	ideal gas constant
R_e	=	equivalent series resistance of the indicating electrode
R_f	=	equivalent series resistive component of faradaic impedance
R_s	=	equivalent series resistance of the solution
R_t	=	total uncompensated series resistance
t	=	time
T	=	absolute temperature
x	=	distance from the electrode surface
z_i	=	ionic charge of species i , with its sign
Z_f	=	faradaic impedance (absolute value)
α, β	=	charge-transfer coefficients, $\beta = (1 - \alpha)$

ϵ =	dielectric constant
ϕ =	corrected phase-angle between the applied a.c. potential and the fundamental harmonic faradaic alternating current
Φ_H =	potential at the outer boundary of the Helmholtz layer (plane of closest approach)
Φ_S =	potential in the bulk of the solution at the outer boundary of the diffuse double- layer
$\Delta\Phi_E$ =	difference of potential between Φ_H and Φ_S
ω =	angular frequency

The Reversible A.C. Polarographic Wave

An ideal reversible process is one in which the charge-transfer rate is so rapid, that the current is purely diffusion controlled and the charge-transfer is described by the thermodynamic Nernst equation. For the system represented by the reaction



the partial-differential equations and initial and boundary conditions for diffusion to a stationary planar electrode have been developed by Smith (9) as follows:

Fick's law for the oxidized and reduced species:

$$\frac{\partial C_O}{\partial t} = D_O \frac{\partial^2 C_O}{\partial x^2} \quad (1)$$

$$\frac{\partial C_R}{\partial t} = D_R \frac{\partial^2 C_R}{\partial x^2} \quad (2)$$

Initial conditions:

for $t = 0$, any x ,

$$C_O = C_O^* \quad (3)$$

$$C_R = C_R^* \quad (4)$$

Boundary conditions:

for $t > 0$, $x \rightarrow \infty$,

$$C_O \rightarrow C_O^* \quad (5)$$

$$C_R \rightarrow C_R^* \quad (6)$$

For $t > 0$, $x = 0$,

$$D_O \frac{\partial C_O}{\partial x} = -D_R \frac{\partial C_R}{\partial x} = \frac{i(t)}{nFA} \quad (7)$$

Equations (1) and (2) imply the assumptions that Fick's law

is applicable to each of the species independently, that coupled chemical reactions exert no influence, and that electrode curvature and motion relative to the solution are negligible. Equation (7) assumes that each reacting species is soluble either in the solution or electrode phase and that adsorption effects are negligible.

Other equations necessary for the development of the final equations which define the reversible a.c. polarographic wave are

$$C_O = C_R (D_R/D_O)^{1/2} \exp \left\{ \frac{nF}{RT} [E(t) - E_{1/2}^R] \right\} \quad (8)$$

and

$$E(t) = E_{d.c.} - \Delta E \sin \omega t \quad (9)$$

Equation (8) is a form of the Nernst equation. Equation (9) defines the total applied potential for a.c. polarography.

Application of the method of the Laplace transformation to Equations (1) through (7) yields expressions which together with Equations (8) and (9) finally yield expressions for the faradaic alternating current and the faradaic impedance. To obtain these expressions, however, it is necessary to consider only sufficiently small amplitudes of the applied alternating potential ($\Delta E \leq \frac{8}{n} \text{ mv}$), to permit linearization of the complex exponential forms encountered. Through the above described mathematical operations the following equations for the alternating current and impedance have been derived by Breyer and Hacobian (22), Delahay and

Adams (23), Matsuda (11), and Tachi and Senda (24):

$$I(\omega t) = \frac{n^2 F^2 A C_O^* (\omega D_O)^{1/2} \Delta E}{4RT \cosh^2 (j/2)} \sin (\omega t + \pi/4) \quad (10)$$

$$I(\omega t) = I_{\text{rev.}} \sin (\omega t + \pi/4) \quad (11)$$

$$Z_f = \frac{4RT \cosh^2 (j/2)}{n^2 F^2 A C_O^* (\omega D_O)^{1/2}} \quad (12)$$

in which

$$j = \frac{nF}{RT} (E_{\text{d.c.}} - E_{1/2}^R) \quad (13)$$

From Equation (10), it can be seen that the faradaic current is proportional to the square root of the angular frequency (ω) and that the phase-angle is equal to 45° ($\pi/4$) for all frequencies.

The Quasi-Reversible A.C. Polarographic Wave

A quasi-reversible electrode process is one in which the current is diffusion and charge-transfer controlled. Theoretical treatment of the a.c. polarographic wave for this case, requires only minor modification in the mathematical formulation of the reversible case. Since the assumption of Nernstian behavior is no longer valid, Equation (8) is replaced by the absolute rate expression, which is

$$\begin{aligned} \frac{i(t)}{nFAk_{a,h}} &= C_{O_{x=0}} \exp \left[- \frac{\alpha nF}{RT} (E(t) - E^0) \right] \\ &- C_{R_{x=0}} \exp \left[\frac{(1 - \alpha)nF}{RT} (E(t) - E^0) \right] \end{aligned} \quad (14)$$

By employing Equations (1) through (7) and Equations (9) and (14), rigorous equations describing the a.c. polarographic wave were derived by Matsuda (25). Smith (26) slightly modified Matsuda's equations for the controlled a.c. potential technique. Both Matsuda's and Smith's solutions are limited to small amplitudes of the alternating potential.

Smith's expression for the faradaic alternating current for a plane electrode is

$$I(\omega t) = I_{\text{rev.}} F(t) \left[\frac{2}{1 + \left(1 + \frac{(2\omega)^{1/2}}{\lambda} \right)^2} \right]^{1/2} \sin(\omega t + \phi) \quad (15)$$

for which $I_{\text{rev.}}$ is defined by Equations (10) and (11), and

$$F(t) = 1 + \left[\frac{(\alpha e^{-j} - \beta) D^{1/2} Q_0(t)}{k_{a,h}} \right] \quad (16)$$

$$\lambda = \frac{k_{a,h} f}{D^{1/2}} \left[e^{-\alpha j} + e^{\beta j} \right] \quad (17)$$

$$\phi = \cot^{-1} \left(1 + \frac{(2\omega)^{1/2}}{\lambda} \right) \quad (18)$$

$$Q_0(t) = \frac{i_{\text{d.c.}}(t)}{nFAC_O^* D_O^{1/2}} \quad (19)$$

$$f = f_O^\beta f_R^\alpha \quad (20)$$

$$D = D_O^\beta D_R^\alpha \quad (21)$$

$$\beta = 1 - \alpha \quad (22)$$

Delmastro and Smith (27) considered spherical diffusion for both the reversible and quasi-reversible cases. It is necessary to apply correction factors for the faradaic current expressions for both cases. However, the expressions relating the phase-angles to the apparent heterogeneous rate constants are unaltered, regardless of whether diffusion is to a plane or spherical electrode or whether the reduced phase is soluble in the electrode.

Evaluation of the apparent heterogeneous rate constant ($k_{a,h}$) and charge-transfer coefficients (α, β), by either Equation (15) or Delmastro and Smith's (27) modified equation, from an a.c. polarogram would be extremely cumbersome. However, the mere knowledge of ϕ , the phase-angle, allows one to determine readily the desired parameters as will be shown from the following considerations.

By substituting Equation (17) into Equation (18), one obtains

$$\cot \phi = 1 + \frac{(2\omega D)^{1/2}}{k_{a,h} f(e^{-\alpha j} + e^{\beta j})} \quad (23)$$

Equation (23) predicts that a plot of $\cot \phi$ versus $\omega^{1/2}$ at a fixed d.c. potential should yield a straight line with an intercept at $\cot \phi = 1$ and a

$$\text{slope} = \frac{(2D)^{1/2}}{k'_{a,h} (e^{-\alpha j} + e^{\beta j})} \quad (24)$$

where

$$k'_{a,h} = k_{a,h} f \quad (25)$$

It can also be seen that as $k_{a,h}$ approaches an infinite value, $\cot \phi$ will approach unity ($\phi = 45^\circ$) as predicted for the reversible case by Equation (10).

The apparent heterogeneous rate constant, $k_{a,h}$ uncorrected for activity effects is the term calculated in this work.

For the special case where $j = 0$, that is the applied d.c. potential is equal to the reversible half-wave potential, one can calculate from the slope and D , defined in Equation (21), a value of $k_{a,h}$ by the following simple expression

$$k_{a,h} = \frac{(D)^{1/2}}{\text{slope } (2)^{1/2}} \quad (26)$$

The charge-transfer coefficients, (α, β) can be calculated from the d.c. potential dependence of the $\cot \phi$ versus $\omega^{1/2}$ plots. The variation of $\cot \phi$ with changing frequency is obtained for two applied potentials, $E_{d.c.,1}$ and $E_{d.c.,2}$. From Equation (23) it is apparent that the values of the slopes of $\cot \phi$ versus $\omega^{1/2}$ from the plots at $E_{d.c.,1}$ and $E_{d.c.,2}$ may be written (if activity effects are neglected)

$$\text{slope } 1 = \frac{(2D)^{1/2}}{k_{a,h}} (e^{-\alpha j_1} + e^{\beta j_1}) \quad (27)$$

$$\text{slope } 2 = \frac{(2D)^{1/2}}{k_{a,h}} (e^{-\alpha j_2} + e^{\beta j_2}) \quad (28)$$

Thus, one can write

$$\frac{\text{slope } 1}{\text{slope } 2} = \frac{(e^{-\alpha j_2} + e^{\beta j_2})}{(e^{-\alpha j_1} + e^{\beta j_1})} = \frac{e^{-\alpha j_2} (1 + e^{\beta j_2})}{e^{-\alpha j_1} (1 + e^{\beta j_1})} \quad (29)$$

or

$$\frac{\text{slope } 1}{\text{slope } 2} = e^{-\alpha(j_2 - j_1)} \frac{(1 + e^{j_2})}{(1 + e^{j_1})} \quad (30)$$

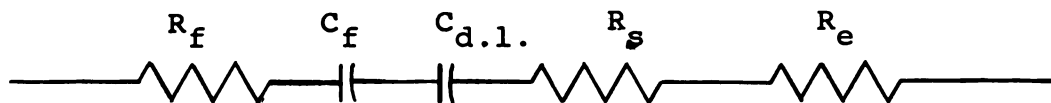
Taking the natural logs of both sides of Equation (30) gives

$$\ln \left(\frac{\text{slope } 1}{\text{slope } 2} \right) = \ln \left(\frac{1 + e^{j_2}}{1 + e^{j_1}} \right) - \alpha(j_2 - j_1) \quad (31)$$

Rearranging yields

$$\alpha = \frac{2.303}{(j_2 - j_1)} \left\{ \log \left(\frac{1 + e^{j_2}}{1 + e^{j_1}} \right) - \log \left(\frac{\text{slope } 1}{\text{slope } 2} \right) \right\} \quad (32)$$

The above equations are derived solely for faradaic current, that is, current arising from the electro-chemical reaction. However, current from the polarographic cell consists of faradaic current and double-layer capacitive currents. To calculate the faradaic current from experimentally obtained total a.c. currents, it is necessary to select an equivalent circuit for the polarographic cell. Several models are possible, since the double-layer capacitance may be placed either in series or in parallel with the faradaic capacitance. Delahay (28) has shown that the same final results are obtained, regardless of the model selected. The following series equivalent circuit is selected, since calculations are simplified:



The polarographic current must pass through resistance offered by the solution and the indicating electrode. R_f and C_f are the faradaic impedances, $C_{d.l.}$ is the capacity of the double-layer, R_s is the resistance of the solution, and R_e is the resistance of the indicating electrode.

To evaluate kinetic parameters for the electrode processes, the faradaic phase-angle must be known. Any measured phase-angle must be corrected for the effects of double-layer capacitance and total uncompensated series resistance. Bauer and Elving (29) derived the following relationship to calculate the corrected phase-angle of the faradaic current:

$$\cot \phi = \frac{\frac{\Delta I}{\Delta E} (\cos \phi' - \frac{\Delta I}{\Delta E} R_t)}{\frac{\Delta I}{\Delta E} \sin \phi' - \omega C_{d.l.} (1 + \left(\frac{\Delta I R_t}{\Delta E}\right)^2 - \frac{2 \Delta I R_t}{\Delta E} \cos \phi')} \quad (33)$$

where ΔI is the amplitude of the alternating current measured and ϕ' is the measured phase-angle between the applied alternating potential and the resulting alternating current.

The A.C. Polarographic Wave at Large Amplitudes

Matsuda (11) derived the first expression for an a.c. polarographic wave which is applicable even when very large amplitudes are applied. Matsuda's equation is valid only for reversible a.c. polarographic waves for the amplitude of the entire complex periodic signal, including higher harmonics. Bauer derived several formulas for large

amplitudes for the special case of very small frequencies ($k_{a,h} \gg \sqrt{\omega D}$), but these are of very limited use and apply only to the reversible case (30).

Smith recently derived equations for the fundamental-harmonic component for a quasi-reversible system valid for larger amplitudes ($\Delta E \leq 35/n$ mv) and $k_{a,h} > 10^{-2}$ (9).

$$I(\omega t) = \frac{n^2 F^2 A C_O^* D_O^{1/2} \Delta E}{RT} \left\{ \left[A_1 + \left(\frac{n F \Delta E}{RT} \right)^2 A_2 \right]^2 + \left[B_1 + \left(\frac{n F \Delta E}{RT} \right)^2 B_2 \right]^2 \right\} \times \sin \left[\omega t + \cot^{-1} \left(\frac{A_1 + (n F \Delta E / RT)^2 A_2}{B_1 + (n F \Delta E / RT)^2 B_2} \right) \right] \quad (34)$$

where

$$A_1 = \frac{(2\omega)^{1/2} (1 + 2^{1/2} z)}{4 \cosh^2 (j/2) [1 + (1 + 2^{1/2} z)^2]} \quad (35)$$

$$B_1 = \frac{(2\omega)^{1/2}}{4 \cosh^2 (j/2) [1 + (1 + 2^{1/2} z)^2]} \quad (36)$$

$$A_2 = \{ (2\omega)^{1/2} [256 \cosh^3 (j/2) [1 + 3.414z + 3.828z^2 + 4.828z^3 + 2.00z^4] \times [1 + (1 + 2^{1/2} z)^2]^{-1}] \} \times \\ \{ 8(\alpha^3 + \beta^3)(1 + 4.828z + 8.655z^2 + 10.241z^3 + 8.827z^4 + 2.828z^5) \times \cosh (j/2) - 12(\alpha e^{-j/2} - \beta e^{j/2}) \\ (2\alpha - 1) \times (1 + 4.828z + 9.517z^2 + 10.517z^3 +$$

$$\begin{aligned}
& 6.356z^4 + 1.885z^5 + \frac{12(\alpha e^{-j/2} - \beta e^{j/2})^2}{\cosh(j/2)} (1 + 4.357z + \\
& 6.104z^2 + 4.161z^3 + 1.333z^4) - 12(\alpha^2 e^{-j/2} + \beta^2 e^{j/2}) \\
& (1 + 4.357z + 7.713z^2 + 6.713z^3 + 2.000z^4) \} \quad (37)
\end{aligned}$$

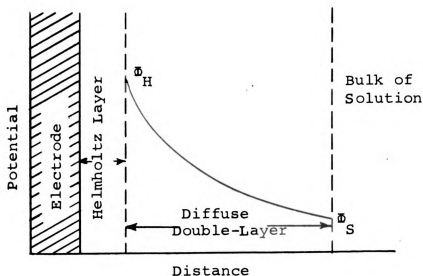
$$\begin{aligned}
B_2 = & \{(2\omega)^{1/2} \left[256 \cosh^3(j/2) [1 + 3.414z + 3.828z^2 + \right. \\
& 4.828z^3 + 2.00z^4] \times [1 + (1 + 2^{1/2}z)^2]^{-1} \} \times \\
& \{ 8(\alpha^3 + \beta^3)(1 + 3.414z + 3.828z^2 + 4.828z^3 + 2.00z^4) \\
& \cosh(j/2) - 12(\alpha e^{-j/2} - \beta e^{j/2})(2\alpha - 1) \times (1 + \\
& 2.747z + 3.747z^2 + 2.552z^3 + 0.862z^4) + \\
& \frac{12(\alpha e^{-j/2} - \beta e^{j/2})^2}{\cosh(j/2)} (1 + 1.805z + z^2 + 0.276z^3) - \\
& 12(\alpha^2 e^{-j/2} + \beta^2 e^{j/2})(1 + 2.471z + 2.609z^2 + 0.276z^3 - \\
& 0.667z^4) \} \quad (38)
\end{aligned}$$

$$z = \omega^{1/2}/\lambda \quad (39)$$

Double-Layer Effects

In the absence of strong interactions between the electrode material and species in solution (specific adsorption), electrode processes may still be perturbed significantly by forces operative within the diffuse double-layer. These influences were not considered in the preceding theoretical discussion.

The following model will show the effects to be considered:



The Helmholtz layer boundary represents the plane of closest approach to the electrode for charged species. These species are prevented from reaching the electrode surface by the primary water layer at the electrode surface, and by their hydration spheres.

