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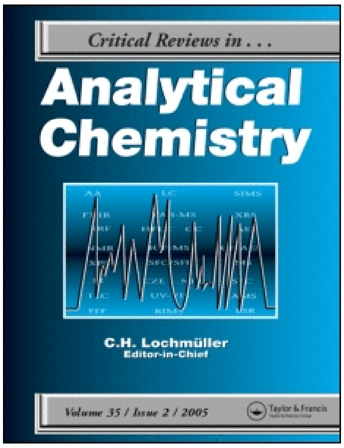

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RECENT DEVELOPMENTS IN ALTERNATING CURRENT POLAROGRAPHY

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I. INTRODUCTION

Shortly after the termination of World War II, independent efforts centered at opposite ends of our planet were undertaken to investigate the applicability of sinusoidally varying test signals of small amplitude in electrochemical measurements. In Australia, a team led by Professor B. Breyer, often referred to as the "father of ac polarography,"[1] pursued a broad spectrum of investigations which led to numerous publications[2] and to the introduction of much of the familiar "jargon" associated with the field--e.g., "ac polarography," "tensammetry," "summit potential," etc. Simultaneously, several groups in Europe, notably those led by Randles,[3-5] and Gerischer[6] effected some elegant applications of small amplitude ac measurements in electrochemical kinetic investigations. Both the Australian and European Schools were concerned with measuring the response of an electrochemical cell (under conditions like those employed in polarography) to a sinusoidal perturbation of small amplitude and with surveying possible applications of such measurements. However, during the early part of this period the isolation of the two schools led to substantial differences in approach and nomenclature so that casual observers sometimes concluded that two distinctly different methodologies were evolving. The Australian group favored an approach which was very similar to conventional (or dc) polarography. A sinusoidally varying potential of small amplitude (10 to 20 millivolts) was superimposed on the usual direct potential (obtained as the sum of an initial voltage and a ramp or linearly increasing voltage) and, with the aid of suitable filters, the resulting fundamental harmonic alternating current was measured as a function of the applied direct potential. The technique was referred to as "ac polarography" and the recording of the amplitude of the alternating current versus dc potential was the "ac polarogram." Such polarograms are characterized by the now familiar peak-shaped response illustrated in Figure 1, the peak being centered in the region of the rising part of the corresponding dc polarogram (compare Figures 2A and 2B)–i.e., where the electrolysis of a particular species (a "faradaic process") ensues. Direct observation of the alternating current magnitude was favored by the Australian workers, apparently because of its compatibility with automatic recording techniques and the desirability of this type of readout format in analytical applications, which was one of their primary concerns. On the other hand, the workers in Europe were primarily interested in electrochemical kinetic applications, where the accuracy of measurement is especially critical. At the time in question the impedance bridge was the most accurate means of characterizing an ac response and, consequently, it became the method of choice with the European school, despite the tedious, manual, point-by-point operations demanded by this device. They formulated data presentation formats in terms of impedance properties rather than currents and referred to their technique as "faradaic impedance measurement." Of course, one should recognize that the distinctions in approach and terminology are only apparent and that the two schools were pursuing fundamentally the same measurement. Faradaic impedance measurements and ac polarography in fact refer to two basically equivalent approaches whereby one can characterize the response of a polarographic cell to a sinusoidal disturbance of small amplitude. The impedance characteristics as a function of direct potential can be transformed into an ac polarogram (including phase angle relations) using the generalized form of Ohm's law, and vice versa.

As the advantages of small-amplitude ac measurements became more widely recognized in the 1950's, a variety of modifications of the original techniques were suggested. The desire to minimize contributions of the sensitivity-limiting background alternating current associated with charging the electrical double layer stimulated the development of techniques such as "square-wave polarography," "phase-selective ac polarography," "second harmonic ac polarography," "faradaic rectification measurements," "intermodulation polarography," and "radio-frequency polarography."[2,7,8] Square-wave polarography utilizes a small-amplitude square wave instead of the sinusoidal applied potential and effects current measurement only near the end of each square-wave half-cycle. The latter operation discriminates against the double-layer charging current, which decays much more rapidly than the faradaic current during a half-cycle. A substantial enhancement of sensitivity is realized. Similar gains are achieved through phase-sensitive detection of the in-phase component of the ac response to a sinusoidal applied potential. This operation substantially reduces the contribution of the charging current component, which is nearly 90° out of phase with the faradaic component. Workers also recognized that phase-selective ac polarography would play an important role in kinetic-mechanistic studies where complete characterization of the ac response (measurement of *both* amplitude and phase relations) is usually necessary. Phase-sensitive detection of the in-phase and quadrature alternating currents provides the desired information. Recognition that the faradaic process is significantly more non-linear than the double-layer charging process stimulated interest in measuring higher-order current components arising from faradaic non-linearity because of the promise of an almost purely faradaic response. Under normal ac polarographic conditions the current function contains, in addition to the fundamental harmonic, a variety of minor ac components at integral multiples of the applied frequency whose measurement is referred to as "second harmonic ac polarography," "third harmonic ac polarography," etc. Also included is a dc component (the "faradaic rectification" component) which exists only in the presence of the applied sinusoidal potential–i.e., it exists *in addition to* the "normal" dc polarographic current. Faradaic non-linearity gives rise to an ac component at the difference frequency (ω_1 - ω_2) whenever one simultaneously applies two sinusoidal potentials of frequencies ω_1 and ω_2. Its measurement is referred to as "intermodulation polarography." Although it was introduced much earlier, rf polarography may be considered to be a rather complex relative of intermodulation polaro-

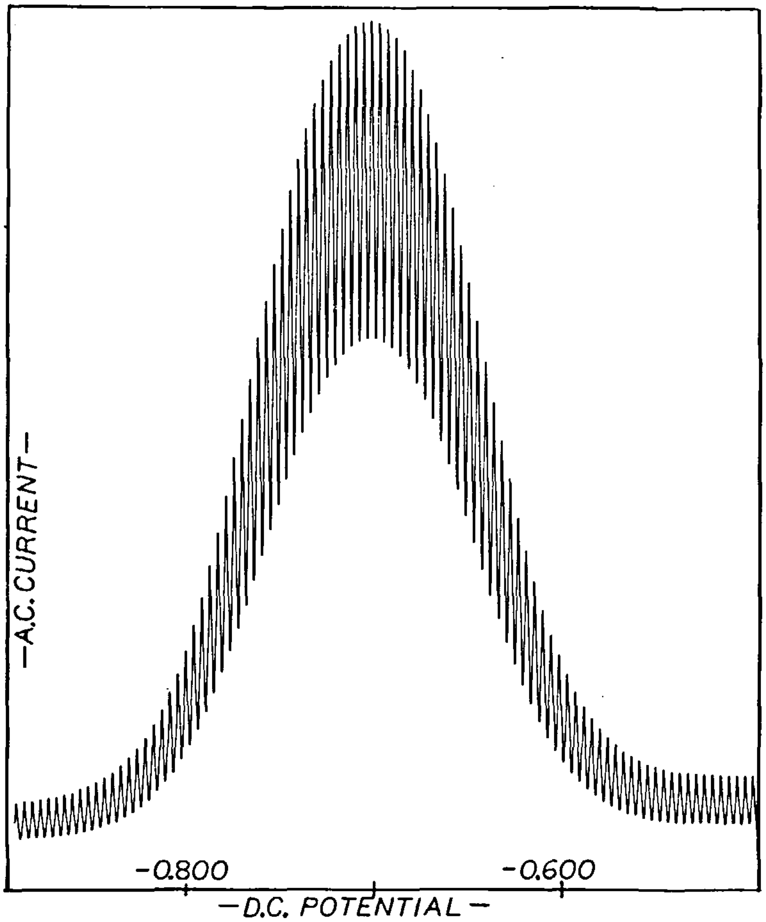

FIGURE 1. Fundamental harmonic ac polarogram. System: 3 x 10^{-3} M Cd^{2+}, 1.0 M Na_2SO_4. Applied: 10 mV peak-to-peak 320-Hz sine wave,dc scan rate 25 mV/min. Measured: 320-Hz component, ordinate uncalibrated. [Reprinted from *Anal. Chem.*, 35, 1811 (1963) by courtesy of the American Chemical Society.]

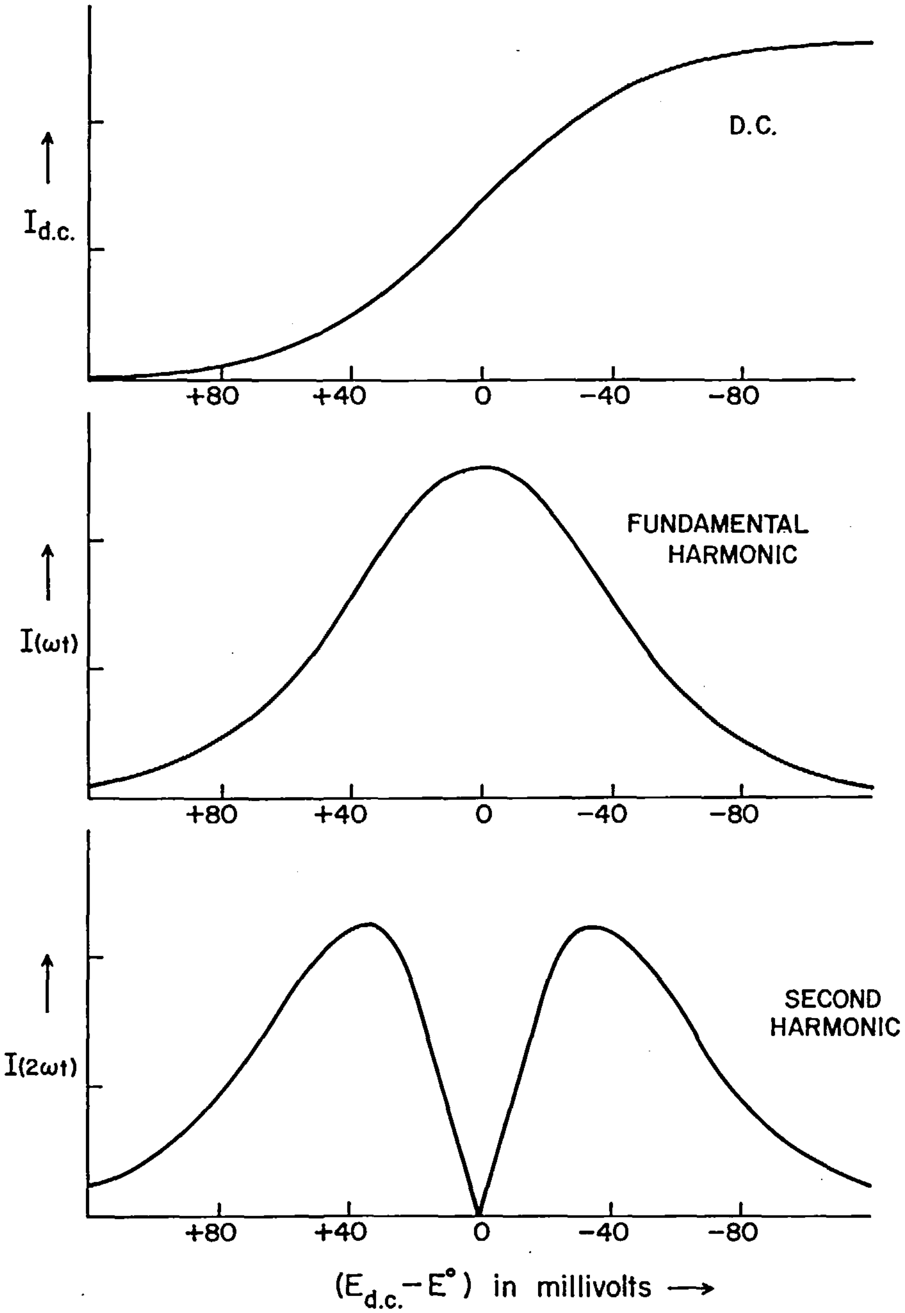

FIGURE 2. Dc, fundamental, and second harmonic ac polarograms with a diffusion-controlled system. (AC polarograms depicted are total current amplitude polarograms–i.e., "conventional" fundamental and second harmonic polarograms. Smooth curves represent currents at the ends of the drop lives–i.e., drop oscillations are not shown). (Reprinted from reference 87 by courtesy of M. Dekker, Inc.)

graphy. Polarograms of these higher-order current components are often characterized by multiple peaks in association with a single dc polarographic process, as illustrated in Figure 2C. The anticipated relatively small contribution of the double-layer charging current to such polarograms is realized.

In addition to witnessing the introduction of numerous modifications in the control and measurement of the experimental parameters, the decade of the 50's also was a period when most of the important phenomenological effects associated with small-amplitude ac measurements were catalogued. Of particular significance was the recognition that a "wave" on the ac polarogram need not be associated with a faradaic process. In the potential realm where a surfactant is desorbed (without electrolysis) one can obtain a sharp peak which is characteristic of the kinetics and thermodynamics of the adsorption-desorption process. The Australian school referred to such peaks as "tensammetric waves" to distinguish them from the normal "faradaic waves." Such observations led to the realization that the small-amplitude ac response of a polarographic cell represented a most useful means of investigating adsorption processes at electrodes and the recognized scope of applicability of such techniques was extended. In a somewhat less dramatic development it was recognized that careful observation of the often-maligned "background current" in ac polarography represented a most useful way of obtaining information on the characteristics of the electrical double layer.

By the end of the 1950's the "ground rules" had been established as far as the variety and applicability of small-amplitude ac measurements were concerned. The various observations that could be made in characterizing the cell response to small-amplitude periodic perturbations had been identified and tested. The types of phenomena which could be usefully investigated by such techniques had been recognized. Little occurred during the 1960's to change this overall picture, and this decade is best characterized as one of consolidation and maturation. The already voluminous array of analytical applications was expanded in number and scope. Various rather large gaps in the quantitative theory were filled. More challenging systems were attacked in quantitative kinetic-mechanistic investigations. Instrumental improvements dramatically enhanced the efficiency with which ac polarographic measurements can be perfomed and lifted certain restrictions related to solvent choice. Finally, the 1960's marked the appearance of the first truly detailed reviews of the subject in question, which are particularly important to those beginning in the field. A detailed monograph by Breyer and Bauer,[2] published in 1963, summarized many of the important developments up to approximately 1961. A review by this writer in 1966[7] emphasized basic principles, instrumentation, and data treatment. Most recently Sluyters and Sluyters-Rehbach[8] presented a detailed summary of physical chemical applications of small amplitude ac measurements which very effectively covered the relevant literature through the year 1967.