The potential measured experimentally is the potential difference between the electrode surface and the bulk of the solution. Since the electroactive species does not reach the electrode surface, and the concentration of reacting particles in the double-layer is different from the bulk of the solution, the electrical energy available for assisting or retarding the electrode reaction is less than the measured value. The potential difference between the plane of closest approach (ϕ_H) and the

bulk of the solution (Φ_S) can not be measured experimentally. Therefore, to correct the rate constants for these effects, it is necessary to calculate a value for $(\Phi_H - \Phi_S)$. The following equation based on the Gouy-Chapman theory is given by Delahay et. al. (31):

$$K_i[(E - E_z) - (\Phi_H - \Phi_S)] = \pm \left\{ \frac{RT\epsilon}{2\pi} \sum C_i^S \left[\exp \left(- \frac{z_i F (\Phi_H - \Phi_S)}{RT} \right) - 1 \right] \right\}^{1/2} \quad (40)$$

Since the equation is non-linear in the variable $(\Phi_H - \Phi_S)$, it can not be solved exactly. Equations of this type can be solved by numerous graphical and numerical methods of analysis. The well-known Newton-Raphson numerical method (32) is selected, since it converges rapidly to give good approximations of the values of $(\Phi_H - \Phi_S)$. Calculations are performed for each supporting electrolyte with the aid of Program Frumkin which is described in the Appendix. To calculate $(\Phi_H - \Phi_S)$ values from Equation (40), it was assumed that the integral double-layer capacitance K_i was equal to the differential capacitance C_{diff} . This is true for the limiting case (21), as the d.c. potential approaches the point of zero charge, E_z , that is

$$\lim_{E \rightarrow E_z} K_i = C_{diff}(E_z) \quad (41)$$

The differential capacitance is equal to the experimental double-layer capacitance divided by the area of the electrode. Using the calculated values for $(\Phi_H - \Phi_S)$, and the following

equation developed by Frumkin as presented by Smith (9), it is possible to calculate corrected values for the apparent heterogeneous rate constants, making the assumption that sinusoidal variations in $\Delta\Phi_E$ may be neglected.

$$k_{a,h} = k_h \exp \left[\frac{(\alpha n - z_O) F \Delta\Phi_E}{RT} \right] \quad (42)$$

where

$$\Delta\Phi_E = \Phi_H - \Phi_S \quad (43)$$

These calculations are performed with the aid of Program Correct which is described in the Appendix.

Activity Effects

The heterogeneous rate constants for cadmium in various supporting electrolytes can be corrected for activity effects according to the following formula (9):

$$k_h = f_O^\beta f_R^\alpha k_h^* \quad (44)$$

While activity coefficients for the reduced form (cadmium amalgam) are known, it is difficult to estimate reasonable values for the activity coefficients of the oxidized forms. Since the supporting electrolytes employed were either 0.5M or 1.0M, Debye-Hückel type calculations can not be used. Furthermore, to make calculations, it is necessary to know the exact form of the oxidized species. This is not readily apparent, since competing complexes are present in some cases, and the electroactive species present in the double-layer may not be the same as the prevalent cadmium

species in the bulk of the solution. In view of these facts, activity corrections were not attempted.

EXPERIMENTAL

Instrumentation

The instruments employed and their applications in this investigation were as follows:

Sargent S-30260 potentiometer to measure all d.c. potentials applied to the cell;

Tektronix Model 502 oscilloscope to measure the amplitude of the a.c. potential applied to the cell and to monitor the tuning of the frequency sensitive amplifier;

Sargent Model S.R., one second full scale deflection, recorder to measure the maximum d.c. currents, rectified a.c. currents, and signals proportional to the phase-angle;

Hewlett-Packard Model 202A signal generator to provide all a.c. potentials;

Hewlett-Packard Electronic Counter Model 521A to calibrate the frequency of the Hewlett-Packard signal generator;

Philbrick Model R-300 power-supply to provide up to 300 ma of ± 300 v d.c.

The A.C. Polarograph

The a.c. polarograph employed was constructed and described in detail by Frischmann(10). The instrument employed operational amplifiers and was similar to one constructed by Smith, (33) except for modifications in the phase-angle detecting circuit which permitted direct linear response recording of the phase-angle to an accuracy of

$\pm 0.5^\circ$, with no high or low level current limitations. Figures 1, 2, and 3 show block diagrams of essential components of the instrument. The main components of the potentiostat consist of operational amplifiers A, B, and C shown in Figure 1. A.C. MODE and D.C. MODE are the units utilized for measuring a.c. or d.c. signals. Amplifier D attenuates the signal to the recorder.

The d.c. potential source, at $E_{d.c.}$, supplied 0 to ± 3 volts with a long term instability of at most 0.1 mv. From this source, any desired potential could be obtained by adjustment of a 10 turn Helipot. The Sargent potentiometer was used to monitor the desired potential before each measurement.

The a.c. potential source provided ranges of 0 to 5.00 ± 0.05 mv or 0 to 50.0 ± 0.5 mv, and any desired potential could be obtained by adjustment of a 10 turn Helipot. The a.c. potential was monitored with the Tektronix oscilloscope before each experiment. The frequency of the signal generator was calibrated with the aid of the electronic counter and typically corresponded to within 0.6% of the dial reading in the frequency range of 30 to 1200 Hz.

The d.c. scanning unit, E_{scan} , was not used in this investigation.

Calibration of D.C. Currents

For d.c. mode operation (Figures 1, 3) a 100K resistor

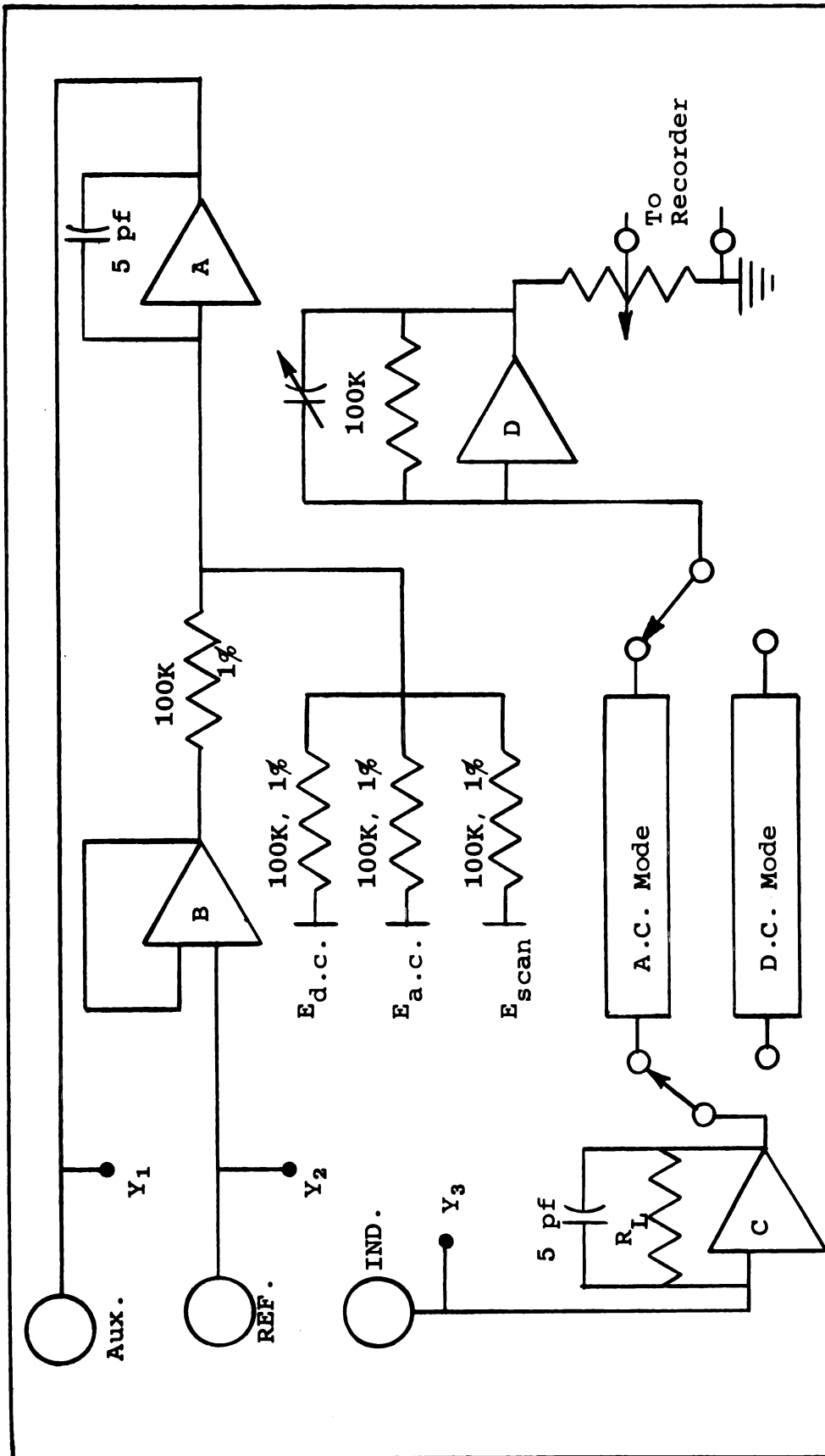


Figure 1. Essential components for an a.c. - d.c. polarograph. Amplifiers A, C, and D are Philbrick USA - 3's. Amplifier B is a combination of a Philbrick K2X-A and a K2-P in the Deford follower configuration (34). Aux., Ref., Ind., are the auxiliary, reference and indicator electrodes respectively. Y₁, Y₂, and Y₃ are the connection points for the calibrating mode (Figure 3).

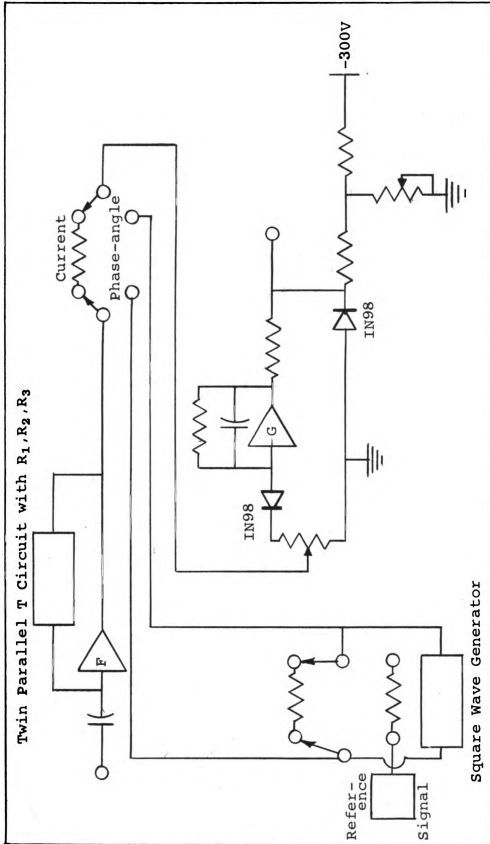


Figure 2. Schematic of the A.C. MODE. Amplifier F, a Philbrick USA-3, is used as the tuned amplifier. Amplifier G, a Philbrick K2X-A, is used as a full-wave rectifier. R_1 , R_2 , and R_3 are 10-turn Helipot.

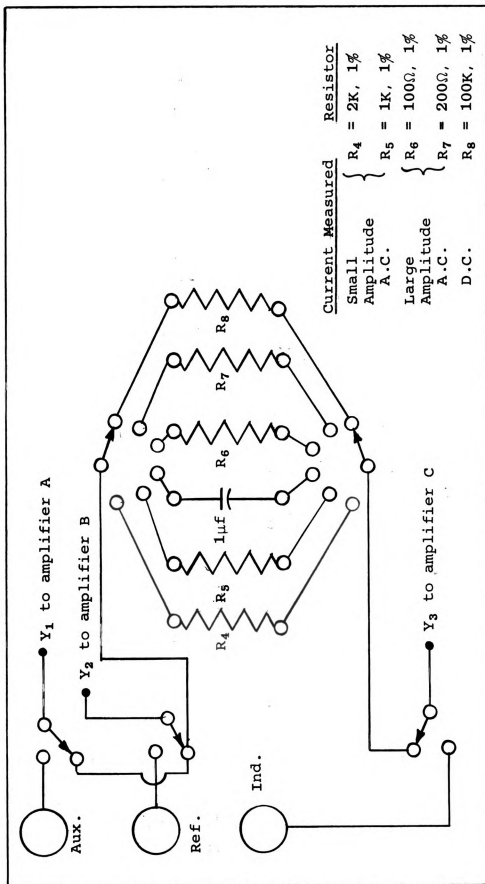


Figure 3. Schematic of the potentiostat switched to the calibrating mode. Y₁, Y₂ and Y₃ are the connection points to the potentiostat (Figure 1).

is introduced between amplifiers C and D. This makes amplifier D a unity gain inverter.

For current calibration, the electrodes are taken out of the circuit and connection to the precision 100K resistor, R_8 , is made as shown in Figure 3. By applying zero volts across R_8 , the zero current level on the recorder is adjusted. A d.c. potential, dependent on the current range to be measured, is applied across R_8 to attain full scale recorder deflection. After the above calibration step, the electrodes are switched into the circuit, and the current flowing through the polarographic cell at a selected potential is recorded.

Calibration of A.C. Currents

To measure fundamental a.c. signals free from noise, amplifier F (Figure 2) must be tuned sharply to the frequency of the signal to be measured. This condition is attained by selection of the proper values of R_1 , R_2 , and R_3 . The role of R_1 in determining the frequency is obvious from the familiar expression, $f_1 = \frac{1}{2\pi R_1 C}$. In the twin parallel T network, R_1 must equal R_2 and R_3 must equal $R_1/2$ for sharp tuning. R_1 , R_2 and R_3 are 10 turn Helipots. The frequency of the a.c. source is adjusted until the output of amplifier F is at a maximum. R_4 , R_5 , R_6 , or R_7 (Figure 3) is then selected to provide the desired current range. A selected a.c. potential is applied across the chosen resistor and the recorder is adjusted to full scale

deflection. To set the low end of the recorder scale, one-tenth of the selected potential is applied across the resistor and the recorder is adjusted to yield one-tenth of the full scale deflection. The low end of the recorder scale is not adjusted to zero reading because of the conductance limitations of the diodes employed in this circuit. Thus the working range of the recorder scale extended from one-tenth of full scale to full scale (from one inch to 10 inches on the recorder chart paper).

After the calibration step, the electrodes are switched into the circuit, and the rectified a.c. current from the cell is recorded.

Phase-Angle Calibration

With amplifier F tuned to the desired frequency, the phase-angle detector is switched in as shown in Figure 2. With an a.c. potential applied across the $1\mu\text{f}$ capacitor in the calibrating circuit (Figure 3) the recorder is adjusted to indicate the 90° phase shift reading, since the a.c. signal through the $1\mu\text{f}$ capacitor leads the applied a.c. potential by 90° . With an a.c. signal across R_4 or R_5 in the calibrating circuit, the phase-shift level of zero degrees is set on the recorder, since the a.c. signal through a resistor is in phase with the applied potential. After the calibration step, the electrodes are switched back into the circuit and the phase-angle from the cell is recorded.

The long term stability of the employed commercial signal generator was about 0.5° , therefore the above calibration was performed before and after each phase-angle measurement.

The accuracy of the phase-angle detector was tested at both large and small amplitudes with the following series RC networks (components of 1% accuracy): 500 ohm and 1.0 μ f; 100 ohm and 1.0 μ f; 50 ohm and 1.0 μ f. The amplitudes employed were 5.00, 25.0, and 50.0 mv. The phase-angles measured agreed within experimental error (~ 3 per cent) to the calculated values throughout the 30 to 1100 Hz frequency range. Data were obtained at fifteen different frequencies. These RC circuits and frequencies yielded a current range from 0.93 μ a to 300 μ a and a phase-angle range from 89.6° to 17.6° .

To perform the experiments at large amplitudes (10.0 to 50.0 mv), it was necessary to decrease the magnitude of the resistors in the calibrating mode (Figure 3) so that the recorder could be calibrated for larger currents from the polarographic cell. This was the only necessary instrumentation change, since the instrument was previously provided with a variable a.c. potential source.

Other Equipment

The polarographic cell employed in this work is shown in Figure 4. Through the side-arm with the two-way stop-cock, nitrogen can either be bubbled through the solution

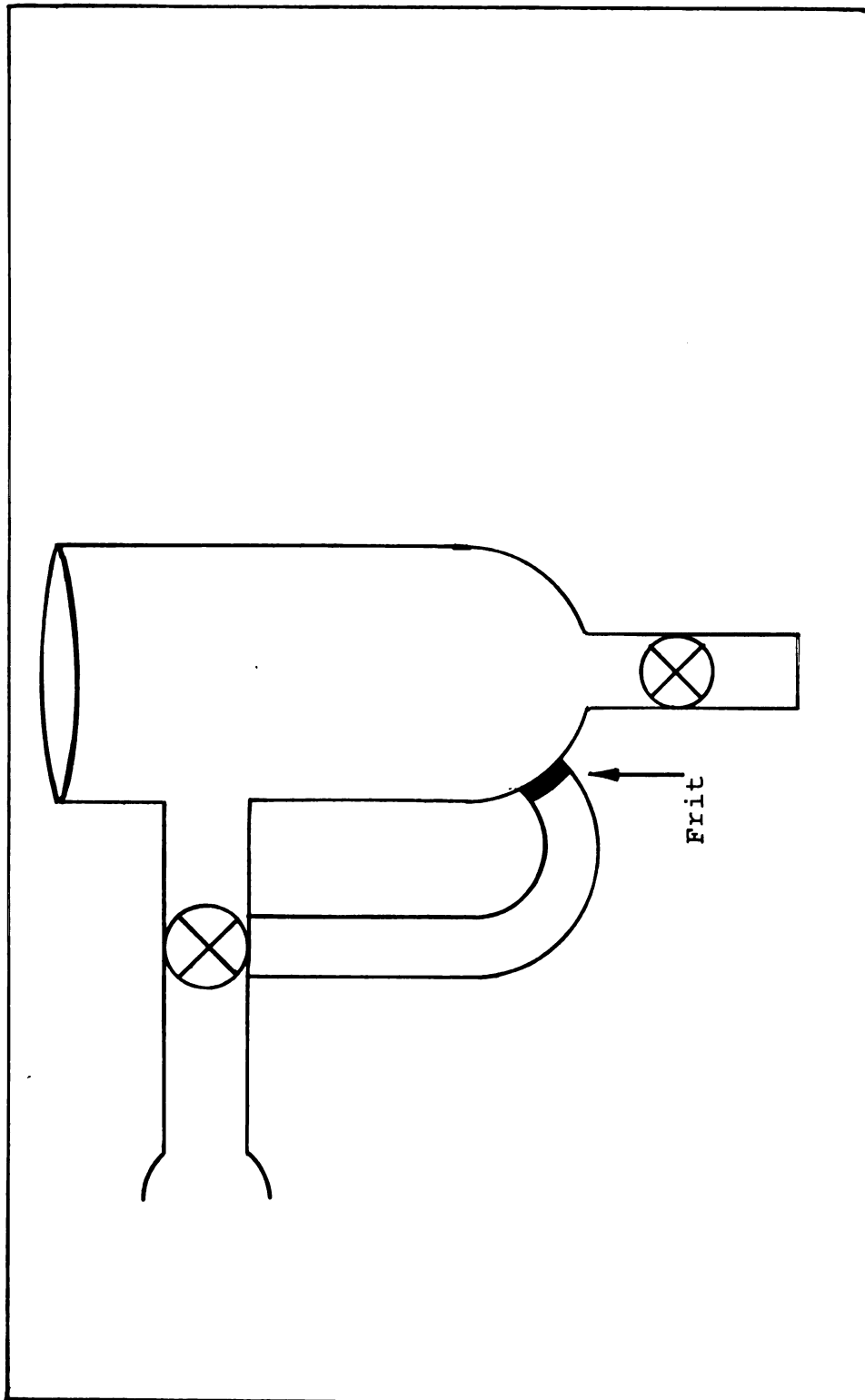


Figure 4. Polarographic cell.

by way of a coarse frit at the bottom of the cell, or blown over the top of the solution. The cell is fitted with a 3-hole rubber stopper through which the dropping mercury electrode, saturated calomel electrode, and the auxiliary electrode (platinum coil) are introduced.