Within these three reviews, encompassing 571 pages devoted to ac polargraphy and related techniques, the reader can find an adequate explanation of the various techniques and concepts referred to rather tersely in the foregoing paragraphs. The above brief historical sketch was presented partly to quickly acquaint the uninformed with the origins of the field, but mainly to establish the subject matter which this writer considers to be within the confines of the topic "ac polarography" and which is appropriate for coverage in this review. Thus, I shall neither recognize the quite artificial distinction between ac polarography and faradaic impedance measurements, nor confine considerations to be the more conventional observables involving the fundamental harmonic current. Developments in all of the various techniques mentioned above involving applications to non-faradaic as well as faradaic processes are viewed as being within the scope of this review. Although a broad subject area is considered relevant, this writer was spared an unduly lengthy task because considerable selectivity has been invoked with regard to the timing and significance of publications in the field. Because the literature has received careful scrutiny through the year 1967,[2,7,8] with a few exceptions the present review will address itself to developments during the 3½ year period, 1968 to mid-1971. In addition, it is the philosophy of the *CRC Critical Review Journals* to present reviews which are not complete literature surveys, but which attempt to focus primarily on the most significant developments. Consequently, the present review represents a distillation of material from a list of nearly 350 publications which this writer has encountered over the 3½ year period in question. The average of nearly 100 publications per year is a measure of the intensity of the research activity concerned with ac polarography and related techniques. The fact that the present review's bibliography contains 145 entries out of the nearly 350 possibilities (excluding a number of supporting references not involving new work) is a measure of the level of selectivity invoked in preparing this review.

II. THEORETICAL DEVELOPMENTS

Progress in the application of modern electrochemical techniques depends to a large measure on the successful development of a quantitative theoretical framework. In the present context, "theory" refers to the development of mathematical formulations which relate the experimental observables to the various *macroscopic* parameters of the electrochemical system, such as potential, temperature, rate constants, etc. In other words, we are referring to the "rate laws" of modern electrochemistry, as opposed to the more fundamental theory which attempts to interpret experimentally-deduced parameters, such as rate constants, on the basis of the *microscopic* characteristics of the reacting system. The latter level of theory is outside the scope of the present survey.

It should be obvious that one can make little progress interpreting data obtained under non-equilibrium conditions if appropriate rate laws are unavailable. Of course, this is particularly true in kinetic-mechanistic applications. On the other hand, the analyst can often "survive" with the aid of simple, empirical calibration curves, although he is "working in the dark" without the guidelines of a sound mathematical theory. The problem of deriving rate laws in homogeneous chemical kinetics is quite trivial, but unfortunately this is not the case in electrochemistry. Because of the importance of diffusive mass transfer as a rate process in most modern electrochemical experiments, the differential forms of electrochemical rate equations amount to boundary-value problems involving second-order partial differential equations. In many cases these boundary-value problems are eminently non-trivial. Consequently, in the past the evolution of many electrochemical techniques was retarded significantly while awaiting the development of a useful set of rate laws encompassing various possible mechanisms. Ac polarography was no exception. It was not until the 1960's that the theoretical framework for small-amplitude sinusoidal measurements was expanded sufficiently to permit the accurate treatment of data associated with moderately complex mechanistic schemes (e.g., systems with adsorption or coupled chemical reactions). Much remains to be accomplished, but the "roadblocks" are negligible and progress to date is satisfactory, particularly over the past five years.

A. Double-Layer Effects and Adsorption Phenomena

1. The Question of a priori Separation of Faradaic and Double-Layer Charging Current

In recent years unprecedented progress has been realized on the problem of quantitatively interpreting the ac polarographic response under conditions where adsorption phenomena play an important role. A large component of this progress was stimulated by efforts to clarify the question of how separation of currents due to faradaic and non-faradaic (double-layer charging currents) processes should be handled whenever the electroactive species influences the double-layer capacity (i.e., as with adsorption).

The "classical" separation approach is to assume that the faradaic and non-faradaic processes behaved as *independent, parallel* impedances whose currents are additive. Consequently, the faradaic current is derived from the total cell current simply by subtracting the double-layer charging current whose characteristics are measured *in the absence* of the faradaic process. Thus, one invokes the assumption that the presence of the electroactive component has no effect on the non-faradaic process. In the context of sinusoidal measurements, one must acknowledge the vectorial nature of the ac signals to properly implement this classical approach.[2,7,8] One must either explicitly or implicitly* measure the amplitude and phase relations of the total and double-layer charging currents so that proper vectorial subtraction can be performed to obtain the faradaic current. This simple *a priori* separation of

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*Implicit measurement of the amplitude and phase relations refers to operations such as balancing an impedance bridge with a precision RC network, or measuring in-phase and quadrature current components with phase-sensitive detectors.

faradaic and non-faradaic currents appeared adequate for the interpretation of the ac response of many systems, as was initially shown by Randles and Somerton,[4,5] Gerischer,[6] and subsequently by many others.[2,7,8] At the same time, it was probably generally recognized on the basis of intuitive considerations and empirical data that this approach left something to be desired in cases involving adsorption of the electroactive component. For example, numerous systems had been reported where a strongly adsorbed electroactive component caused a significant change in the double-layer charging current at direct potentials well-removed from the faradaic wave.

Presumably, the latter type of evidence stimulated Sluyters and co-workers at Utrecht[8] to develop in the early 60's a method which permitted one to obtain the double-layer charging current *in the presence* of the faradaic process. Consequently, the need to base separation of faradaic and non-faradaic currents on a measurement made in the absence of the faradaic process was eliminated and the possibility that the double layer is influenced by the faradaic reaction was acknowledged. However, the technique of the Utrecht group retained the concept that the electrical double layer behaved as an ideal capacitance in parallel with a faradaic impedance. Using this "second-generation" approach to the separation of faradaic and non-faradaic contributions, Sluyters and co-workers were able to show that certain systems which yielded "anomalous" faradaic behavior when ac data were treated by the classical method became "normal" when subjected to their technique. A noteworthy example was the $Tl^+/Tl(Hg)$ system.[8] Their results suggested that the anomalies observed arose because the double-layer charging current was not the same in the presence and in the absence of the faradaic process, thus invalidating the classical separation scheme. Although the origin of the rather substantial effect of the faradaic process on the double-layer charging current was not fully appreciated at first, the results of the Utrecht school were satisfying from a phenomenological viewpoint and emphasized that the act of separating faradaic and non-faradaic contributions should not be taken lightly.

The foregoing contributions of Sluyters and co-workers were a clear suggestion that electrochemists had to mend their ways with regard to the question at hand. However, their message was apparently too mild to penetrate an existing barrier of complacency. On the other hand, a series of papers by Delahay and co-workers appearing in 1966[9,10] (see references 11 and 12 for a complete bibliography) provided a sufficiently strident cry for repentance that the message was heeded by all, and for a time the foundations of electrochemical kinetics were subject to considerable agitation. Many of the established specialists in the field were swept up in the ensuing controversy which highlighted one of the more exciting periods in the recent history of electrochemical kinetics. The level of activity, debate, and confusion which reigned for a period of about two years can only be partially appreciated by examining the published literature. Nevertheless, even the "public" response to the challenge of Delahay et al. must be viewed as convincing evidence that despite some inertia the field of electrochemistry remains vibrant and healthy.