The constructional details of the reference electrode employed are shown in Figure 5. The reference electrode was separated from the polarographic solution by an isolation compartment which contained the supporting electrolyte. Both the reference electrode and the isolation compartments were tightly stoppered to minimize any flow of solution through the frits. Isolating the reference electrode minimizes contamination of the polarographic solution by foreign ions from the side arm of the reference electrode.

The auxiliary electrode, a platinum wire coil, is separated from the polarographic solution by a fine frit. Its isolation compartment always contained the polarographic solution. The frit prevented the free diffusion of oxidation products to the dropping mercury electrode.

Reagents

Reagents were employed without further purification.

The chemicals, and sources are as follows:

Cadmium Nitrate, Tetrahydrate	Baker's Analyzed Reagent
Disodium Salt of Ethylenediamine tetraacetic Acid (EDTA) Dihydrate	Mallinckrodt Analytical Reagent

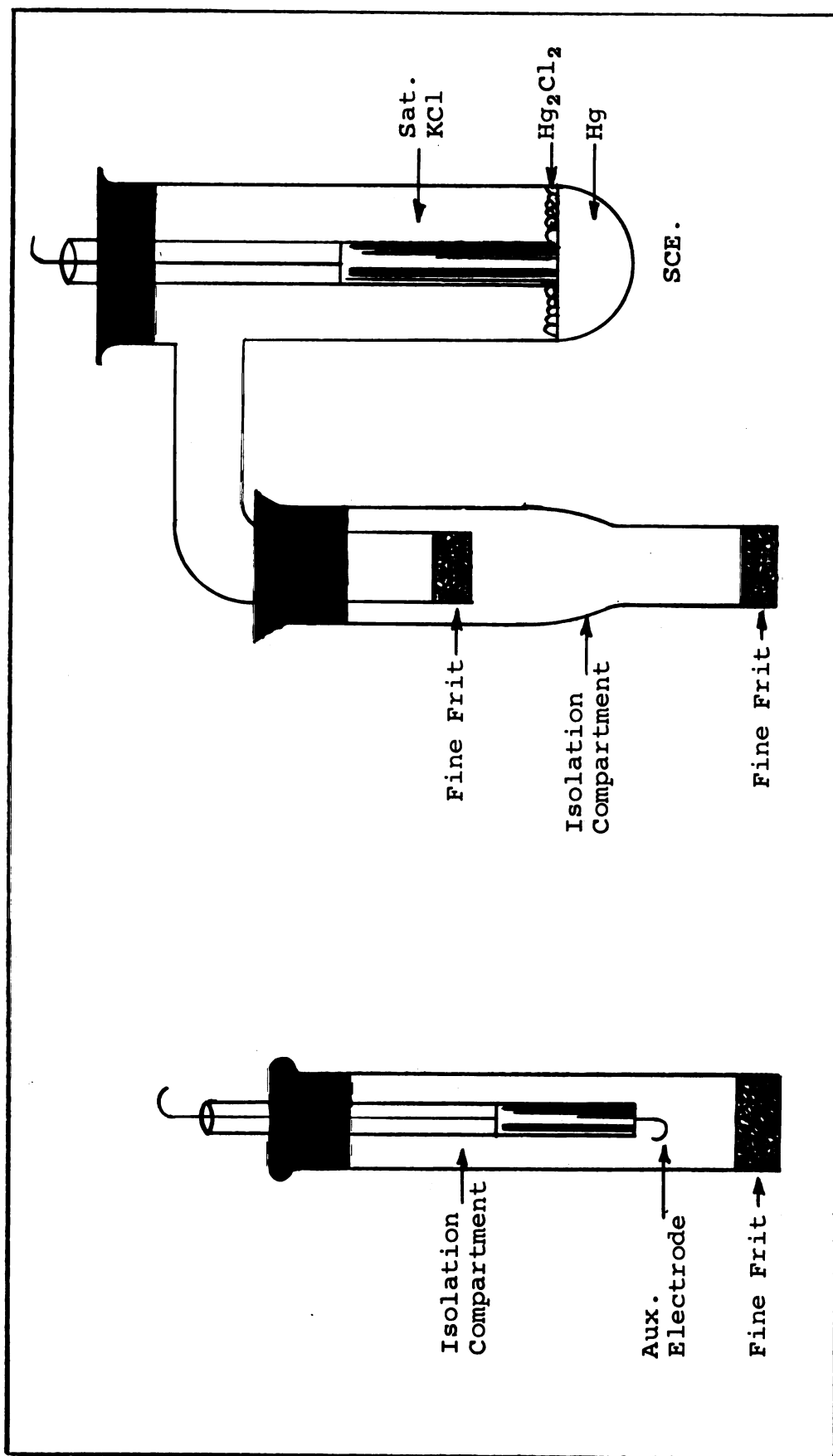


Figure 5. Auxiliary and reference electrodes.

Hydrochloric Acid	Baker's Analyzed Reagent
Mercury	Two sources: Chicago Apparatus Company, Triple Distilled, Chemically Pure; Purified in this Laboratory.
Nitrogen	Prepurified, 99.996% The Matheson Company
Perchloric Acid	Baker's Analyzed Reagent
Potassium Chloride	Matheson, Coleman and Bell A.C.S. Reagent
Potassium Nitrate	Matheson, Coleman, and Bell A.C.S. Reagent
Sodium Chloride	Baker's Analyzed Reagent
Sodium Perchlorate Monohydrate	G. Frederick Smith Chemical Company
Sodium Sulfate (Anhydrous)	Baker's Analyzed Reagent
Sulfuric Acid	Baker's Analyzed Reagent

Mercury Purification

Mercury which had previously been used for electro-chemistry was purified by the following process. Mercury was filtered into a large filter flask to remove gross contamination, and one liter of 1M nitric acid was then added. A glass tube inserted through a rubber stopper located in the neck of the flask extended below the mercury surface. When suction was applied to the side arm of the flask, the air entering through the glass tube provided vigorous mixing. After one day of aeration and nitric acid washing, the wash solution was removed, and the mercury was rinsed several times with distilled water. One liter of 1M

sodium hydroxide was added to the filter flask and the washing process continued for one day. The sodium hydroxide was used to remove grease and other such organic impurities from the mercury. The wash solution was then removed and the mercury was again rinsed several times with distilled water. This process was continued for one week, alternating the nitric acid and sodium hydroxide treatment each day. In the final wash, the mercury was rinsed with 1 liter of distilled water to which a few drops of concentrated nitric acid were added to prevent oxide formation. The mercury was separated from the water and the last traces of water were removed by blotting the mercury surface with filter paper. It was then filtered twice through pinholes in filter paper and then stored in special hard glass bottles. The cleaned mercury was used for both a.c. and d.c. polarography, cyclic voltammetry and stripping analysis. No anomalous results were obtained in any of these methods, indicating that the mercury was equal in quality to commercial triple-distilled mercury used for electrochemical purposes. It was possible to clean up to 35 pounds of mercury at one time, using this method.

Preparation of Solutions

A 0.0100M Cd(II) stock solution was prepared from $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and standardized by EDTA titration (35).

The supporting electrolyte solutions were prepared by weighing solids, or pipetting electrolyte solutions, and

diluting to volume. The acid supporting electrolytes were standardized with previously standardized sodium hydroxide.

The sample solutions were prepared by appropriate dilution of the cadmium nitrate stock aliquots to which the desired amount of electrolyte had been added. None of the solutions contained maximum suppressor.

Half of the solutions were prepared from the laboratory distilled water supply and half were prepared from triple-distilled water. Duplicate experiments run on similar solutions prepared with water from the two sources yielded, within experimental error, no different results.

Dissolved oxygen was removed from all solutions in the polarographic cell by bubbling with nitrogen for a period of 20 minutes. Nitrogen was also swept continuously over the surface of the solution during the duration of an experiment. Last traces of oxygen were removed from the nitrogen by bubbling it through an acid vanadous sulfate solution, dilute sodium hydroxide, and water, before passing it into the polarographic cell.

All polarograms were run at $24 \pm 1^\circ$.

Evaluation of $C_{d.l.}$, K_i and R_t

The determination of the capacity of the double-layer ($C_{d.l.}$) and total uncompensated resistance (R_t) is accomplished by applying a 5 mv a.c. potential of known frequency to the cell containing only supporting electrolyte,

and measuring the amplitude of the resulting a.c. current and its phase-angle.

Since the capacity of the double-layer changes with the d.c. potential and the electrode area, current and phase-angles are determined at maximum drop size at each d.c. potential of interest.

The capacity of the double-layer is calculated by

$$C_{d.l.} = \frac{\Delta I}{\omega \Delta E \sin \phi} \quad (45)$$

and total series resistance by

$$R_t = \frac{\Delta E}{\Delta I} \cos \phi \quad (46)$$

The evaluation of $C_{d.l.}$ and R_t was performed at fifteen different frequencies. It was found that the values obtained were independent of frequency within experimental error. However, since the value of $\cos \phi$ changes rapidly at phase-angles greater than 88° , only the values at frequencies greater than 100Hz were used. This resulted in averaging ten values to obtain $C_{d.l.}$ and R_t in each supporting electrolyte at each d.c. potential.

The above experiments were also performed with an applied a.c. potential of 50.0 mv for the large amplitude studies. The data thus obtained, were used to evaluate $C_{d.l.}$ and R_t for the various supporting electrolytes. Since the values obtained at large amplitudes agreed within experimental error to the values obtained at small amplitudes,

the values of $C_{d.l.}$ and R_t determined at 5 mv were used for all calculations at all amplitudes.

To evaluate K_i , the value of the integral double-layer capacity per unit electrode area, it was necessary to determine the area of a mercury drop, at maximum drop size, in each supporting electrolyte, at the desired d.c. potential. This was accomplished by weighing 20 drops of mercury delivered by the capillary in the desired supporting electrolyte, and then calculating the drop area assuming that the drop is a sphere, using a value of 13.54 g/cc for the density of mercury at 24° (36).

Evaluation of $k_{a,h}$ and α

Values for the apparent (uncorrected) heterogeneous rate constants, $(k_{a,h})$ were calculated with the aid of Equations (21) and (26). The slope necessary for use in Equation (26) was determined from the $\cot \phi$ versus $\omega^{1/2}$ plot (Equation (23)) evaluated at a d.c. potential corresponding to $E_{1/2}^R$. The data necessary for this plot were determined by measuring the a.c. current and the phase-angle at fifteen different frequencies between 30 and 1200 Hz. All measurements were made at maximum drop size. The experiments were performed with a.c. potentials of 5.00, 10.0, 15.0, 20.0, 25.0, 30.0, 35.0, 40.0, 45.0, and 50.0 mv. All phase-angles were corrected for double-layer capacitance and total uncompensated series resistance effects by

Equation (33), using Program AC which is described in the Appendix. With this program the least squares slopes for $\cot \phi$ versus $\omega^{1/2}$ plots of these corrected phase-angles can also be calculated.

Values for the charge-transfer coefficients (α, β) were calculated with the aid of Equations (22) and (32). The slopes necessary for use in Equation (32) included the slopes evaluated above at $E_{1/2}^R$, and slopes evaluated in the same way from similar experiments carried out at $E_{1/4}$ and $E_{3/4}$.

DISCUSSION OF RESULTS

Evaluation of $E_{1/4}$, $E_{1/2}^R$, $E_{3/4}$ and D

Values of the experimental half-wave potential, $E_{1/2}^R$, and the calculated diffusion coefficient, D , for aqueous Cd(II) in various supporting electrolytes are tabulated in Table I. The values of $E_{1/4}$, $E_{1/2}^R$, and $E_{3/4}$ used in this work were those determined by Frischmann (10) from d.c. polarograms. The values were obtained from the $E_{d.c.}$ versus $\log \frac{i_d - i}{i}$ plots at points where the intercepts were equal to 0.477, 0, and -0.477. $E_{1/4}$ and $E_{3/4}$ were displaced 14 mv from $E_{1/2}^R$ in all media.

The values of D_0 , the diffusion coefficient of the oxidized species, (Cd(II)), in various supporting electrolytes, necessary for the calculation of D , were determined by Frischmann (10). The values were calculated from d.c. polarographic data, with the aid of the Lingane-Loveridge equation (37). Employing these values and the value of D_R , the diffusion coefficient of the reduced species, (Cd(Hg)), of 1.61×10^{-5} cm²/sec obtained by Bauer and Elving (38), values for D were calculated with the aid of Equation (21).

Evaluation of the Apparent Heterogeneous Rate Constant, $k_{a,h}$, at Large Amplitudes of the Applied A.C. Potential

Typical plots of $\cot \phi$ versus $\omega^{1/2}$ at $E_{d.c.} = E_{1/2}^R$ at various amplitudes of the applied a.c. potential are shown in Figures 6-10, for 5×10^{-4} M Cd(II) in 1.0M sulfuric acid. The data were obtained at $E_{1/2}^R$, since maximum

Table I $E_{1/2}^R$ and D values for $5.0 \times 10^{-4} \text{M Cd(II)}$ in various supporting electrolytes.

Supporting Electrolyte	$E_{1/2}^R$ versus SCE, v	$D^* \times 10^6 \text{ cm}^2/\text{sec}$
1.0M Na_2SO_4	-0.606	5.51
1.0M H_2SO_4	-0.597	7.54
1.0M KNO_3	-0.585	10.20

$$^* D = D_O^\beta D_R^\alpha .$$

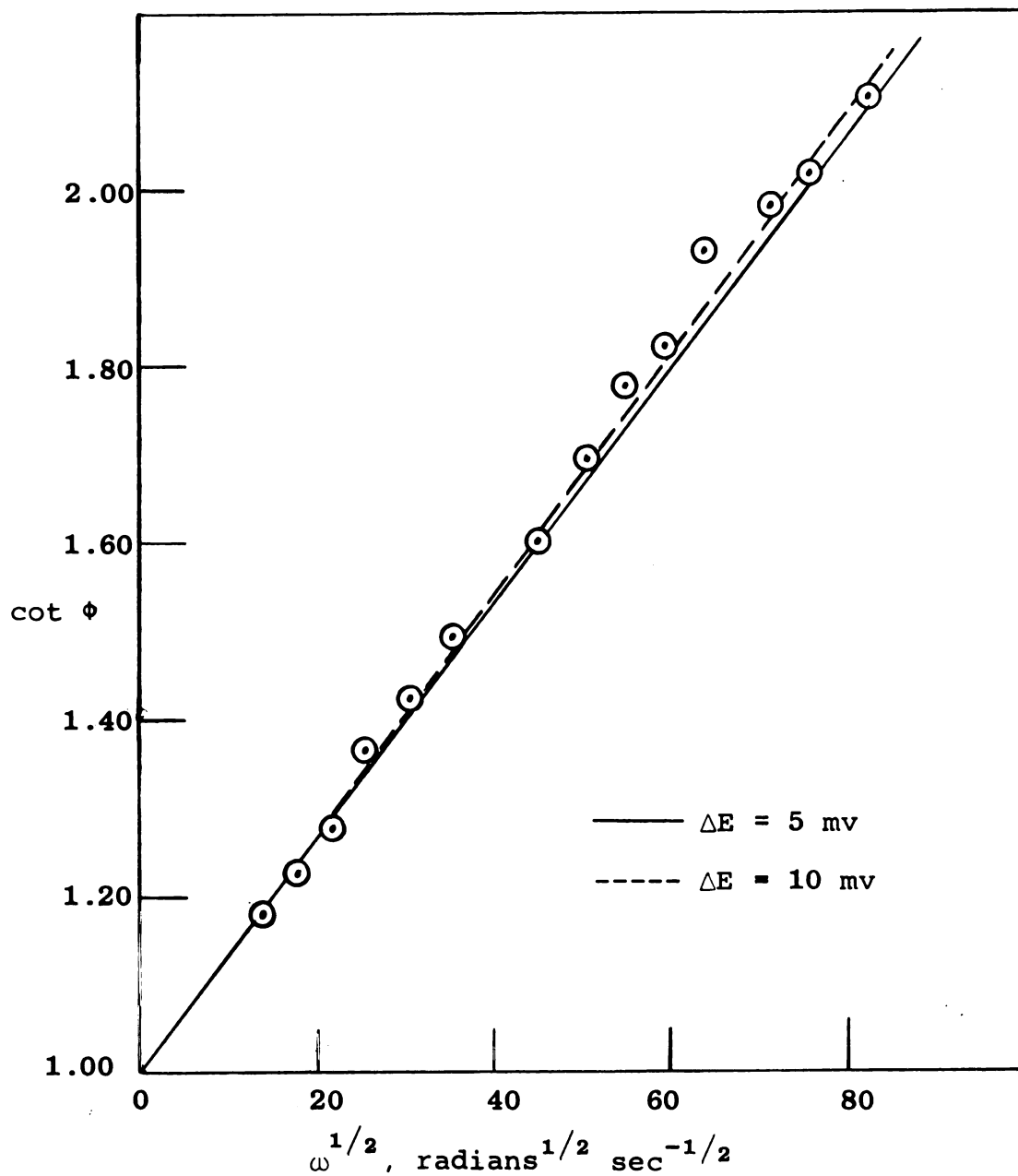


Figure 6. Variation of the corrected phase-angle with the square root of angular frequency for $5.0 \times 10^{-4} \text{M Cd(II)}$ in $1.0 \text{M H}_2\text{SO}_4$ at $E_{\text{d.c.}} = E_{1/2}^R$ and with an applied a.c. potential of 10 mv.