Delahay set the fuse to the debate when he questioned the operational significance of the concept that faradaic and non-faradaic processes are separable in the *a priori* sense. Both the classical and second generation methods were under attack. In effect, Delahay[9,10] pointed out that if an electroactive component contributes significantly to the differential double-layer capacity, then as the faradaic process induces concentration changes of the electroactive species, the double-layer capacity will correspondingly change with time in a manner controlled by the rates of the various faradaic processes (mass transfer, heterogeneous charge transfer, etc.). In effect, the faradaic and non-faradaic processes are strongly coupled under such circumstances. In the context of a sinusoidal perturbation, the double-layer charging current will not be a linear function of frequency with a 90° phase angle (relative to the potential across the double layer), as in the case of an ideal capacitor. Rather, the charging current will exhibit non-ideal amplitude and phase characteristics which are determined by the faradaic process. To take account of this effect, Delahay[9,10] proposed the use of three basic equations;

$$D_O \frac{\partial C_O}{\partial x} - \frac{d\Gamma_O}{dt} = D_R \frac{\partial C_R}{\partial x} + \frac{d\Gamma_R}{dt} \quad (1)$$

$$t > 0,\ x = 0;\quad i = nFA\left(- D_O \frac{\partial C_O}{\partial x} + \frac{d\Gamma_O}{dt}\right) + \frac{dq}{dt} \quad (2)$$

$$i_f = nFA\left(-D_O \frac{\partial C_O}{\partial x} + \frac{d\Gamma_O}{dt}\right) \qquad (3)$$

to replace the normally-employed boundary conditions which are invoked in most electrochemical boundary value problems, such as

$$D_O \frac{\partial C_O}{\partial x} = D_R \frac{\partial C_R}{\partial x} \qquad (4)$$

$$t > 0; \quad x = 0$$

$$i_f = -nFAD_O \frac{\partial C_O}{\partial x} \qquad (5)$$

(Notation definitions are given below*).

The terms $d\Gamma_i/dt$ in Equations 1 to 3 "correct" the flux expressions of Equations 4 and 5 for the fact that if the species O and R are adsorbed on the electrode, fluctuations in their surface excesses contribute to the fluxes in much the same manner as the electrolysis process. Neither this idea nor Equations 1 and 3 were novel. The new feature is the suggestion embodied in Equation 2 that one must develop and apply theoretical relationships for the total cell current, rather than relying on *a priori* separation of faradaic and non-faradaic currents and theoretical relations for the faradaic current alone. The "coupling" of the faradaic and non-faradaic processes is implicit in Equation 2, since the charge, q, depends on Γ_o and Γ_R, as well as on the Γ's for the supporting electrolyte, etc.

It is unlikely that knowledgable workers in the field questioned either the basic premise that a significant effect of an electroactive component on the double-layer capacity will lead to strong coupling of the faradaic and non-faradaic processes, or the equations proposed to account for this effect (Equations 1 to 3). These ideas appear to be quite sound. Difficulties arose concerning some conceptual ideas and especially Delahay's report that the "coupling" effect would be important, not only with strong specific adsorption but also with systems exhibiting rather modest non-specific adsorption due to electrostatic effects in the electrical double layer. The latter statement indicted as questionable many of the widely-heralded "classical" investigations using sinusoidal methods, and other relaxation techniques. The conceptual difficulties and some originally-hidden mathematical inconsistencies in Delahay's original treatment were reasonably well resolved by the beginning of 1968, where this review's responsibilities begin. However, some debate still existed regarding the conditions under which the "coupling effect" is important. For example, Delahay and co-workers maintained that significant coupling manifestations would arise with systems such as Zn^{+2} in 0.1 *M* KCl, whereas Sluyters et al. presented experimental data to the contrary and questioned the numerical calculations of the former. The fact that some confusion remained on this point as the year 1968 commenced is quite evident from the reviews of the (almost) independent observers, Anson[11] and Reinmuth.[12] These reviews, together with Reference 8, consider at length the *a priori* separation question and are highly recommended to the reader who wishes to examine in detail the developments on this question through the year 1967, which the present prelude merely summarizes. Despite this residuum of controversy, by 1968 understanding of the faradaic-non-faradaic separation problem had been clarified considerably. Of notable significance was the finding that when properly developed, the Delahay theory provided an explanation for systems such as $Tl^+/Tl(Hg)$ (mentioned above) and Hg_2^{++}/Hg[8] where the second-generation separation method of Sluyters et al. yielded an apparently ideal double-layer capacity whose magnitude in the presence of faradaic currents was considerably larger than in their absence.[8] This is precisely what is predicted by the equations which account for the coupling effect in the limit of *weak* reactant adsorption and *very rapid* charge-transfer kinetics.[8] This writer feels that if the efforts initiated by Delahay had yielded nothing more, they were justified by the fact that they led to a sound theoretical explanation of the paradoxical (to some of us[7]) behavior exhibited by the $Tl^+/Tl(Hg)$ and Hg_2^{+2}/Hg systems. In addition to this specific point, some of the general conditions which enhance faradaic-non-

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*C_i represent concentrations of species i, D_i are diffusion coefficients, Γ_i are surface excesses, i is the total cell current, i_f is the faradaic current, q is the double-layer charge, n is the number of electrons transferred, F is Faraday's constant, A is the electrode area, t is time, x is distance from electrode surface, subscripts O and R denote oxidized and reduced forms, respectively, the equations assume anodic currents are positive.

faradaic coupling had been identified. Besides the obvious fact that increasing Γ_o and/or Γ_R accentuates the effect, it also was recognized that coupling will be more likely if (a) adsorption is highly-potential dependent or (b) charge-transfer kinetics are fast. The latter two items are readily recognized as conditions which enhance the $d\Gamma/dt$ terms in Equations 1 to 3. It is important to note that condition (a) is almost always fulfilled in the potential region corresponding to the rising part of an ac polarographic wave, for the occurrence of the faradaic process causes the concentrations of the species O and R just outside the double layer to fluctuate rapidly with potential, inducing corresponding fluctuations in the Γ's (unless adsorption kinetics are abnormally sluggish). Consequently, if efforts to unravel the question of separability of faradaic and non-faradaic currents are relevant for any electrochemical relaxation technique, this technique must be ac polarography. Finally, another significant fact which surfaced in the pre-1968 period was the extreme complexity of the data-analysis problem whenever the coupling effect was significant. It was thought at first that at least eight double-layer parameters had to be determined, in addition to the normal parameters associated with the faradaic process, *provided adsorption equilibrium prevails.* Reinmuth has commented aptly on the significance of this problem.[12]

Early in 1968 Delahay and Holub[13] published a revised derivation of the coupling effect in ac measurements with a reversible electrode process and adsorption equilibrium. It was designed to correct some mathematical deficiencies in an earlier derivation and to present some new calculations illustrating the extent of the departure of the coupling theory from the classical approach. The differences depicted were quite substantial, although the reader should take care not to be misled by the extremely wide frequency range employed in Figure 1 of Reference 13, where the frequency domain normally employed in ac polarographic measurements is compressed into a small segment near the origin. It is noteworthy that these calculations employed data which had been questioned previously by Sluyters and co-workers.[14] One must conclude that when this paper was written, these two groups had not resolved their differences. In fact, this latter work stimulated further controversy when the Utrecht group found that they could not reproduce the derivation of Delahay and Holub. Consequently, Sluyters and co-workers[15] presented a derivation of their own which produced results originally attributed to Reinmuth.[16] They pointed out that only three independent double-layer parameters had to be determined to analyze data with a reversible system, so the apparent complexity of the data-analysis problem appears to be not as severe as originally stated. Experimental data on the Pb^{++} system in KNO_3-KCl mixtures seemed to be consistent with Reinmuth's equations. In response, Delahay[17] acknowledged that equations in Ref. 13 are incorrect due to errors in transcription, not derivation, and showed how his properly transcribed equations and those presented by Sluyters et al. are in agreement. Delahay also agreed that three independent double-layer parameters were needed and discussed at length some approaches to data analysis.[17] If this exchange suggested to the "innocent bystander" that agreement between the adversaries on the faradaic-non-faradaic coupling question was incipient, the contents of two additional publications[18,19] should convince one that almost complete agreement prevailed by late 1968. Holub[18] showed in a very elegant and general manner how one can incorporate the coupling effect in derivations of the response functions for various electrochemical relaxation techniques. In a paper which applied Holub's equations to some transient relaxation methods, Delahay and Susbielles[19] conceded the final point in their disagreement with the Utrecht group by acknowledging that their previous calculations (including Reference 13) had used incorrectly estimated double-layer parameters. Upon utilizing more realistic values of these parameters they concluded[19] that their treatment predicts a significant coupling effect* "only if there is marked

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*In the context of Delahay's remarks as well as those of Sluyters et al.,[15] a significant coupling effect appears to be one which invalidates *both* the classical and second-generation separation approaches, as defined above. In other words, all *a priori* methods must be invalid and a "third generation" *a posteriori* approach must be necessary. This is an artificial distinction since some of us might view systems such as $Tl^+/Tl(Hg)$, where only the classical method is incorrect, as manifesting a coupling effect. After all, the faradaic process does influence the non-faradaic one in the case of thallium.

specific adsorption of reactant or product."

At this point the question of when the coupling effect would be important had traversed a full circle. Once again, the prevailing view was that faradaic-non-faradaic coupling must be considered only under rather special (and obvious) circumstances, with strong specific adsorption being the most obvious and accessible sufficient condition. However, the possibility that a significant coupling effect (in the Delahay-Sluyters context) might be observed with non-specific adsorption was not ruled out completely by the Utrecht group. In a recent paper,[20] Timmer, Sluyters-Rehbach, and Sluyters reconsidered the coupling theory, particularly with regard to (a) calculating the double-layer parameters and (b) the question of the importance of non-specific adsorption. The relevant equations for the case of adsorption equilibrium were presented, together with data-analysis guidelines in a format whose unusual clarity and practicality are uncharacteristic of publications on this subject. If an investigator faces the prospect of utilizing the coupling theory for the first time, I recommend that Reference 20 be consulted before proceeding. Upon analyzing the coupling theory, Timmer et al. deduced that one might observe a significant coupling effect due to non-specific adsorption, provided the system exhibited the following characteristics:

"1. The electrode reaction at a mercury electrode should proceed as reversibly as possible with no kinetic complications; i.e., diffusion and charge transfer should be rate determining.

2. The oxidized species must be a divalent (or trivalent) cation that is not appreciably complexed by the anions of the supporting electrolyte, with a corresponding decrease of the effective charge. The reduced species should preferentially form an amalgam.

3. The reactants are not specifically adsorbed at the interface, for otherwise it will be unlikely that the existence of non-specific adsorption can be verified.

4. The standard potential of the system must be as negative as possible. At these potentials $-\Phi_2$* is large and cations are strongly attracted in the double layer. In the same potential region the supporting electrolyte reduction should not interfere.

5. The electrode reaction should be studied in 1-1 supporting electrolytes of low concentrations, because then $-\Phi_2$* is larger. Moreover, the ratio C_o/C_s* can be chosen larger, providing a favorable condition for strong adsorption of C_o."

Despite this careful theoretical study, a Herculean experimental effort on a judiciously selected system, $Ba^{+2}/Ba(Hg)$ in LiCl solutions, failed to uncover a significant coupling effect. Apparently the $Ba^{+2}/Ba(Hg)$ reaction does not adequately fulfill requirement 1 above. Most likely a coupling effect with non-specific adsorption will be elucidated someday. However, the apparently rigid and numerous requirements specified above suggest that if specific adsorption is not evident with a system under investigation, one should not lie awake at night worrying about faradaic-non-faradaic coupling, unless one is working with an abnormally low concentration ($\lesssim$0.1 *M*) of supporting electrolyte, where additional well-known problems (e.g., ion migration) are evident, not to mention some new ones. It appears from the latest theoretical conclusions in the literature that at ordinary concentrations of supporting electrolyte, one has about as much chance of finding a significant coupling effect (in the Delahay-Sluyters context) due to non-specific adsorption as of being struck by lightning on a clear day in the Antarctic.

At the time of this writing, the most recent, and possibly the most impressive, publication dealing with the coupling effect is one that applies the coupling concept to the theory for faradaic rectification measurements.[21] Among the most important hidden messages in this paper is that one should interpret with care the frequently mentioned fact that observables arising from faradaic non-linearity (second harmonic currents, faradaic rectification signals, etc.) contain only relatively small contributions due to the double-layer charging process. It is true that in such measurements the observed "background current" arising from double-layer charging is quite small, and even completely negligible at normal frequencies and electroactive component concentrations. However, the absence of a non-faradaic background signal does not necessarily mean that one can ignore the non-faradaic process. The theoretical work of DeLeeuwe, Timmer, Sluyters-

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*C_s is the concentration of supporting electrolyte; Φ_2 is the potential at the plane of closest approach.

Rehbach, and Sluyters[21] shows quite clearly that despite the absence of a measurable non-faradaic background, a non-faradaic contribution is hidden under the "faradaic" wave when specific adsorption is present due to faradaic-non-faradaic coupling. Using their coupling theory in its most rigorous form, DeLeeuwe et al.[21] were able to obtain results for the Hg_2^{2+} system over the frequency range 50 kHz to 10 MHz which were consistent with low-frequency impedance and galvanostatic pulse measurements. This is noteworthy because it is only within about the past five years that the observation of consistency in system parameters obtained with different electrochemical relaxation techniques has been the rule rather than the exception. At the beginning of 1970, most of the early difficulties along these lines were well understood and agreement between methods was becoming somewhat routine. However, the Hg^{2+}/Hg system remained a "problem child" until Reference 21 appeared.

Among the remaining theoretical papers which have appeared on the coupling topic is one by Baticle and co-workers[22] which is worth consulting if one is interested in solid electrode work. The rather approximate nature of this theory is, in a way, a reflection of the difficulty one faces in handling faradaic-non-faradaic coupling with solid electrodes. After all, with the exception of electrodes composed of single crystal planes, the non-faradaic process does not need the aid of a faradaic step to behave non-ideally; it does quite well on its own.[23]

The foregoing theoretical studies dealing with faradaic-non-faradaic coupling are based on the assumption of double-layer equilibrium–i.e., the Γ's are assumed to have values that represent equilibrium with the concentrations outside the double layer. It has been known for some time that equilibration in the adsorption of certain large organic molecules is sufficiently slow that the double layer is not in equilibrium under ac polarographic conditions. Clearly, such effects can alter the nature of the faradaic-non-faradaic coupling process. One must introduce adsorption kinetics into the coupling theory to account for this effect. No one has attempted this, as far as this writer knows, perhaps because the obvious complexities of the data analysis problem discourage even the more ambitious investigators. However, the questions raised by Delahay regarding separation of faradaic and non-faradaic responses served also to focus attention on the general question of the non-equilibrium double layer, although not in the context of coupling theory (e.g., double-layer relaxation in the absence of a faradaic process was considered). Because this latter type of investigation has not dealt explicitly with the coupling question, it is considered separately. Nevertheless, one should not overlook the crucial significance of conclusions reached regarding double-layer relaxation on the entire question of separation of faradaic and non-faradaic responses.