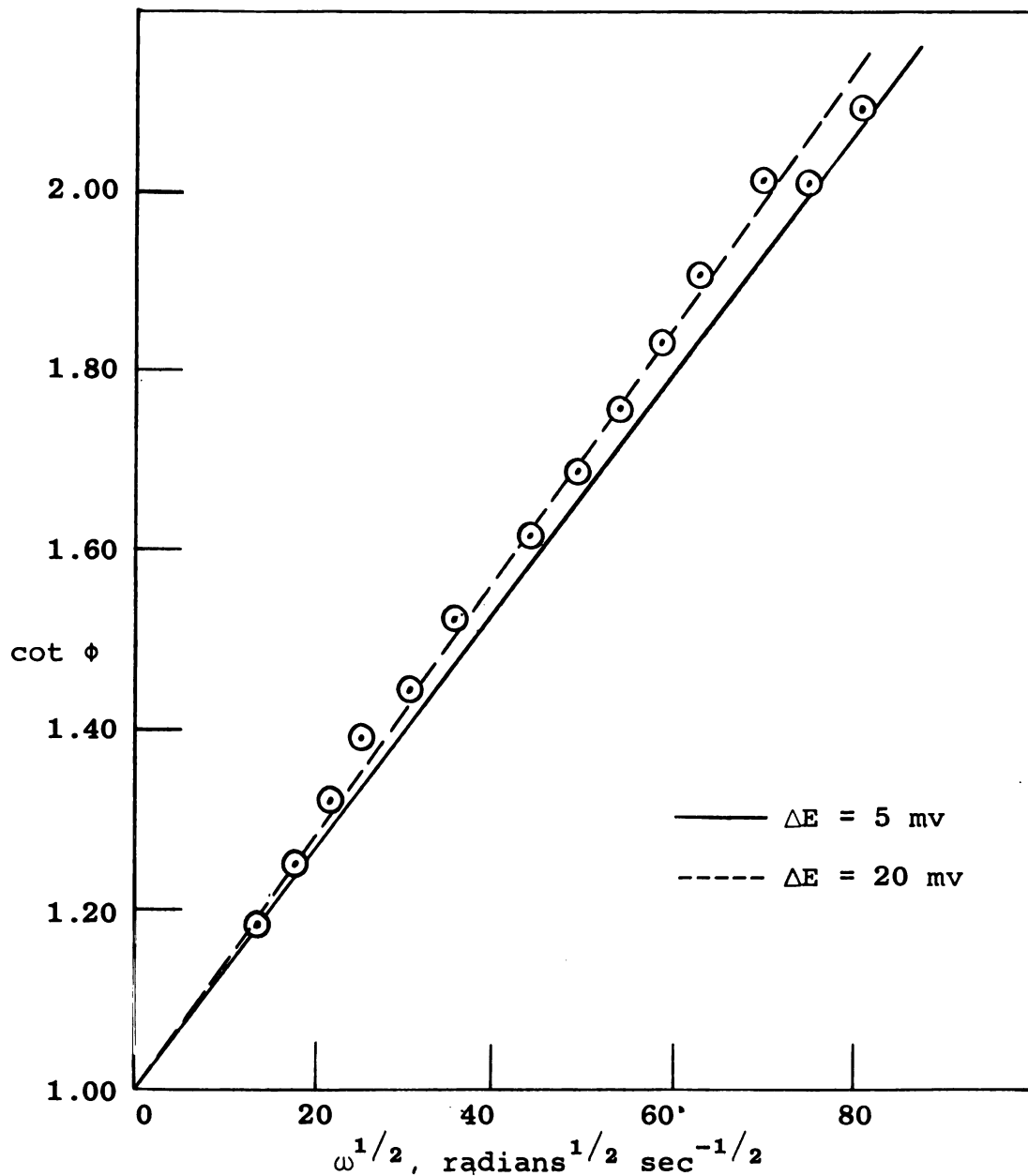


Figure 7. Variation of the corrected phase-angle with the square root of angular frequency for $5.0 \times 10^{-4} \text{M Cd(II)}$ in $1.0 \text{M H}_2\text{SO}_4$ at $E_{\text{d.c.}} = E_{1/2}^{\text{R}}$ and with an applied a.c. potential of 20 mv.

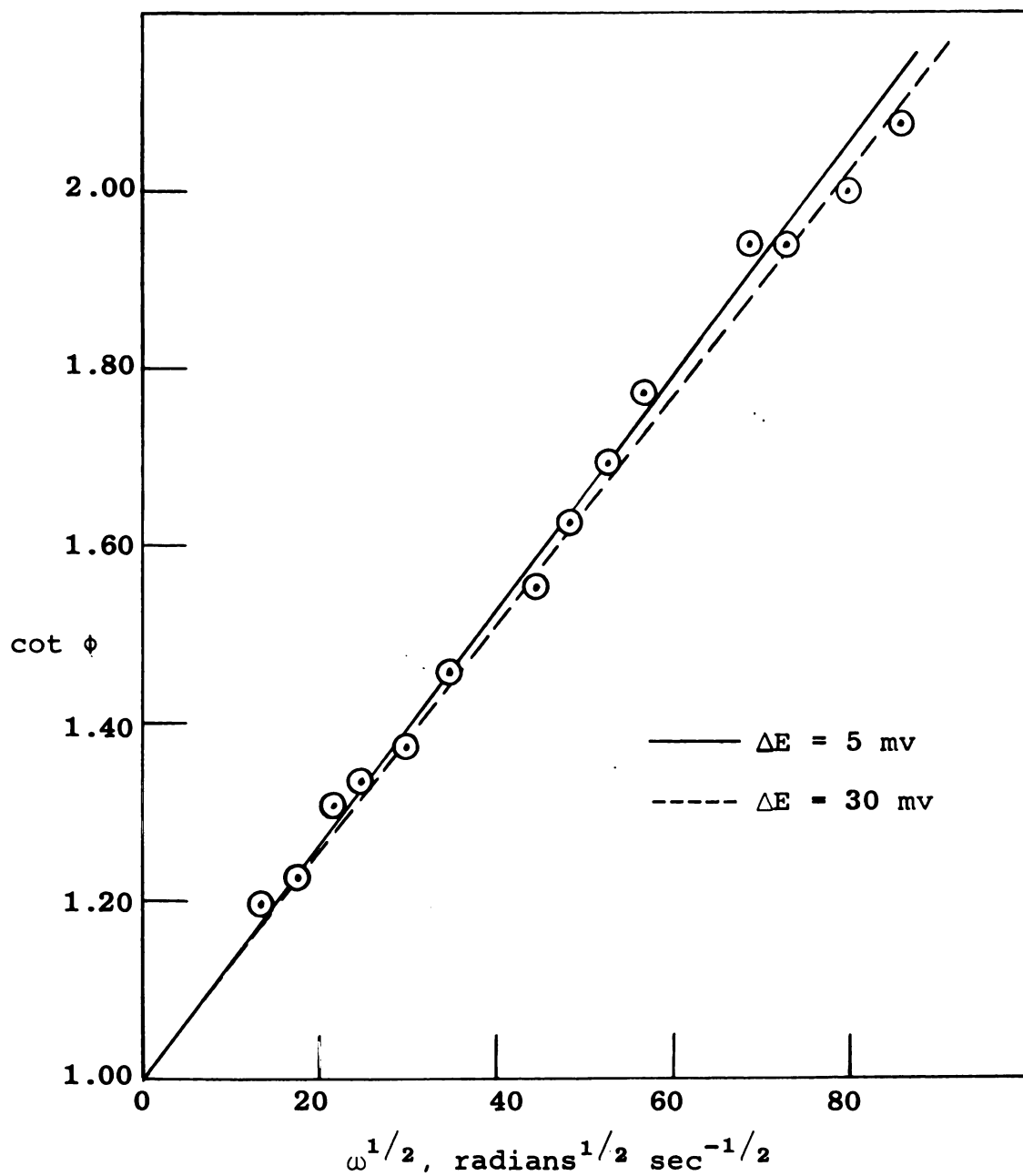


Figure 8. Variation of the corrected phase-angle with the square root of angular frequency for $5.0 \times 10^{-4} \text{M Cd(II)}$ in $1.0 \text{M H}_2\text{SO}_4$ at $E_{\text{d.c.}} = E_{1/2}^R$ and with an applied a.c. potential of 30 mv.

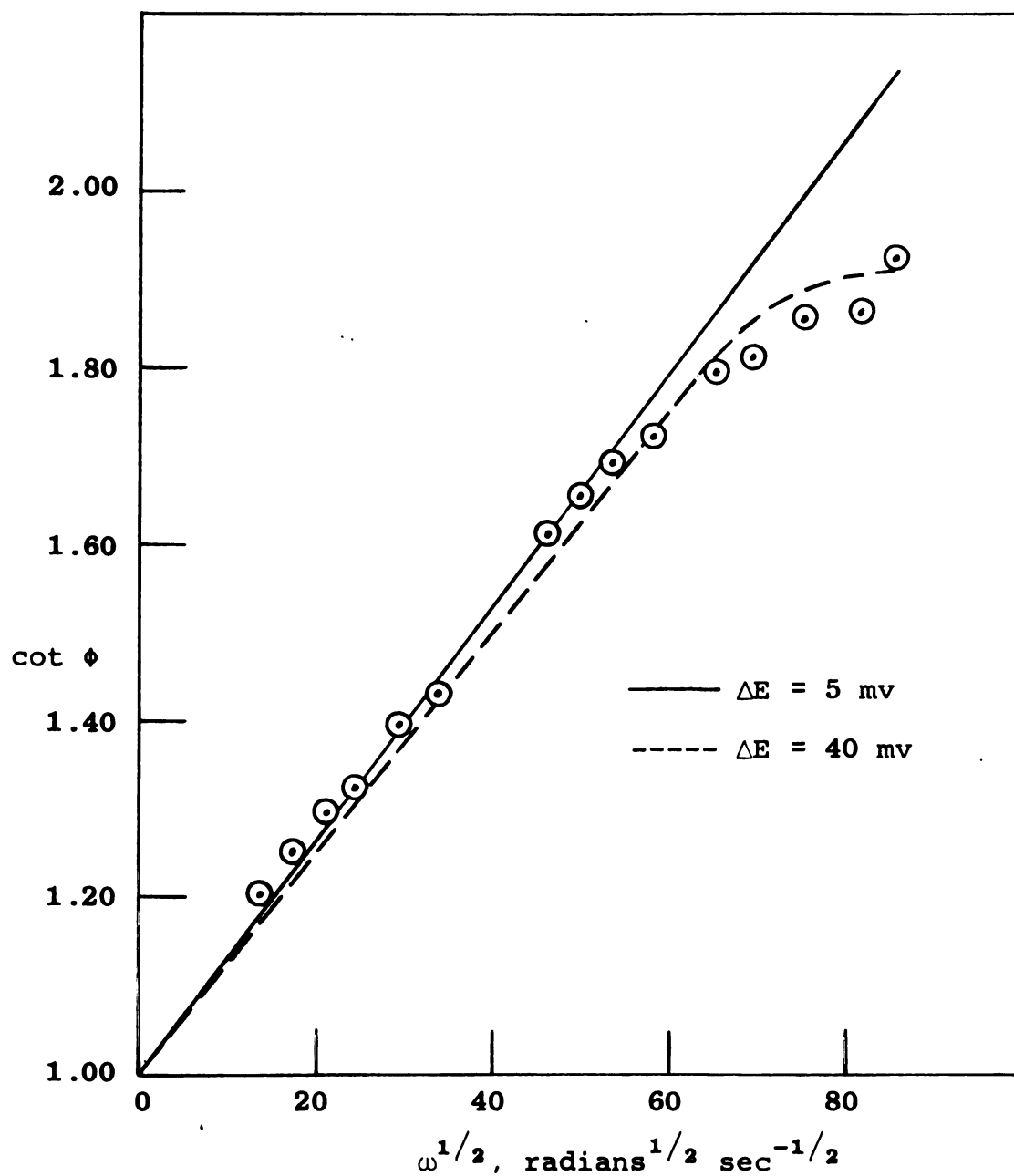


Figure 9. Variation of the corrected phase-angle with the square root of angular frequency for $5.0 \times 10^{-4} \text{ M Cd(II)}$ in $1.0 \text{ M H}_2\text{SO}_4$ at $E_{\text{d.c.}} = E_{1/2}^R$ and with an applied a.c. potential of 40 mv.

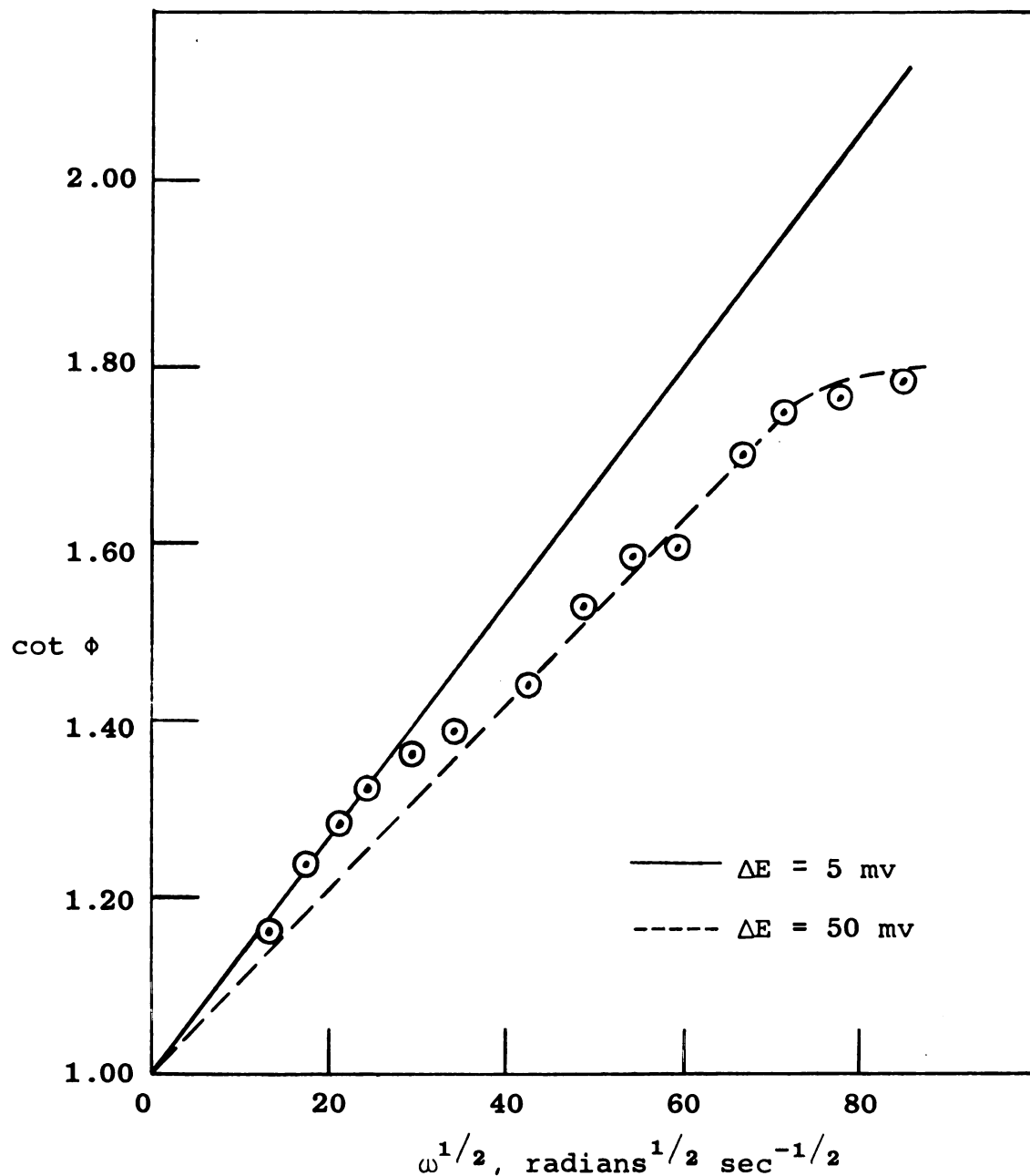


Figure 10. Variation of the corrected phase-angle with the square root of angular frequency for $5.0 \times 10^{-4} \text{ M Cd(II)}$ in $1.0 \text{ M H}_2\text{SO}_4$ at $E_{\text{d.c.}} = E_{1/2}^R$ and with an applied a.c. potential of 50 mv.

deviation in quantities measured to evaluate $k_{a,h}$ would be expected at this d.c. potential. Several supporting electrolytes were employed, to obtain a variation in the value of $k_{a,h}$. The values necessary for correcting the phase-angles used in these plots are listed in Table II for both large and small amplitudes.

Table III lists the variation of the apparent heterogeneous rate constant with changing amplitude of the applied a.c. potential for $5.0 \times 10^{-4} \text{ M Cd(II)}$ in various supporting electrolytes, as well as the values of the slopes from the $\cot \phi$ versus $\omega^{1/2}$ plots used in the calculations. From Table III it is apparent that if $k_{a,h}$ is between 0.05 and 0.20 cm/sec, its value, as determined by the low amplitude equation does not vary markedly to the upper limit of amplitudes tested.

This is true even though the slopes demonstrate some variation, since $k_{a,h}$ values are not strongly sensitive to changes in the slope. Although the $k_{a,h}$ values show good agreement, some deviations in the data become apparent above 30 mv as is shown in Figures 9 and 10. These deviations occur as a distinct falling off from linearity in the $\cot \phi$ versus $\omega^{1/2}$ plots at frequencies above 800 Hz, with the magnitude of the error increasing directly with the frequency. In all of these plots, the intercept is still one on the $\cot \phi$ axis at zero frequency, as is predicted by Equation (23).

Table II. Experimental values for $C_{d.l.}$ and R_t , constants for the evaluation of $k_{a,h}$ in various supporting electrolytes.