2. *Double-Layer Relaxation Effects*

a. Surfactant-Induced Relaxation

Actually, the establishment of a non-equilibrium diffuse double layer and the observation of its subsequent relaxation behavior is not a new area of electrochemical investigation. Such effects are especially well known in aqueous solutions containing large surface-active organic solute molecules and have been studied at great length, with sinusoidal perturbations being one of the favored approaches. Double-layer relaxation phenomena are observed readily in such systems because the surfactant is normally present in small concentrations relative to the solvent and supporting electrolyte and because of relatively sluggish kinetics attending mass transport of the surfactant and/or the establishment of the adsorbed state. Consequently, a potential perturbation on an electrode in contact with such solutions is followed by establishment of a non-equilibrium double layer due to the greater "agility" and abundance of the solvent-supporting electrolyte pair, followed by a relatively slow reorganization of the double layer as the organic moiety is transported to the electrode and achieves its equilibrium surface conformation. Cases where diffusion and/or adsorption kinetics are rate-controlling have been established on an experimental and theoretical basis for such surfactant-induced relaxation. The so-called tensammetric wave,[2] which occasionally appears on ac polarograms, is one manifestation of a surfactant-induced double-layer relaxation. Thorough reviews of the subject are available.[2,8,24]

Although theoretical treatment of the effects of surfactant-induced double-layer relaxation on ac measurements has been a fairly active field through most of the 1960's, it has been relatively quiet for the last three years. Armstrong, Race, and Thirsk,[25] Race,[26] deLevie and Pospisil,[27] and

Takahashi[28] have presented some noteworthy papers which are addressed (at least in part) to finding more efficient schemes for the analysis of ac impedance data with surfactant-induced double-layer relaxation. These contributions introduce no new basic theoretical concepts. Rather, they reformulate in more efficient formats previously derived theoretical expressions for the common situations where the relaxation is controlled by diffusion of the surfactant and/or by the heterogeneous adsorption process. The reformulations in all cases reveal the utility of data analysis via some type of experiment-theory comparison involving the complex plane. The use of the concept of relaxation times is also shown to be useful.Experimentalists should take note of these contributions.

Apparently the only recently presented novel theoretical concept involving the type of process in question is presented in papers by Armstrong, Porter, and Thirsk[29] and Armstrong.[30] These papers propose, and convincingly demonstrate on a theoretical basis, that a homogeneous chemical reaction coupled to an adsorption process can influence the ac response under appropriate conditions. The mechanism in question may be represented as:

$$S_2 \underset{k'}{\overset{k}{\rightleftharpoons}} S_1 \rightleftharpoons S_{1,ADS}$$

where S_1 and $S_{1,ADS}$ represent unadsorbed and adsorbed surfactant, respectively. S_2 is a surface-inactive species which is transformable to S_1 via a homogeneous chemical process characterized by the forward and reverse rate constants, k and k′, respectively. The theoretical treatment assumes adsorption equilibrium, so rate parameters are not assigned to the adsorption step, $S_1 \rightleftharpoons S_{1,ADS}$. Although the specific mechanistic model considered is rather simple and somewhat restricted, it serves quite admirably to illustrate an interesting general concept. This is that an electrochemical relaxation technique such as ac polarography might be used to obtain kinetic and thermodynamic information about a homogeneous chemical step, *even if all species involved in the homogeneous chemical process are electroinactive.* The rather dramatic event of actual charge transfer, which is the usual "handle" employed, is not a necessary condition for such studies. All that is required to adequately perturb the chemical step is some experimentally controllable interaction at the electrode surface and, apparently, the relatively subtle (compared to charge transfer) phenomenon known as adsorption will suffice.

Armstrong's theoretical expressions[30] are formulated in terms of three relaxation times given by

$$\tau_{D1} = D^{-1}\left(\frac{\partial\Gamma}{\partial C_o}\right)^2 \tag{6}$$

$$\tau_{D2} = D^{-1}\left(\frac{\partial\Gamma}{\partial C_o}\right)^2\left(\frac{C_o}{C_o' + C_o}\right) \tag{7}$$

$$\tau_R = (k_o D)^{-\frac{1}{2}}\left(\frac{\partial\Gamma}{\partial C_o}\right) \tag{8}$$

where D is the diffusion coefficient for S_1 and S_2 (assumed equal). Γ is the surface excess of $S_{1\,ADS}$. C_o' and C_o, are the bulk concentrations of

TABLE 1*

Observable Relaxation Times for Spanning the Relaxation Process Under Various Conditions

Conditions	Times
$\omega \gg k_o$	τ_{D1}
ω comparable with k_o, $C_o \ll C_o'$	$\tau_{D1} + \tau_R$
$\omega \ll k_o$, $k_o^{1/2}C_o \ll \omega^{1/2}C_o'$	τ_R
$\omega \ll k_o$, $k_o^{1/2}C_o$ comparable with $\omega^{1/2}C_o'$	$\tau_R + \tau_{D2}$
$\omega \ll k_o$, $k_o^{1/2}C_o \gg \omega^{1/2}C_o'$	τ_{D2}

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S_1 and S_2, respectively, and k_o is given by

$$k_o = k\left(1 + \frac{C_o}{C'_o}\right) \qquad (9)$$

τ_{D1} and τ_{D2} are relaxation times associated with diffusion of species S_1 and S_2. τ_R is the relaxation time arising from the chemical reaction. Armstrong's analysis of the theoretical expressions indicates that the ac response will be influenced most visibly when τ_R lies between τ_{D1} and τ_{D2}. A more specific set of conditions is given in Table 1. Although the requirements for obtaining a measurable effect of the chemical reaction are somewhat strict, appropriate conditions should be obtainable in many cases, particularly when the ratio C'_o/C_o is conveniently controllable. The possible utilization of this concept is particularly appealing in the biochemical area where electroinactive, surface-active, water-soluble, macromolecules abound. One should not be overly surprised if someday the concept in question is applied to the kinetic characterization of a process such as an enzyme-substrate interaction.

b. Double-Layer Relaxation Arising from Finite Ionic Mobility

Until very recently, the surfactant-induced double-layer relaxation was the only one generally recognized as being important under experimental conditions normally associated with ac polarography and other electrochemical relaxation techniques. However, the reexamination of the nonequilibrium diffuse double layer which Delahay stimulated has brought a new dimension to the electrochemist's viewpoint regarding the conditions required for a double-layer relaxation. Specifically, this recent work has emphasized that the existence of surfactant is not a necessary condition for observing double-layer relaxation effects on the time (or frequency) scale associated with electrochemical kinetic measurements. A solution containing only solvent and supporting electrolyte ions can exhibit a noticeable relaxation time under certain conditions due simply to the finite values of the ionic mobilities. Those contributing to this work have been Barker,[31] Anson and coworkers,[32,33] Newman,[34] Baker and Buckle,[35] Buck,[36] MacDonald,[37] and Feldberg.[38] Each of these authors has contributed to the theoretical characterization of the problem. Anson et al. also present definitive experimental data.