Supporting Electrolyte	$C_{d.l.}, \mu F^*$		$R_t^*, \text{ ohms}$	
	10 mv	100 mv	10 mv	100 mv
1.0M Na_2SO_4	0.833	0.834	77.2	78.7
1.0M H_2SO_4	0.952	0.956	58.9	60.4
1.0M KNO_3	1.14	1.14	76.4	78.0

* Determined at $E_1^R/2$.

Table III. Variation of the apparent heterogeneous rate constant with changing amplitude of applied a.c. potential for 5.0×10^{-4} M Cd(II) in various supporting electrolytes evaluated at $E_{1/2}^R$.

ΔE	1.0M Na_2SO_4		1.0M H_2SO_4		1.0M KNO_3	
	slope $\times 10^2$	$k_{a,h'}$ cm/sec	slope $\times 10^2$	$k_{a,h'}$ cm/sec	slope $\times 10^3$	$k_{a,h'}$ cm/sec
5	2.69	0.06	1.32	0.15	3.66	0.62
10	2.28	0.07	1.35	0.14	2.11	1.07
15	2.40	0.07	1.45	0.13	2.41	0.94
20	2.24	0.07	1.38	0.14	2.39	0.95
25	2.26	0.07	1.37	0.14	2.43	0.93
30	2.21	0.08	1.30	0.15	2.18	1.04
35	2.20	0.08	1.21	0.16	1.82	1.24
40	2.14	0.08	1.26	0.15	1.46	1.55
45	2.03	0.08	1.21	0.16	1.50	1.51
50	2.13	0.08	1.06	0.18	1.13	2.00

In a recent monograph (9), Smith presents theoretical a.c. polarograms and a.c. polarographic phase-angles for a specific hypothetical system for ΔE of 5, 20, 30, and 40 mv. He demonstrates that $\cot \phi$ should decrease with increasing values of ΔE at the d.c. potential equal to $E_1^R/2$. Although the magnitudes of these changes cannot be compared directly with the experimental values listed above due to differences in constant parameters involved, one can see that the changes follow the same pattern. Smith's theoretical figures, as well as the above experimental data indicate that the changes are relatively small if the apparent heterogeneous rate constant is in the range 0.01 to 0.20 cm/sec, as is the case for Cd(II) in the various sulfate media.

Apparent heterogeneous rate constants for Cd(II) in 1.0M KNO₃ calculated from slopes obtained from Figure 11 show much greater variation than the values obtained in sulfate media. This is primarily due to the fact that the heterogeneous rate constant in this medium is considerably faster, and thus changes in the slope produce a much greater change in the value of $k_{a,h}$. Rate constants of the order of 1.0 cm/sec or faster are difficult to determine accurately by the technique of a.c. polarography. Figure 11 data were included to demonstrate what might be expected if large amplitudes are employed on these systems. Although the values of $k_{a,h}$ show deviation as ΔE increases, no deviation from expected behavior, that is linearity in the $\cot \phi$ versus $\omega^{1/2}$ plot with a resulting intercept of one on

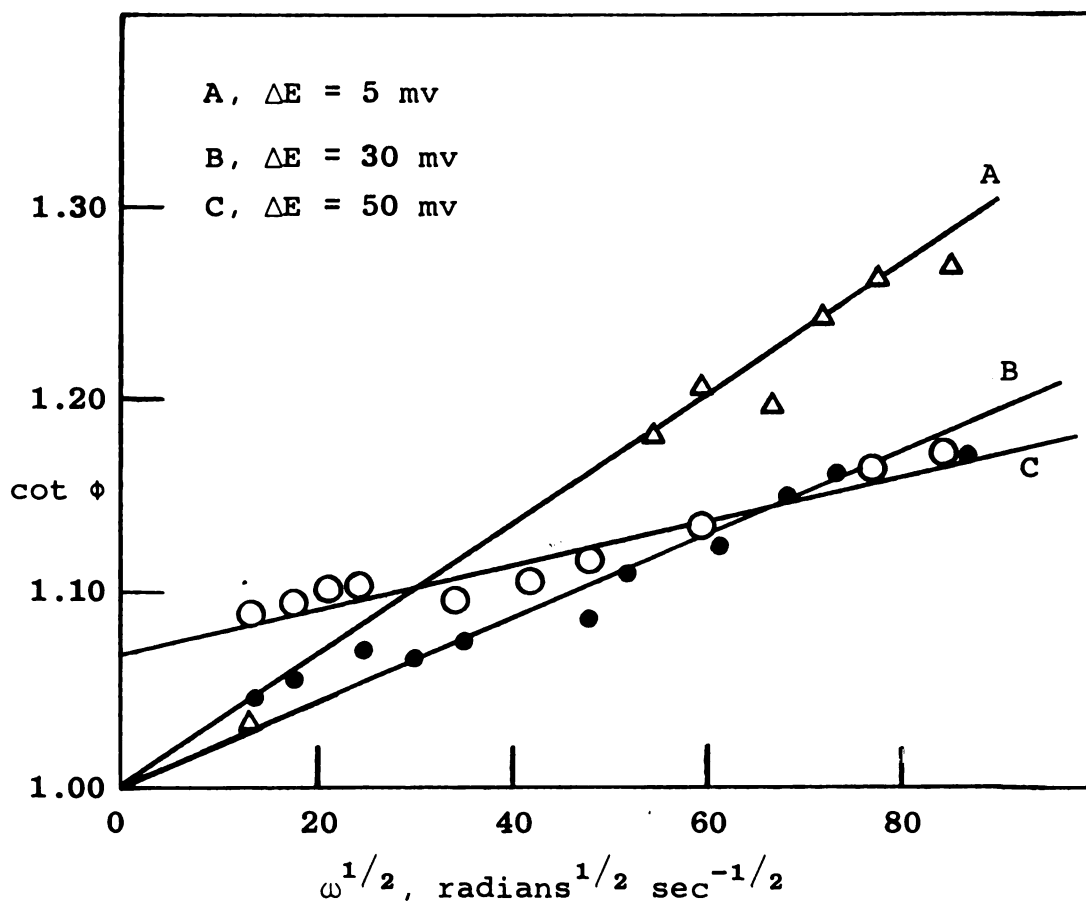


Figure 11. Variation of the corrected phase-angle with the square root of angular frequency for $5.0 \times 10^{-4} \text{M Cd(II)}$ in 1.0M KNO_3 at $E_{\text{d.c.}} = E_{1/2}^R$, and with applied a.c. potentials of 5, 30, and 50 mv.

the $\cot \phi$ axis at zero frequency, is observed until ΔE exceeds 30 mv. At this point, the $\cot \phi$ intercept at zero frequency becomes greater than one, the value predicted by theory. Again, the error becomes increasingly large as ΔE increases.

Evaluation of the Charge-Transfer Coefficient, α , at Large Amplitudes of the Applied A.C. Potential

The values of the charge-transfer coefficient, α , obtained from the ratio of slopes $(\frac{\Delta \cot \phi}{\Delta \omega^{1/2}})$ at two different d.c. potentials are tabulated in Tables IV and V as well as the values of the slopes used in the calculations. The $C_{d.1.}$ and R_t values used to correct the phase-angles to evaluate these slopes are listed in Table VI. Typical plots of $\cot \phi$ versus $\omega^{1/2}$, necessary for the evaluation of the above slopes, at $E_{d.c.} = E_{1/4}$ and $E_{d.c.} = E_{3/4}$ at various amplitudes of the applied a.c. potential are shown in Figures 12-21 for $5 \times 10^{-4} M$ Cd(II) in 1.0M sulfuric acid.

From Tables IV and V it can be seen that α values, as determined by the low amplitude equation, do not vary markedly up to an amplitude of 40 mv. Although the α values show good agreement, some deviations in the data become apparent above 20 mv, as is shown in Figures 13-16, and 18-21. These deviations occur as a distinct falling off from linearity in the $\cot \phi$ versus $\omega^{1/2}$ plots at frequencies above 600 Hz, with the magnitude of the error increasing directly with the frequency. In all of these plots, the

Table IV. Variation of the charge-transfer coefficient with changing amplitude of applied a.c. potential for $5.0 \times 10^{-4} \text{M Cd(II)}$ in $1.0\text{M H}_2\text{SO}_4$.

ΔE	Slope $\times 10^3$, at $E_{1/4}$	Slope $\times 10^2$, at $E_{3/4}$	α^a	α^b
5	8.71	1.57	0.23	0.22
10	8.29	1.58	0.20	0.21
15	8.00	1.46	0.22	0.20
20	8.21	1.59	0.20	0.20
25	8.26	1.54	0.21	0.22
30	8.27	1.58	0.20	0.20
35	8.37	1.54	0.22	0.22
40	8.23	1.40	0.25	0.26
45	8.31	1.39	0.26	0.26
50	7.76	1.38	0.23	0.24

^a Obtained from the ratio of slopes at $E_{3/4}$ and $E_{1/4}$, see Equation (32).

^b Obtained from an average of α 's evaluated from the ratio of slopes at $E_{1/2}$ and $E_{1/4}$, and $E_{3/4}$ and $E_{1/2}$, see Equation (32).

Table V. Variation of the charge-transfer coefficient with changing amplitude of applied a.c. potential for $5.0 \times 10^{-4} \text{M Cd(II)}$ in $1.0 \text{M Na}_2\text{SO}_4$.

ΔE	Slope $\times 10^2$, at $E_{1/4}$	Slope $\times 10^2$, at $E_{3/4}$	α^a	α^b
5	1.77	3.15	0.24	0.24
10	1.50	2.58	0.25	0.25
15	1.48	2.69	0.23	0.25
20	1.45	2.55	0.24	0.24
25	1.59	2.73	0.25	0.25
30	1.55	2.60	0.26	0.26
35	1.49	2.42	0.28	0.28
40	1.52	2.43	0.28	0.28
45	1.49	2.32	0.30	0.30
50	1.62	2.41	0.32	0.32

^a Obtained from ratio of slopes at $E_{3/4}$ and $E_{1/4}$, see Equation (32).

^b Obtained from an average of α 's evaluated from the ratio of slopes at $E_{1/2}$ and $E_{1/4}$ and at $E_{3/4}$ and $E_{1/2}$, see Equation (32).

Table VI. Experimental values for $C_{d.1}$ and R_t , constants for the evaluation of α in various supporting electrolytes.

Supporting Electrolyte	$E_{1/4}^*$		$E_{3/4}^*$	
	$C_{d.1}, \mu f$	$R_t, ohms$	$C_{d.1}, \mu f$	$R_t, ohms$
1.0M H_2SO_4	0.966	56.0	0.912	56.0
1.0M Na_2SO_4	0.844	78.7	0.816	74.3

* All values listed at $E_{3/4}$, as well as the values for 1.0M H_2SO_4 at $E_{1/4}$ were obtained with a different D.M.E. This D.M.E. was also used to obtain the other data necessary for the evaluation of α in these media.

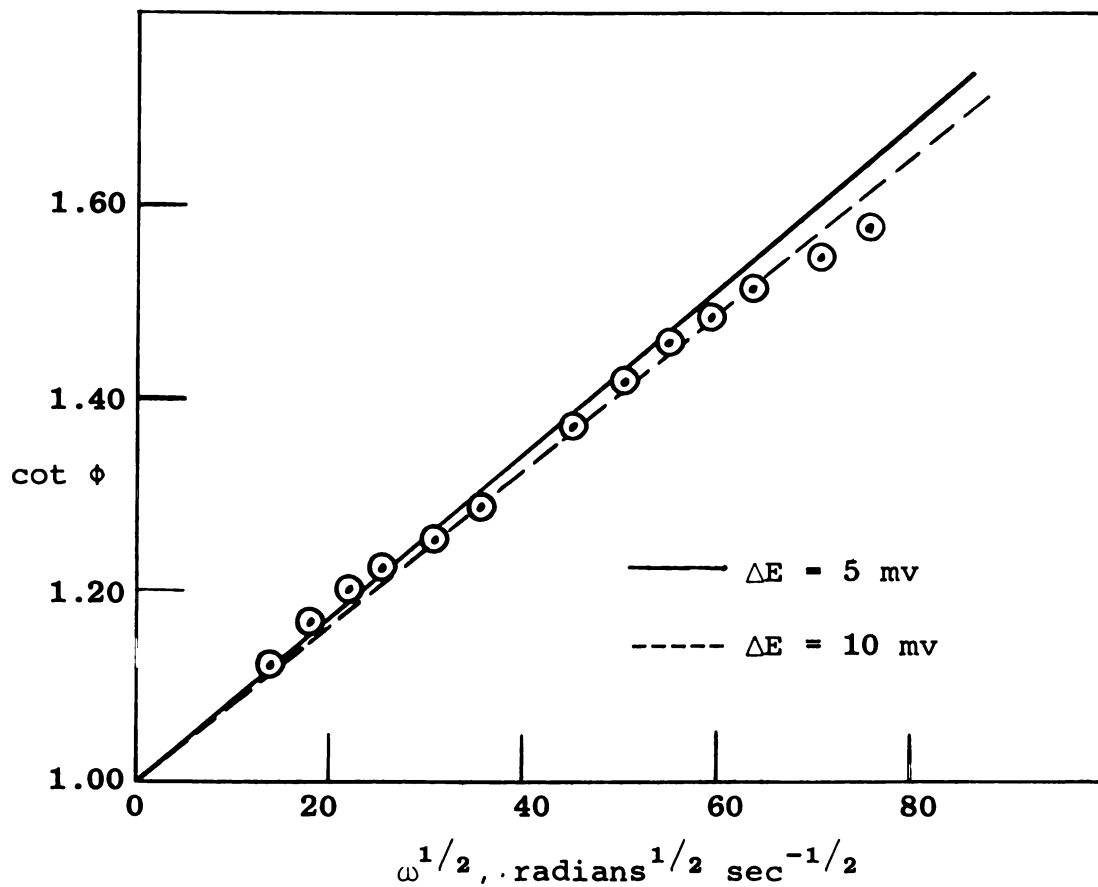


Figure 12. Variation of the corrected phase-angle with the square root of angular frequency for $5.0 \times 10^{-4} \text{ M Cd(II)}$ in $1.0 \text{ M H}_2\text{SO}_4$ at $E_{\text{d.c.}} = E_1/4$ and with an applied a.c. potential of 10 mv.

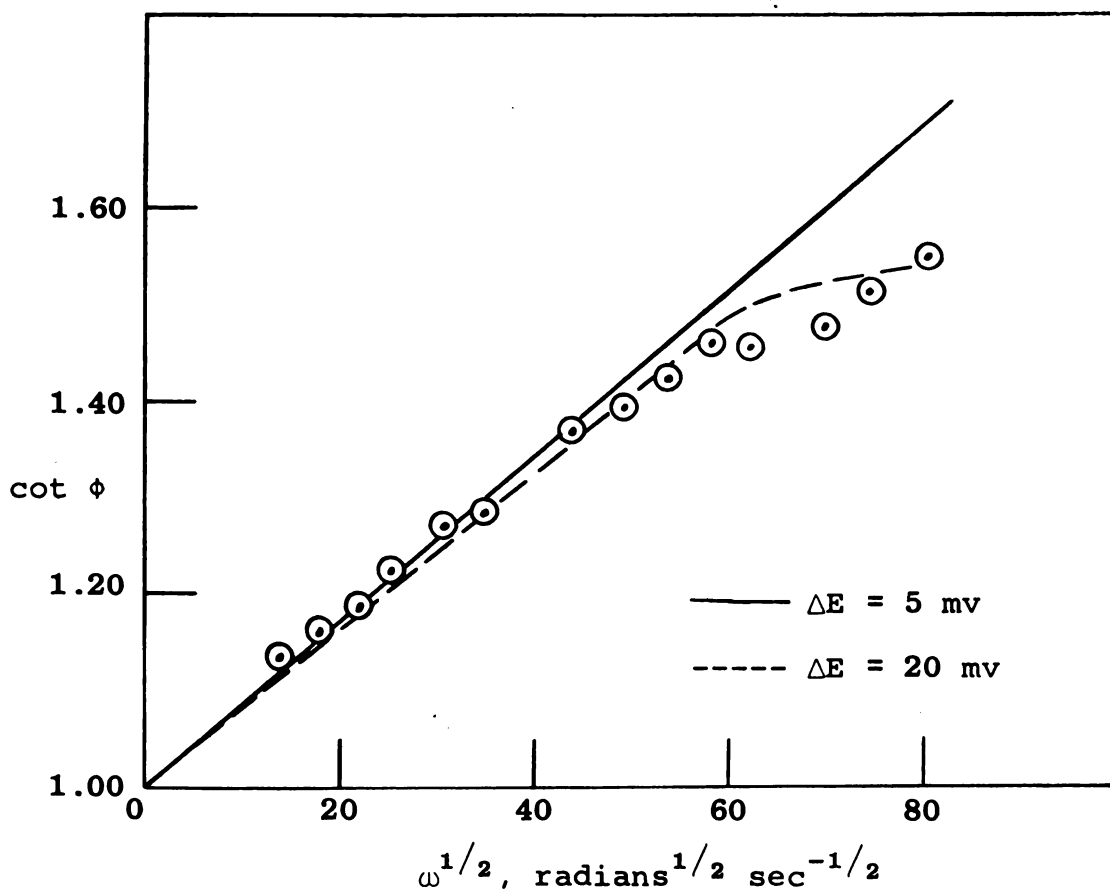


Figure 13. Variation of the corrected phase-angle with the square root of angular frequency for $5.0 \times 10^{-4} \text{M Cd(II)}$ in $1.0 \text{M H}_2\text{SO}_4$ at $E_{\text{d.c.}} = E_{1/4}$ and with an applied a.c. potential of 20 mv.

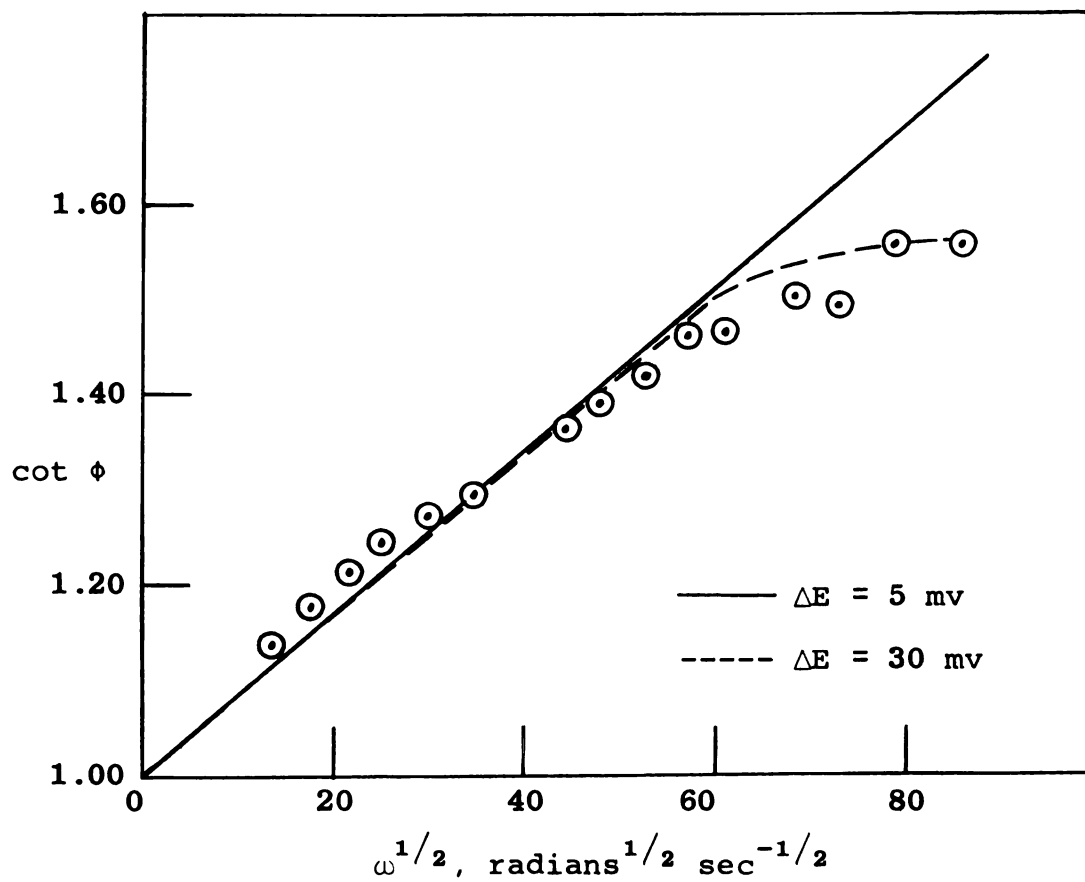


Figure 14. Variation of the corrected phase-angle with the square root of angular frequency for $5.0 \times 10^{-4} \text{ M Cd(II)}$ in $1.0 \text{ M H}_2\text{SO}_4$ at $E_{\text{d.c.}} = E_{1/4}$ and with an applied a.c. potential of 30 mv.

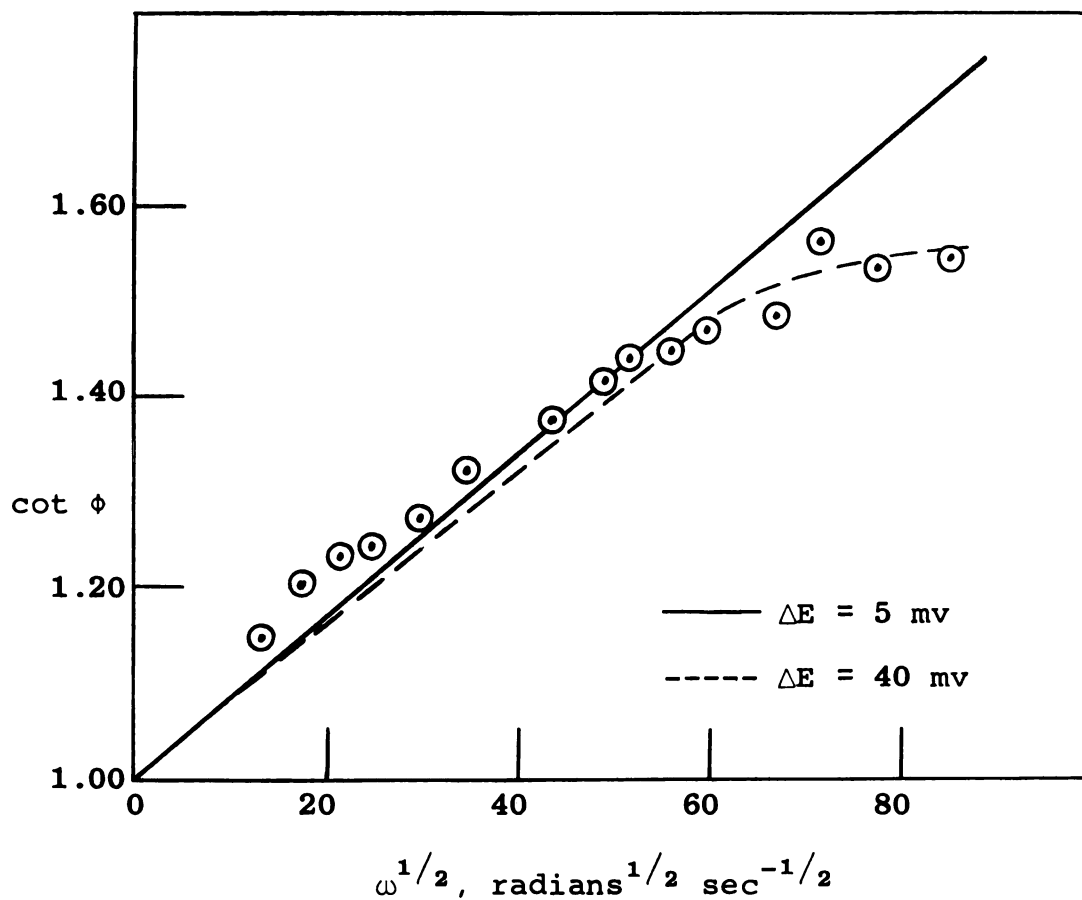


Figure 15. Variation of the corrected phase-angle with the square root of angular frequency for $5.0 \times 10^{-4} \text{ M Cd(II)}$ in $1.0 \text{ M H}_2\text{SO}_4$ at $E_{\text{d.c.}} = E_{1/4}$ and with an applied a.c. potential of 40 mv.

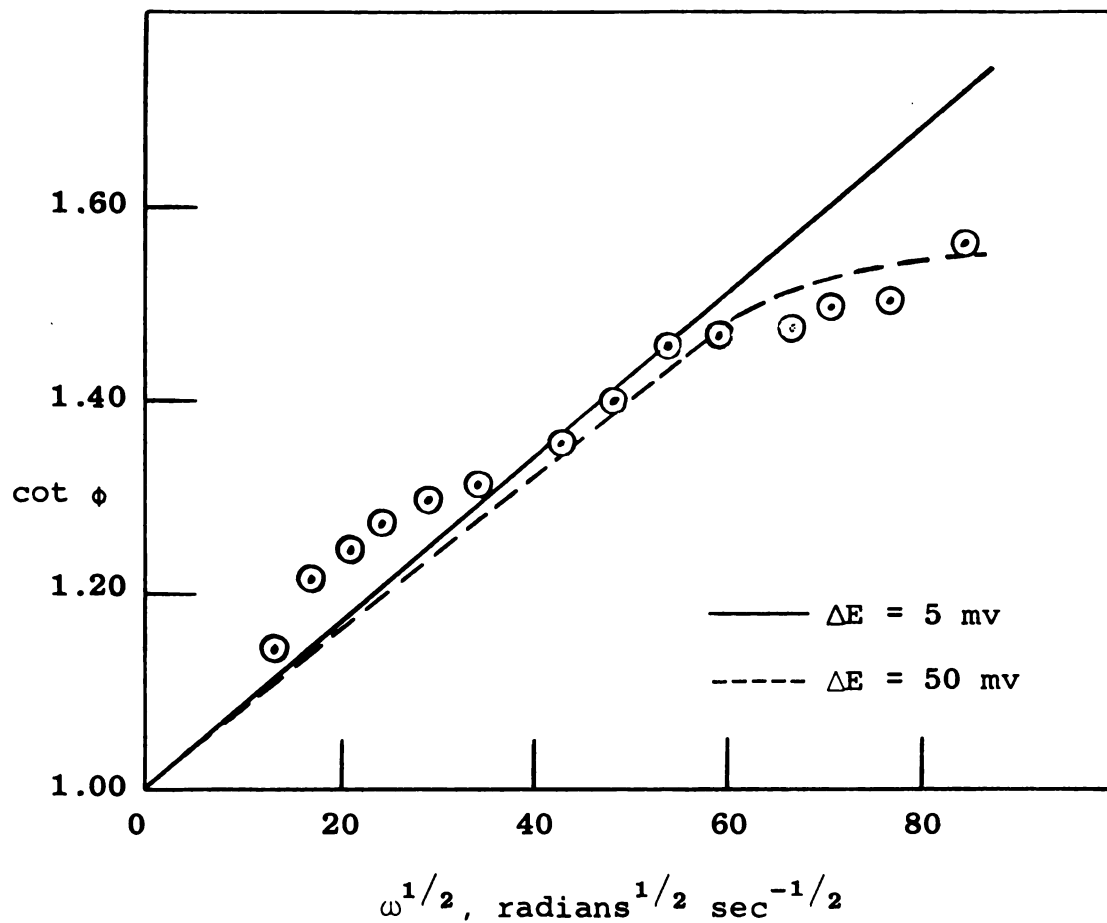


Figure 16. Variation of the corrected phase-angle with the square root of angular frequency for $5.0 \times 10^{-4} \text{ M Cd(II)}$ in $1.0 \text{ M H}_2\text{SO}_4$ at $E_{\text{d.c.}} = E_{1/4}$ and with an applied a.c. potential of 50 mv.

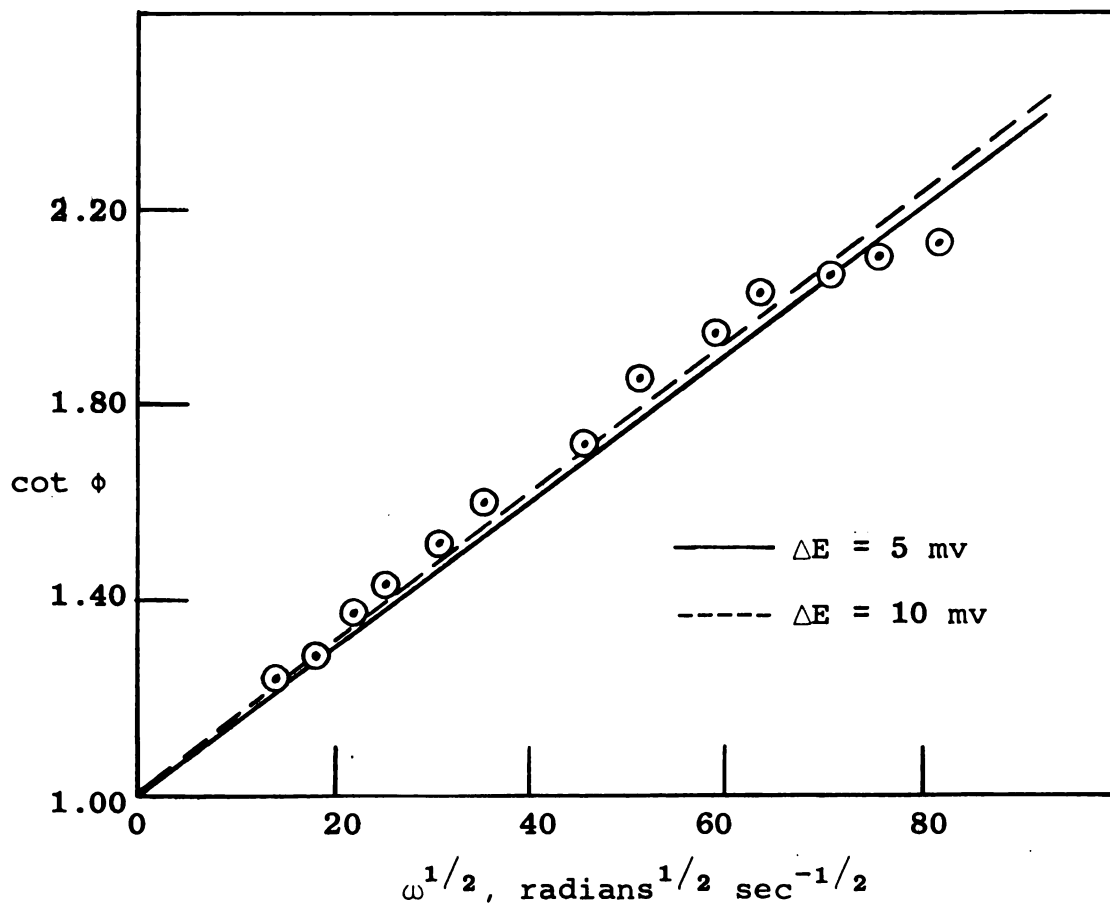


Figure 17. Variation of the corrected phase-angle with the square root of angular frequency for $5.0 \times 10^{-4} \text{ M Cd(II)}$ in $1.0 \text{ M H}_2\text{SO}_4$ at $E_{\text{d.c.}} = E_{3/4}$ and with an applied a.c. potential of 10 mv .

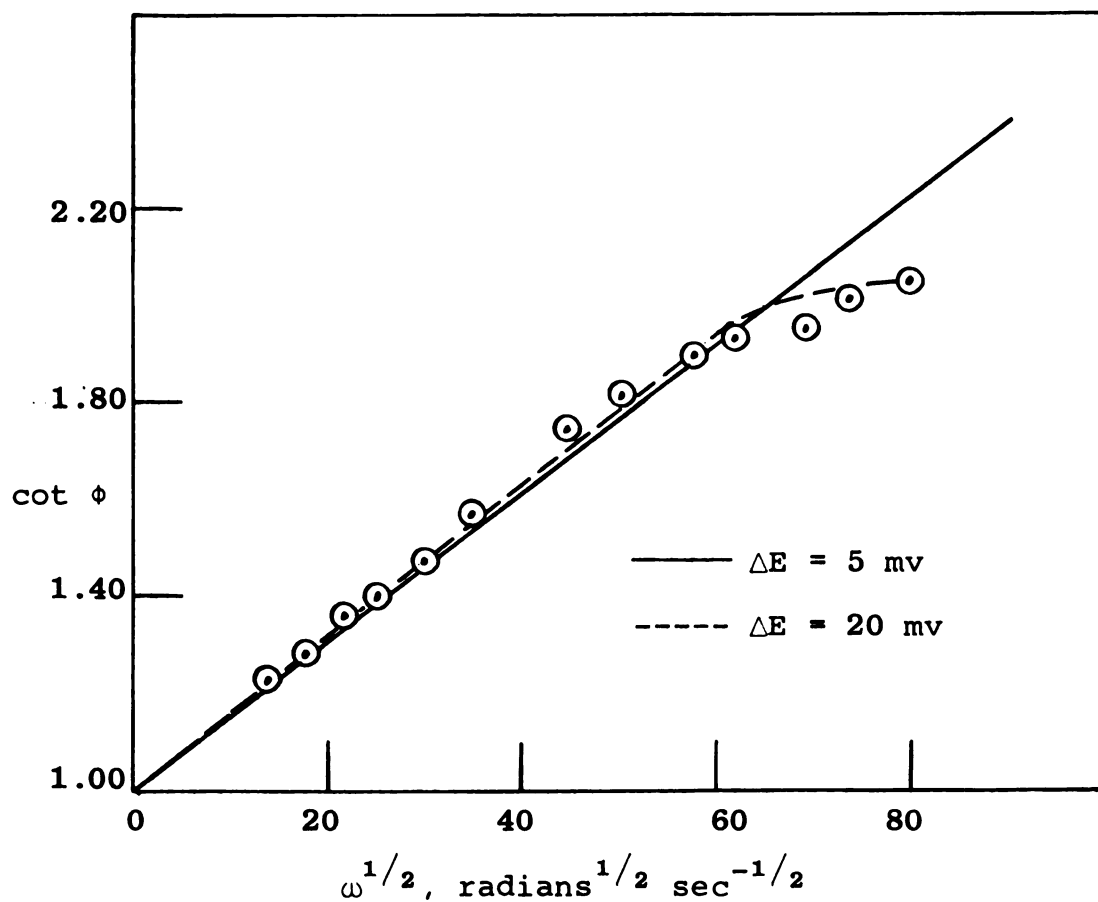


Figure 18. Variation of the corrected phase-angle with the square root of angular frequency for $5.0 \times 10^{-4} \text{ M Cd(II)}$ in $1.0 \text{ M H}_2\text{SO}_4$ at $E_{\text{d.c.}} = E_{3/4}$ and with an applied a.c. potential of 20 mv.