The theoretical treatment of double-layer relaxation arising from finite ionic mobility is extremely difficult because the boundary value problem must account for both diffusion and ionic migration. Attempts to formulate analytical solutions[31-37] have been understandably approximate and show poor quantitative agreement with respect to some aspects of the problem. Perhaps a numerical approach to this problem[38] is our best hope. However, there is general agreement on the qualitative and semi-quantitative aspects of the relaxation phenomena. First, all theoretical treatments (and experiment) lead to the conclusion that somewhat special conditions must prevail in order to observe such relaxation effects in the frequency range normally employed in ac polarography. The most frequently quoted "special condition" is that the electrolyte must be dilute (e.g., $\ll 0.1$ *M*), but fused salts and thin-layer cells have been cited[37] as additional possibilities. There also appears to be reasonable agreement regarding the underlying processes responsible for the non-equilibrium state. Three relaxation phenomena have been identified as possibly important. In order of increasing time constant (decreasing rapidity) they are (a) relaxation of the ionic atmosphere—i.e., a Debye-type relaxation,[34-37] (b) "salt-diffusion" relaxation,[31-34,38] and (c) "ion-exchange" relaxation.[33] The first and most rapid of these is the familiar relaxation phenomenon associated with motion of ions due solely to the influence of an electric field (migration)—i.e., the rate-determining process in most conductivity measurements. When an ideally polarized electrode is rapidly charged the attendant electric field causes anions and cations to migrate rapidly in opposite directions, leading to space-charge polarization in the vicinity of the electrodes. Newman[34] has estimated that for an electrode in a 0.001 *M* KCl solution (aqueous), this disturbance can extend about 5300 Å into the solution, a distance which far exceeds the dimensions of the equilibrium diffuse double layer. After the occurrence of this initial process, which requires of the order of 1 μs in millimolar electrolyte,[34] the disturbance region is comprised of relatively pure solvent. The attendant concentration gradient leads to the onset of back-diffusion of supporting electrolyte which proceeds with a significantly longer time constant in dilute electrolytes. In a system composed of a solvent and a single electrolyte, the relaxation associated with back-diffusion of salt is characterized by a single time constant and has been referred to as "salt-diffusion relaxation."[33] Relaxation times of the order of 0.1 to 1 *ms* characterize salt-diffusion relaxation in millimolar electrolytes.[33] Last, but definitely not least, is an effect revealed by Anson and co-workers.[33] They pointed out that in *mixed electrolytes* there can be two identifiable relaxation processes associated with back-diffusion of the electrolyte. This occurs when the salt mixture is comprised of univalent ions plus some highly charged ions (preferably with an excess of the former). In such a system the diffuse double-layer equilibrium state is characterized by preferential inclusion of the more highly charged ions. However, the mobilities of the latter are inferior to the ions of lower charge. Consequently, after the initial charging (Debye relaxation) one first observes a relatively rapid "normal" salt-diffusion relaxation yielding an "intermediate" diffuse double layer, which is dominated by the more mobile univalent ions. This is followed by a transition to a so-called "ion-exchange relaxation" in which the slower, highly charged ions finally reach the double layer, displace some of the univalent ions, and achieve their equilibrium status. Diffuse double-layer relaxation which includes an ion-exchange component can exhibit rather long relaxation times (e.g., ~30 ms. in 4.98 m*M* HCl + 0.05 m*M* $BaCl_2$ + 0.05 m*M* $LaCl_3$[33]). Incidentally, perhaps the most successful theory-experiment comparison of a double-layer relaxation arising from finite ionic mobility has been presented for the case of an ion-exchange relaxation.

Despite the academically interesting aspects of these relaxation effects, the reader at this point may be questioning the wisdom of devoting space in this review to phenomena which can be ignored with impunity under "conventional" ac polarographic conditions (relatively concentrated electrolytes combined with frequencies usually less than 10 to 30 kHz.). In the light of most existing applications of ac polarography, such an objection is understandable. However, the reader should be aware of faint "rumblings" in the literature which are suggesting that we broaden our viewpoint of conditions appropriate for ac polarographic measurements (and other forms of voltammetry). In particular, recent advances in potential-control circuitry (see section IIIB-2) have led some workers[39-42] to suggest and/or demonstrate the feasibility of performing electrochemical measurements, including ac polarography,[39,40] in very *dilute electrolytes*. Because some rather compelling reasons can be given for effecting measurements in dilute electrolytes, particularly in the context of analytical applications, it appears likely that such studies will become more frequent. In this event, concepts such as ion-exchange relaxation, salt-diffusion relaxation, etc. will no longer be irrelevant curiosities. These concepts should make the ac polarographer recognize that if the electrolyte is diluted sufficiently, the electrical double layer will begin to behave quite unlike a pure capacitance. Consequently, many of the simple guidelines and electronic tricks for minimizing contributions of charging current (e.g., square-wave polarography, phase-selective ac polarography) will become less effective.* Under such conditions the concept of separating faradaic and non-faradaic currents is considerably complicated by the non-equilibration of the double layer, even if *a priori* separability could be assumed (which is unlikely in most cases). In other words, the recent advances in the theory of double-layer relaxation phenomena are reviewed here to emphasize that workers contemplating ac polarography in dilute electrolytes must recognize that they are opening a new Pandora's box. The demons released will, in many cases, invalidate the convenient and comfortable concept of the electrical double layer as an independent capacitance in parallel with the faradaic process. These new problems should not be considered sufficiently formidable to justify abandonment of dilute electrolyte electrochemistry, but their existence must be recognized so that work in the area can proceed intelligently

3. Electrocrystallization Effects.

Until recently, the accepted theoretical basis for interpreting the ac response with solid metal-metal ion electrode processes differed little from the theory originally derived for cases where both redox forms are soluble species (e.g., metal ion-metal ion or metal ion-metal amalgam systems). In other words, the rate processes considered were

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*Barker[31] has pointed out that even in electrolytes of normal concentration ($\geqslant$ 0.1 M), the usually negligible double-layer relaxation effects may become important or even the limiting factor in high-sensitivity measurements. When one is trying to detect a small faradaic signal in the presence of a much larger charging current by square-wave polarography, or the like, even a minute double-layer relaxation can be important.

bulk diffusion, heterogeneous charge transfer, and/or coupled homogeneous chemical reactions. In many cases, the theory for the simple quasi-reversible case (rate control by diffusion and heterogeneous charge transfer) seemed to adequately describe the ac response with metal-metal ion electrodes and, consequently it was used to calculate the standard heterogeneous charge-transfer rate constant k_s (or the exchange current density i_o). This procedure was shown to contain a significant possible source of error in a theoretical treatment by Fleischmann, Rangarajan, and Thirsk.[43] These workers considered possible kinetic effects of adatom transport (diffusion) along the metallic crystal surface to lattice-building sites, in addition to bulk diffusion and heterogeneous charge transfer. The lattice incorporation step was assumed to be in equilibrium. Although this theoretical treatment contains several interesting features, the one of most immediate importance is the prediction that even though adatom transport is kinetically important, the shape of the ac frequency response profile can "mimic" simple quasi-reversible behavior over a wide frequency range. For example, although the intercept will be altered by surface diffusion, plots of the resistive component of the faradaic impedance will exhibit the "classical" linear behavior usually associated with the quasi-reversible case. Under such conditions, the calculated value of the heterogeneous charge-transfer rate constant k_s may be substantially in error unless one accounts for surface diffusion. Such error may characterize much of the data in the literature which pertain to metal-metal ion systems.

Rangarajan[44] has expanded the consideration of this question recently and presented the theoretical results shown in Figure 3. As one can see, the classical linear dependence of R_s on $\omega^{-1/2}$ is exhibited over a wide frequency range, even though surface diffusion effects are important in this range. The region where adatom transport causes a discernible non-linearity is confined to the region where $\omega < 10$, which is below the normal frequency realm employed in ac polarography. If one invokes the "classical" treatment of linear $R_s - \omega^{-1/2}$ data and calculates k_s or i_o from the infinite-frequency intercept (charge-transfer resistance, R_t) without accounting for surface-diffusion effects, errors corresponding to factors of 4.14 and 2.0 would result in the case of curves (a) and (b), respectively, of Figure 3.