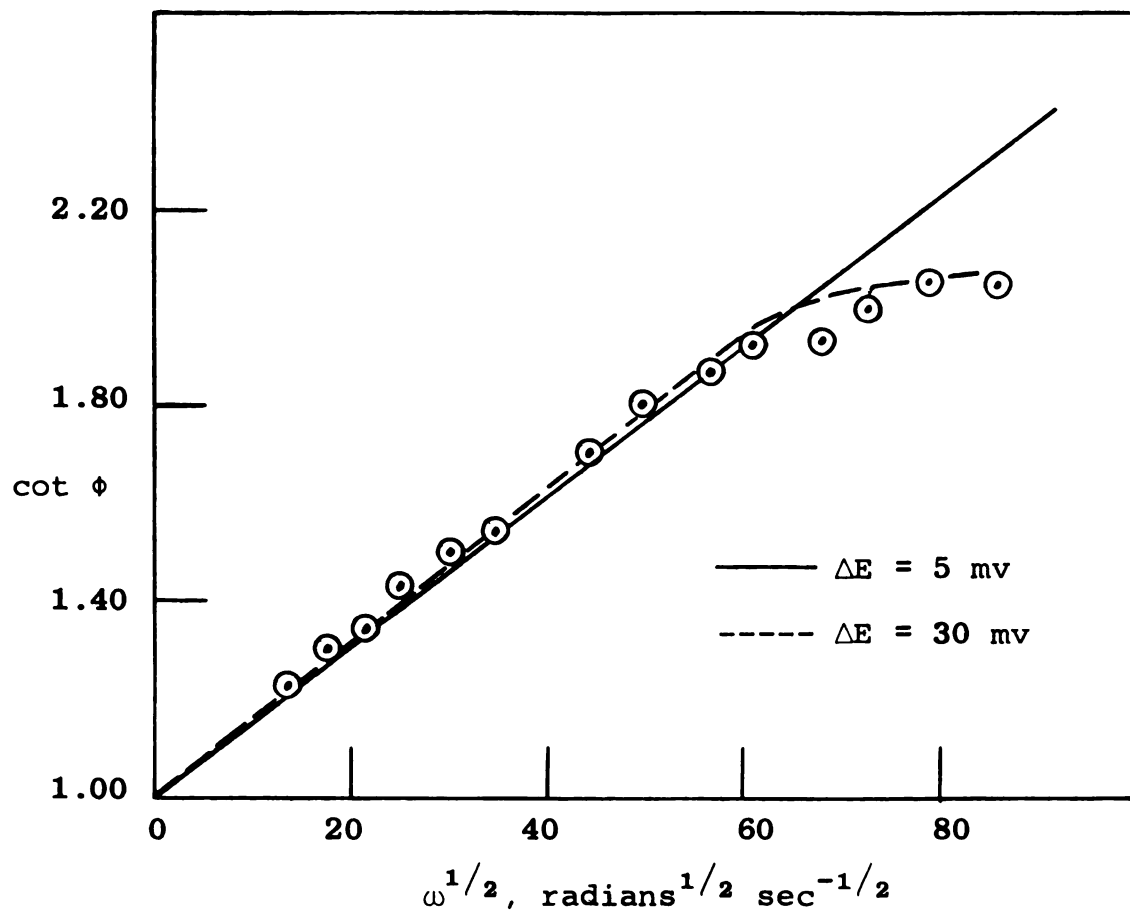


Figure 19. Variation of the corrected phase-angle with the square root of angular frequency for $5.0 \times 10^{-4} \text{M Cd(II)}$ in $1.0 \text{M H}_2\text{SO}_4$ at $E_{\text{d.c.}} = E_{3/4}$ and with an applied a.c. potential of 30 mv.

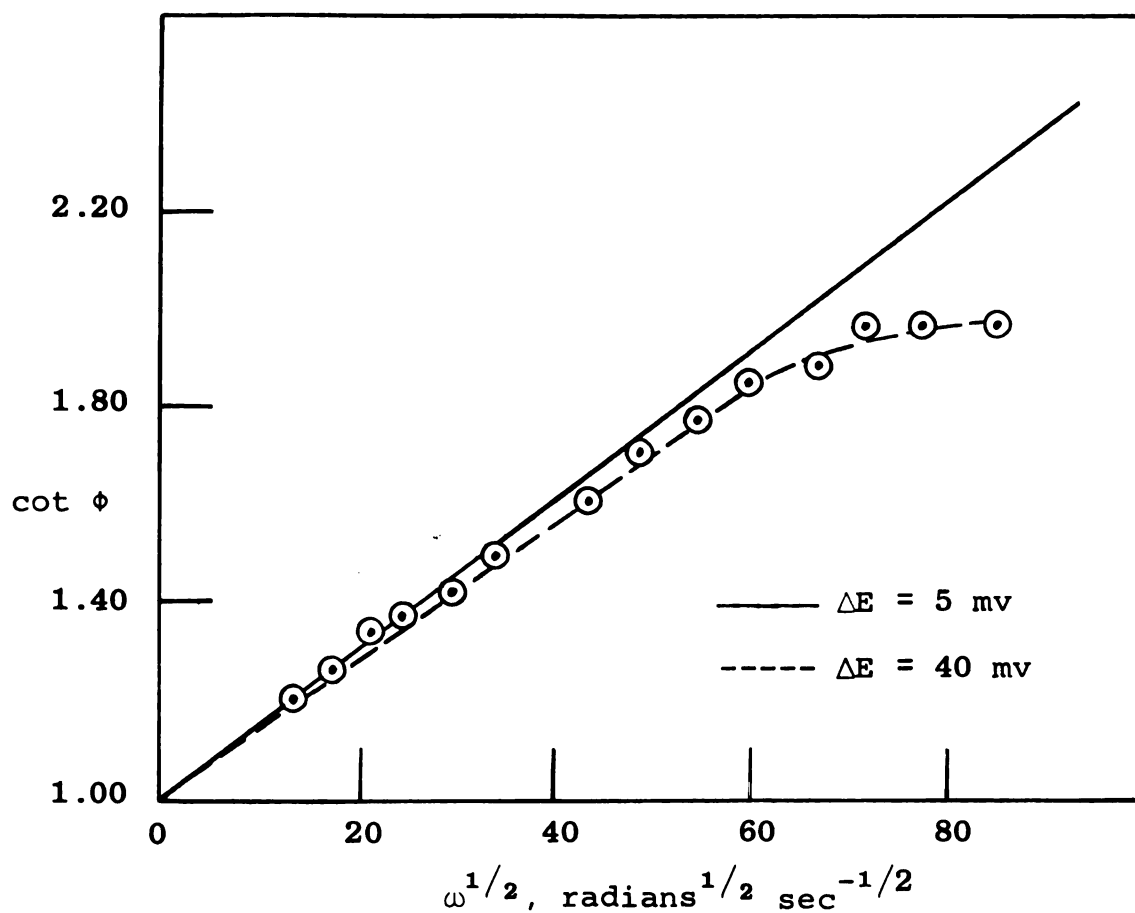


Figure 20. Variation of the corrected phase-angle with the square root of angular frequency for $5.0 \times 10^{-4} \text{M Cd(II)}$ in $1.0 \text{M H}_2\text{SO}_4$ at $E_{\text{d.c.}} = E_{3/4}$ and with an applied a.c. potential of 40 mv.

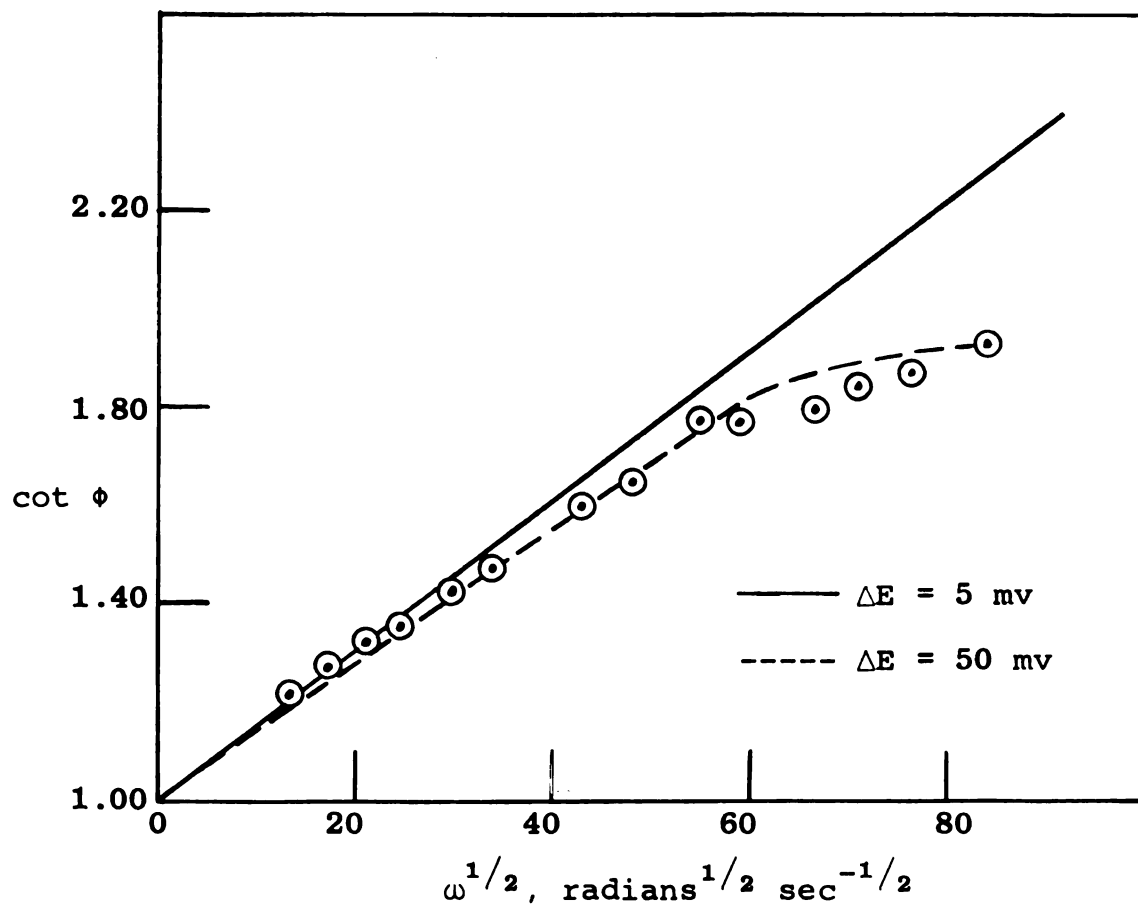


Figure 21. Variation of the corrected phase-angle with the square root of angular frequency for $5.0 \times 10^{-4} \text{ M Cd(II)}$ in $1.0 \text{ M H}_2\text{SO}_4$ at $E_{\text{d.c.}} = E_{3/4}$ and with and applied a.c. potential of 50 mv .

intercept is one on the $\cot \phi$ axis at zero frequency, as is predicted by Equation (23).

By comparing Figures 12-21 to Figures 5-10, it is obvious that although the deviations from linearity in these plots occur at lower amplitudes and frequencies at $E_1/4$ and $E_3/4$ than at $E_1^R/2$, the changes in the slope $\frac{\Delta \cot \phi}{\Delta \omega^{1/2}}$ are smaller at $E_1/4$ and $E_3/4$. This leads to the conclusion that acceptable values of α can be obtained at large amplitudes even though α is more sensitive to changes in the slope of $\cot \phi$ versus $\omega^{1/2}$ plots than is $k_{a,h}$. Smith's (9) plots of $\cot \phi$ versus $E_{d.c.}$ for a hypothetical system at amplitudes of 5, 20, 30, and 40 mv predict smaller slope changes at $E_1/4$ and $E_3/4$, than at $E_1^R/2$, in agreement with the results obtained in this study. These conclusions are only valid for charge-transfer coefficients of systems having apparent heterogeneous rate constants in the range 0.01 to 0.20 cm/sec as is the case for Cd(II) in the various sulfate media.

Charge-transfer coefficients for Cd(II) in 1.0M KNO_3 were not evaluated, since the ratio of the uncertainties in the slopes became competitive with the values of the ratio of the slopes.

Evaluation of $\Delta \bar{\Phi}_E$

Values of the applied d.c. potential, the potential at the point of zero charge and the integral double-layer capacitance used to calculate $\Delta \bar{\Phi}_E$ for 1.0mM Cd(II) in

various supporting electrolytes, are tabulated in Table VII. The values of E listed are equal to $E_{1/2}^R$ for 1.0 mM Cd(II) in each supporting electrolyte, respectively, since the apparent heterogeneous rate constants were evaluated at this d.c. potential. The concentrations employed in the calculation of $\Delta\Phi_E$ were the bulk concentrations of each ionic species expressed in moles/cm³ and the charges (z_i) were the ionic charges with their respective signs.

Evaluation of k_h , the Corrected Heterogeneous Rate Constant

Table VIII lists the uncorrected and corrected values of the heterogeneous rate constants for 1.0mM Cd(II) in various supporting electrolytes, as well as the $\Delta\Phi_E$ and charge-transfer coefficients used for the corrections. The values of $k_{a,h}$ and α listed in Table VIII were obtained in a previous study in this laboratory by Frischmann (10). Low amplitude a.c. potentials (5 mv) were employed and the experiments and calculations were performed exactly as described in this work. The value of z_0 necessary for the calculation of the corrected heterogeneous rate constant is the ionic charge (with the appropriate sign) of the oxidized form. The oxidized form was assumed to be Cd⁺⁺ in all supporting electrolytes except the chloride media, where the various chloride complexes of cadmium were considered.

From Table VIII, it is apparent that the only cadmium species which gives a value for the corrected heterogeneous rate constant which correlates with corrected values in the

Table VII. Values of the applied d.c. potential, E , the potential at the point of zero charge, E_z , and the integral double-layer capacitance, K_i , used to calculate $\Delta\Phi_E$ for 1.0mM Cd(II) in various supporting electrolytes.

Supporting Electrolyte	E^a versus SCE, v	E_z versus SCE, v	$K_i, \mu\text{f}/\text{cm}^2$
0.5M Na_2SO_4	-0.604	-0.427 ^b	22.0
1.0M Na_2SO_4	-0.606	-0.427 ^b	22.6
0.5M H_2SO_4	-0.594	-0.427 ^b	23.2
1.0M H_2SO_4	-0.597	-0.427 ^b	25.7
1.0M KNO_3	-0.585	-0.573 ^c	30.9
1.0M HClO_4	-0.607	-0.544 ^c	29.5
1.0M NaClO_4	-0.573	-0.544 ^c	31.5
1.0M KCl	-0.642	-0.517 ^b	29.9
1.0M NaCl	-0.635	-0.518 ^b	29.1
1.0M HCl	-0.644	-0.517 ^b	30.2

$$^a E = E_{1/2}^R.$$

^bData from Conway (39).

^cData from Kolthoff and Lingane (40).

Table VIII. Comparison of apparent and corrected heterogeneous rate constants for 1.0mM Cd(II) in various supporting electrolytes.

Supporting Electrolyte	$\Delta \bar{E}_E^a, v$	α	$k_{a,h}^b, \text{cm/sec}$	$k_h^b, \text{cm/sec}$
0.5M Na ₂ SO ₄	0.0375	0.21	0.076	0.77
1.0M Na ₂ SO ₄	0.0301	0.20	0.063	0.41
0.5M H ₂ SO ₄	0.0377	0.27	0.14	1.2
1.0M H ₂ SO ₄	0.0321	0.24	0.12	0.81
1.0M KNO ₃	0.0108	0.50	0.63	0.96
1.0M HClO ₄	0.0431	0.26	0.25	3.0
1.0M NaClO ₄	0.0254	0.31	0.34	1.3
1.0M KCl	0.0676	0.44	1.2	1.6(CdCl ⁺) 23. (Cd ⁺⁺) 0.12(CdCl ₂) 0.0084(CdCl ₃ ⁻) 0.0006(CdCl ₄ ⁼)
1.0M NaCl	0.0636	0.46	1.2	1.5(CdCl ⁺)
1.0M HCl	0.0687	0.42	0.94	1.4(CdCl ⁺)

^aCalculated with the aid of Equation (40) using data from Table VII.

^bCalculated with the aid of Equation (42).

other supporting electrolytes, is CdCl^+ . This is not unreasonable, since various cadmium-chloride complexes are undoubtedly present in the bulk of the solution, and the species most prevalent in the bulk of the solution, are not necessarily the species most prevalent in the electrical double-layer, where the charge-transfer rate is determined.

It should be emphasized that the corrections which were made did not take specific adsorption into account. Therefore if adsorption is an important complication in the chloride media, the conclusions which were drawn about the species which undergoes charge-transfer are not valid. However, no evidence of adsorption complications was observed by Frischmann while recording a.c. polarograms with the chloride media.

From Table VIII, it is also apparent that values of corrected heterogeneous rate constants for Cd(II) in various supporting electrolytes cover a considerably smaller range than the apparent (uncorrected) rate constants. The range of uncorrected values is from 0.063 cm/sec for 1.0mM Cd(II) in 1.0M Na_2SO_4 to 1.2 cm/sec for 1.0mM Cd(II) in 1.0M KCl , while the range of corrected values in the same respective supporting electrolytes is 0.41 cm/sec to 1.6 cm/sec.

Even though the overall range of the corrected values is definitely smaller than the overall uncorrected range, several anomalies are obvious in Table VIII. The corrected

rate constants in the various sulfate media are not in as good agreement as would be expected, and the corrected value of k_h in 1.0M HClO_4 appears to be too large. These facts, however, may be explained by the following considerations. Values for corrected rate constants depend directly on experimentally determined values of the apparent rate constants which are at best known within ± 20 per cent. Therefore, the fact that uncorrected rate constants for Cd(II) in 0.5M and 1.0M Na_2SO_4 have very similar values may be fortuitous.

Since errors in the values of quantities used to calculate the corrected rate constants would also contribute to the above deviations, it was decided to calculate a probable range of values for the corrected rate constants in each supporting electrolyte. To accomplish this, maximum and minimum values for $\Delta\phi_E$ were calculated for each supporting electrolyte, by assuming the following reasonable error levels in experimentally determined values necessary for the calculation of $\Delta\phi_E$: $C_i \pm 3$ per cent, E and $E_z \pm 3$ mv, $K_i \pm 6$ per cent.

The stated error levels were employed with the aid of Equation (40) to calculate the two extreme values for $\Delta\phi_E$ for various supporting electrolytes listed in Table IX. These values for $\Delta\phi_E^{\max}$ and $\Delta\phi_E^{\min}$, values of $k_{a,h} \pm 20$ per cent, and $\alpha \pm 0.03$ units, were employed with the aid of Equation (42) to calculate the probable ranges for values of the corrected heterogeneous rate constants for

Table IX. Probable ranges for values of corrected heterogeneous rate constants for 1.0mM Cd(II) in various supporting electrolytes, calculated from error estimates.

Supporting Electrolyte	$\Delta\Phi_E^{\max}, v$	$\Delta\Phi_E^{\min}, v$	$k_h^{\max}, \text{cm/sec}$	$k_h^{\min}, \text{cm/sec}$
0.5M Na ₂ SO ₄	0.0397	0.0353	1.2	0.50
1.0M Na ₂ SO ₄	0.0321	0.0277	0.61	0.27
0.5M H ₂ SO ₄	0.0399	0.0354	1.8	0.76
1.0M H ₂ SO ₄	0.0341	0.0297	1.1	0.54
1.0M KNO ₃	0.0178	0.0047	1.6	0.59
1.0M HClO ₄	0.0493	0.0362	6.0	1.5
1.0M NaClO ₄	0.0327	0.0182	2.6	0.68
1.0M KCl	0.0728	0.0614	2.6(CdCl ⁺)	1.1
			45. (Cd ⁺⁺)	12.
			0.22(CdCl ₂)	0.061
			0.020(CdCl ₃ ⁻)	0.0036
			0.0018(CdCl ₄ ⁼)	0.0002
1.0M NaCl	0.0688	0.0574	2.3(CdCl ⁺)	0.96
1.0M HCl	0.0740	0.0626	2.4(CdCl ⁺)	0.87

1.0mM Cd(II) in various supporting electrolytes listed in Table IX.

The ranges of values for the corrected heterogeneous rate constants for Cd(II) overlap in all cases, except in 1.0M Na₂SO₄ and 1.0M HClO₄. Even in these media, the limits of the probable ranges are close to overlapping the limits of rate constants in the other supporting electrolytes. This would indicate that the Frumkin double-layer effect is an important factor in explaining the reported ranges of values for aqueous Cd(II) in the supporting electrolytes considered in this work. Exact agreement among the rate constants corrected in this manner would not be expected, since activity effects and migration of the electroactive species within the diffuse double-layer also have an effect on the rate of the electron-transfer.

Activity Effects

Although activity corrections were not attempted because of the high concentration of supporting electrolytes, some conclusions can be drawn concerning the results of such corrections. From Equation (44) it can be shown that corrections for activity coefficients different from unity would result in an increase in the corrected heterogeneous rate constants. Since the activity corrections should be larger in the various sulfate media than in the perchlorate or chloride media, the probable overlap in the rate constant

values corrected for both Frumkin double-layer effects, and for activity effects would be more complete than the overlap apparent in the values tabulated in Table IX.

SUGGESTED FURTHER WORK

Since it has been demonstrated that it is possible to apply considerably larger a.c. potentials than was formerly accepted, to evaluate $k_{a,h}$ and α with the aid of $\cot \phi$ versus $\omega^{1/2}$ plots for Cd(II), it would also be interesting to test experimentally, phase-angle dependence on the d.c. potential, for this system at a selected low and high frequency, employing the larger a.c. amplitudes. Plots of $\cot \phi$ versus d.c. potential would be obtained, from which conclusions regarding the mechanism of the electrode process could be drawn.

If a preceding or succeeding chemical reaction proceeds at a rate comparable to the charge-transfer rate, departure from linearity is observed in the $\cot \phi$ versus $\omega^{1/2}$ plots as well as changes in the normal bell-shaped wave obtained when $\cot \phi$ is plotted against applied d.c. It would be interesting to test at large amplitudes, systems which demonstrate the kinetic complications mentioned above at low amplitudes, to establish whether the expected deviations are enhanced.

The small amplitude a.c. polarographic experiments for Cd(II) should be repeated with the supporting electrolyte concentration reduced to 0.05 to 0.1M. This would allow an estimation of the activity coefficients for Cd(II) in the various supporting electrolytes with the aid of the extended Debye-Hückel equation. The apparent heterogeneous rate constants could then be corrected for Frumkin double-layer effects and activity effects to determine if the

rate constant values converge to a single value. This work would also demonstrate the effect of supporting electrolyte concentration on the charge-transfer rate.

The small amplitude experiments should also be repeated for Cd(II) in supporting electrolytes containing ions such as I^- or SCN^- which are readily adsorbed. Adsorption corrections could then be attempted for the various known adsorbing supporting electrolytes at various concentrations, to test the validity of accepted adsorption corrections.

Double-layer corrections including adsorption effects as well as the Frumkin correction (no adsorption) could then be made and the corrected rate constants could be compared to those obtained for media containing ions which are not strongly adsorbed.

SUMMARY AND CONCLUSIONS

Experiments were performed with aqueous solutions of Cd(II) in various supporting electrolytes at amplitudes of the applied a.c. potential from 5 to 50 mv, to determine the effect of increasing amplitudes on values of $k_{a,h}$ and α , calculated with the aid of the low amplitude equations.

Apparent heterogeneous rate constants evaluated from $\cot \phi$ versus $\omega^{1/2}$ plots for $5.0 \times 10^{-4} \text{M}$ Cd(II) in 1.0M H_2SO_4 at 5, 10, 15, 20, 25, 30, 35, 40, 45, and 50 mv were 0.15, 0.14, 0.13, 0.14, 0.14, 0.15, 0.16, 0.15, 0.16, and 0.18 cm/sec, respectively. Charge-transfer coefficients for the same system at the same respective amplitudes were 0.22, 0.21, 0.20, 0.20, 0.22, 0.20, 0.22, 0.26, 0.26, and 0.24. For an identical Cd(II) concentration in 1.0M Na_2SO_4 , the range in $k_{a,h}$ values was 0.06 to 0.08 cm/sec and the charge-transfer coefficients varied from 0.24 to 0.32 for the stated amplitudes.

Although acceptable values of α and $k_{a,h}$ were obtained for the above systems, deviations from linearity in the $\cot \phi$ versus $\omega^{1/2}$ plots above 30 mv and 800 Hz at $E_{1/2}^R$ and above 20 mv and 600 Hz at $E_{1/4}$ and $E_{3/4}$ were observed. The deviations increased with increasing amplitude in all cases. Intercepts of one on the $\cot \phi$ axis as predicted by the low amplitude equations, were obtained in the $\cot \phi$ versus $\omega^{1/2}$ plots at all d.c. potentials and all a.c. amplitudes.

Studies of $5.0 \times 10^{-4} \text{M}$ Cd(II) in 1.0M KNO_3 gave $k_{a,h}$ values from 0.62 cm/sec at 5 mv, to 2.0 cm/sec at 50 mv. Intercepts of greater than one on the $\cot \phi$ axis were

obtained in the $\cot \phi$ versus $\omega^{1/2}$ plots, a departure from accepted low amplitude theory, at applied amplitudes greater than 30 mv. Charge-transfer coefficients could not be obtained for this system, since the ratio of the uncertainties in the slopes necessary for the calculation, became competitive with the values of the ratio of the slopes.

The results of this study show that if the apparent heterogeneous rate constant is in the range 0.01 to 0.50 cm/sec, acceptable values of α and $k_{a,h}$ can be obtained with the aid of low amplitude equations, with no deviation from theory up to amplitudes of at least 30 mv. This is considerably larger than the $8/n$ mv limit of low amplitude theory, which would be 4 mv for Cd(II).

Frumkin double-layer corrections were applied to apparent heterogeneous rate constants for 1.0mM aqueous Cd(II) in 0.5M Na₂SO₄, 1.0M Na₂SO₄, 0.5M H₂SO₄, 1.0M H₂SO₄, 1.0M KNO₃, 1.0M NaClO₄, 1.0M HClO₄, 1.0M KCl, 1.0M NaCl, and 1.0M HCl, and the following corrected rate constants were obtained respectively: 0.77, 0.41, 1.2, 0.81, 0.96, 1.3, 3.0, 1.6, 1.5, and 1.4 cm/sec. These values have considerably less spread than the uncorrected values, which have a range of 0.063 cm/sec in 1.0M Na₂SO₄, to 1.2 cm/sec in 1.0M KCl. The only cadmium species in chloride media which yields rate constant values which agree with the remaining corrected rate constants, is CdCl⁺.

Maximum and minimum probable values of $\Delta \Phi_E$, the potential difference necessary for the Frumkin double-layer

corrections on the apparent heterogeneous rate constant were calculated by assuming reasonable error levels of ± 6 per cent for the integral double-layer capacitance, ± 3 per cent for the bulk concentration of each ionic species present in the solution, and ± 3 mv for the applied d.c. potential and the same level for the potential at the point of zero charge.

Assuming also an error of ± 0.03 units in the charge-transfer coefficient and ± 20 per cent error in $k_{a,h}$, the probable ranges of the corrected rate constants were calculated. These ranges overlapped for all supporting electrolytes with the exception of 1M Na_2SO_4 and 1M HClO_4 .

Activity corrections were not made, since it is difficult to obtain values of the activity coefficient of the oxidized species in the various 1.0M supporting electrolytes, but it is predicted that the corrections would make the overlap of the rate constants in the various media even more complete.

The results of this study show that Frumkin double-layer corrections cause the range of the apparent heterogeneous rate constants for aqueous Cd(II) in the media investigated, to converge. Thus, other complications such as preceding reactions or specific adsorption do not significantly influence the rate of the charge transfer.

Even though the Frumkin double-layer corrections help to explain the observed range of rate constants for Cd(II) in the various media it would appear that Cd(II) is not

the ideal choice as an electrochemical test ion, since it is known that Cd(II) forms various complexes with commonly used supporting electrolyte anions.

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APPENDIX

Computer Programs

Many of the calculations reported in this work were performed on a Control Data type 3600 digital computer. The programs were written in FORTRAN language, since this system is widely used and compatible with most modern computers. The programs and instructions for their use are listed below. Derivations and references for the formulas employed in the programs are included in the text.

Program A.C.

This program is used to correct the measured phase-angle for uncompensated solution resistance and double-layer capacitance effects. It is also used to calculate the least squares slope of the resulting data assuming an intercept of one at zero frequency. The following data are read in:

Card 1 - IM, ID, IY, which is the date in numbers,
columns 1 - 2 = month
3 - 4 = day
5 - 6 = year

Card 2 - N RUN, which is the total number of sets
of data
columns 1 - 2

Card 3 - SENT, which is a sentence describing the set
of data
columns 1 - 80 - will print out any numbers,
letters or symbols

Card 4 - N DATA, which is the total number of data
points in a given set of data

columns 1 - 2

Card 6 - constants for a given set of data

columns 1 - 10, VOLT which is ΔE in volts in the
text

columns 11 - 20, R which is R_t in ohms in the text.

Card 7 - data

columns 1 - 10, PHIP, which is ϕ' in degrees in
the text

columns 11 - 20, OMEG, which is the frequency in
Hz in the text

columns 21 - 30, CURR, which is the current in
amperes in the text

(must be in E field and right hand justi-
fied e.g. $6.925 \times 10^6 = 6.925E - 006$)

columns 31 - 40, D.C., which is the d.c. potential
with its sign in the text

columns 41 - 50, CAPDL, which is the measured
double-layer capacity, $C_{d.l.}$, in
farads in the text

(must be in E field and right hand
justified)

Cards 8 - etc. - new data, same format as card 7

Repeat cards 3 - 7 if desired

The output involves printing the date, the sentence, PHIP,
OMEGA, VOLT, R, CAPDL, CURR, COTAN, ANGLE, DC, ROMEGA,

and SLOPE, where PHIP is now the angle in radians, OMEG is the angular frequency, VOLT, R, CAPDL, CURR, and D.C. are the same as on the data cards, and COTAN is the cotangent of the corrected phase-angle which is $\cot \phi$ in the text, ANGLE is the corrected phase-angle in degrees, ROMEGA is the square root of the angular frequency, which is $\omega^{1/2}$ in the text, and SLOPE is the least squares slope with an intercept of 1.0 for the plot of $\cot \phi$ versus $\omega^{1/2}$. All of the above numbers are printed in scientific notation with 6 figures.

The performance of this program was checked by hand calculation.

```

PROGRAM AC
  DIMENSION SENT(50),X(50),Y(50)
  READ 600, IM, ID, IY
  600 FORMAT (3I2)
  READ 10, NRUN
  2 READ 5, (SENT(I), I=1,10)
  5 FORMAT (10A8)
  READ 10, NDATA
  10 FORMAT (I2)
  PRINT 15
  ND=NDATA
  15 FORMAT (1H1////////)
  PRINT 20
  20 FORMAT (40X, 22HCORRECTED PHASE ANGLES//)
  PRINT 21, (SENT(I), I=1,5)
  21 FORMAT (40X, 5A8////////)
  I=0
  PRINT 601, IM, ID, IY
  601 FORMAT (100X, 7H DATE I2, 1H/ I2, 1H/ I2////////)
  PRINT 25
  250FORMAT (4X, 4HPHIP, 9X, 5HOMEGA, 7X, 4HVOLT, 11X, 1HR, 11X,
15HCAPDL, 7X, 4HCURR, 10X, 5HCOTAN, 8X, 5HANGLE, 11X, 2HDC,
210X, 6HROMEGA////)
  READ 30, VOLT, R
  30 FORMAT (2F10.0, E10.0, F10.0, E10.0)
  PHIP = 3.141592*PHIP/180.
  OMEG = 2.*3.14159*OMEG
  ROMEQ = SQRTF(OMEG)
  A = CURR/VOLT
  B = A*R
  TEMP = A*(COSF(PHIP) - B)
  TEMP2 = A*SINF(PHIP) - OMEG*CAPDL*(1. + B**2. - 2.*B*COSF(PHIP))
  ANS = TEMP/TEMP2
  ANGLE = 1./ANS

```

```

ANGLE = ATANF(ANGLE)
ANGLE = 180.*ANGLE/3.141592
PRINT 40, PHIP, OMEG, VOLT, R, CAPDL, CURR, ANS, ANGLE, DC, ROMEQ
I=I+1
  X(I)=ROMEG
  Y(I)=ANS
40 FORMAT (10E13.5)
  NDATA = NDATA - 1
  IF(NDATA)45,45,1
45 CONTINUE
  NRUN = NRUN - 1
  SXY=0
  SX=0.
  SX2=0.
  D=ND
  DO 100 I=1,ND
    SX2=SX2+X(I)**2
    SXY=SXY+X(I)*Y(I)
100 SX=SX+X(I)
    B=(SXY-SX)/SX2
  PRINT 121
121 FORMAT(////)
  PRINT103,B
103 FORMAT(7HSLOPE = E13.5)
  IF(NRUN)46,46,2
46 END

```

Program Frumkin

This program calculates a value for ROOT, which is $(\Phi_H - \Phi_S)$ or $\Delta\Phi_E$ in the text. The following data are read in:

Card 1 - ANAM, which is a sentence describing the set of data

columns 2 - 80 - will print out any numbers, letters, or symbols

Card 2 - data

columns 1 - 10, IN, which is the number of guesses

columns 11 - 20, AI, which is K_i in μf in the text

columns 21 - 30, POT, which is $(E - E_z)$ in volts, in the text

columns 31 - 40, CP, which is C_+^S in moles/cm³, in the text

columns 41 - 50, CM, which is C_-^S in moles/cm³, in the text

columns 51 - 60, ZP, which is Z_+ in the text

columns 61 - 70, ZM, which is Z_- without its sign, in the text

Card 3 - etc. XG, the guesses, 1 per card

columns 1 - 10

Repeat Cards 1 - 3, if desired

The output involves printing the sentence, the ROOT, which is the answer for $\Delta\Phi_E$ in volts to 9 figures with its sign, and GUESS, the value printed as XG on card 3. The

output also includes the number of trials necessary to find the ROOT, or SYSTEM DIVERGES, with the value when the number of trials necessary to calculate the ROOT exceeds 99.

The performance of this program was checked by calculating values reported in the literature by Delahay (32), using Delahay's data. Another check was made by putting computer values for ΔG_E back into Equation (40) to be certain that this made both sides of the equation equal.

```

PROGRAM FRUMKIN
  DIMENSION ANAM(10)
  1 READ3, (ANAM(J), J=1, 10)
  3 FORMAT(10A8)
  IF (EOF, 60) 2, 105
  105 PRINT4, (ANAM(J), J=1, 10)
  4 FORMAT(///10A8/)
  READ12, IN, AI, POT, CP, CM, ZP, ZM
  AI=AI*1.0E-006
  12 FORMAT(I10, 6F10.4)
  DO100M=1, IN
  READS, XG
  5 FORMAT( F10.4)
  X1=XG
  I=1
  102 VAR1=2.745E-009*(CP*EXPF(-39.06*ZP*X1)-CP+CM*EXPF(39.06*ZM*X1)-CM)
  VAR2=.5*(1./SQRTF(VAR1))
  VAR3=1.072E-007*CM*ZM*EXPF(39.06*ZM*X1)
  DERX=-AI-VAR2*(1.072E-007*CP*ZP*EXPF(-39.06*ZP*X1)+VAR3)
  EQNX=-AI*(POT-X1)-SQRTF(VAR1)
  X2=X1-(EQNX/DERX)
  IF (ABSF((X2-X1)/X2)-.00005) 100, 100, 101
  101 X1=X2
  I=I+1
  IF (I-99) 102, 103, 103
  103 PRINT 10
  10 FORMAT(15HSYSTEM DIVERGES )
  100 PRINT 11, X1, XG, I
  11 FORMAT(6HROOT =F11.8, 3X7HGUESS =F8.4, 6HLOOKED14, 13H TO FIND ROOT )
  GO TO 1
  2 END

```

Program Correct

This program calculates a value for HET, which is k_h , or k_h^* , the corrected heterogeneous rate constant in the text. This rate constant may be corrected for activity effects, Frumkin double-layer effects (k_h), or both (k_h^*).

The following data are read in:

Card 1 - a sentence describing the set of data

columns 1 - 49 - will print out any numbers, letters,
or symbols

Card 2 - data

columns 1 - 10, AHET, which is $k_{a,h}$, the apparent
heterogeneous rate constant
in the text

columns 11 - 20, QN, which is n in the text

columns 21 - 30, ZO, which is z_0 , with its sign,
in the text

columns 31 - 40, DELPHI, which is $\Delta\phi_E$ in volts,
in the text

columns 41 - 50, FO, which is f_0 in the text

columns 51 - 60, FR, which is f_R in the text

columns 61 - 70, A, which is α in the text

Repeat cards 1 - 2 if desired.

The output involves printing the sentence, and the corrected heterogeneous rate constant to six figures.

The performance of this program was checked by hand calculation.

```

      PROGRAM CORRECT
10 READ 2
   2 FORMAT(49H
      IF (EOF,60)4,5
   5 PRINT 2
      READ 1,AHET,QN,ZO,DELPHI,FO,FR,A
   1 FORMAT(7F10.0)
      B=1.0-A
      HET=AHET/(FO**B*FR**A*EXPF(39.06*DELPHI*(A*QN-ZO)))
      PRINT 3,HET
   3 FORMAT(//'*CORRECTED HETEROGENOUS RATE CONSTANT =*,F11.5///)
      GO TO 10
   4 END

```