The ac response with electrocrystallization was considered from another viewpoint by Levart and Schuhmann. These authors examined and presented a derivation of the ac response of a metal-metal ion electrode with a pure binary electrolyte–i.e., in the absence of supporting electrolyte. As was mentioned earlier, mass transport under such circumstances is influenced by ion migration as well as by diffusion. The attending mathematical complexities forced the authors to adopt a variety of simplifications which limited the scope of the treatment. The kinetic complications accounted for were mass transport (diffusion and migration) and *irreversible* charge transfer. Double-layer relaxation effects were ignored, which restricts the treatment to relatively concentrated electrolytes (above about 0.01 M). Adsorption and surface diffusion of adatoms also was not considered. Finally, solution of the mass-transfer problem was based on the rather approximate Nernst diffusion-layer concept. Nevertheless, the results are interesting and validly demonstrate some important semi-quantitative concepts. Perhaps the most fundamental result of this treatment is the demonstration that for the conditions considered, none of the properties of the cell impedance is *a priori* separable. The ohmic resistance, double-layer capacity, and faradaic impedance are all strongly coupled and mutually influence one another. This writer is certain that a more rigorous treatment will not only confirm this somewhat expected finding but also will demonstrate it more forcefully, particularly if double-layer relaxation effects in dilute electrolytes are considered. Despite this awe-inspiring complication, the authors conclude that by appropriate procedures such systems, which are rather relevant from an industrial viewpoint, can be effectively studied by ac methods.

4. *Other Adsorption and Double-layer Effects*

When organizing a review of any reasonably active scientific area, one inevitably encounters papers which fit equally well under more than one category, regardless of the organizational format. The present review is no exception. In the case of theory relevant to ac polarography with double-layer and adsorption effects, one finds several important papers which are equally concerned with effects of coupled homogeneous chemical reactions. A case involving a homogeneous chemical reaction coupled to a "pure" adsorption step (no faradaic component) already was discussed above.[29,30] Two additional important theoretical developments which consider the combined effects of homogeneous chemical reactions, the double-layer and heterogeneous charge transfer are discussed in the next section which highlights theory for systems with coupled homogeneous chemical reactions. This somewhat arbitrary organizational plan is implemented primarily to "even the score" and give equal emphasis to both homogeneous chemical reactions and adsorption-double-layer effects for those papers addressed to both subjects. This hopefully avoids leaving an implicit impression that elucidation of adsorption or double-layer phenomena is viewed as the more important physical-chemical application of ac polarography and vice versa.

B. Systems with Coupled Homogeneous Chemical Reactions

The theory for the ac polarographic response with mechanisms involving coupled homogeneous chemical reactions has continued to receive close attention over the past three years. In general, one finds three considerations which stimulate the development of a theoretical framework for this type of mechanism. First, one may be interested in applying ac polarography to the kinetic-

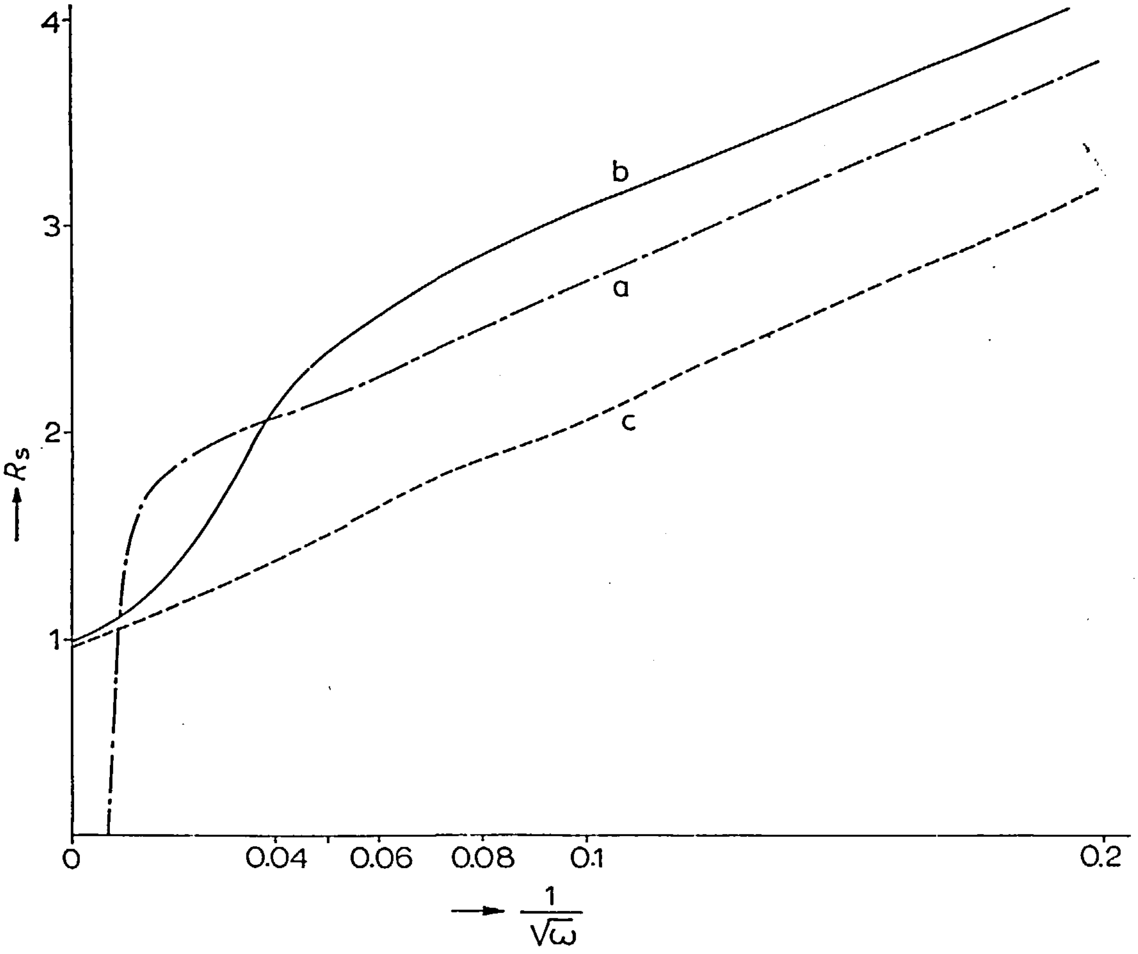

FIGURE 3. Plot of resistive component of faradaic impedance (R_s) versus $\omega^{-1/2}$ for system involving electrocrystallization. (a) —·— R_t^{app} ~4.14 R_t. (b) —— $R_t^{app} = 2R_t$. (c) —— $\omega_c = 10$. (R_t^{app} = apparent charge-transfer resistance R_t) R_s is plotted in units of R_t. Curve (a) is shifted *down* by 2.5 units and should converge on the R_s axis with curves (b) and (c) as $\omega^{-1/2} \rightarrow 0$ (at $R_s = 1$). ω_c is approximately equal to the transition frequency for R_s ($\omega_c = 10$ corresponds to negligible effect of adatom transport over frequency range considered. (Reprinted from reference 44 by courtesy of Elsevier Publishing Co.)

mechanistic characterization of fast homogeneous chemical processes. When it is coupled to the heterogeneous charge-transfer step, a homogeneous chemical reaction can significantly and characteristically alter ac polarographic behavior. These influences provide useful quantitative insights into the nature of the chemical step, provided that the relevant rate laws (theory) are available. Second, one may be concerned primarily with the measurement of heterogeneous charge-transfer rates, which for two decades has been the most common and successful kinetic application of ac polarography. In this context, an encounter with kinetic effects of a homogeneous chemical reaction means that the system under investigation is intractable, unless a theory exists which properly characterizes effects of the chemical step and allows one to "correct for" the chemical perturbation. Finally, the influence of a homogeneous chemical process on the position (direct potential) and magnitude of the ac wave has important implications for analytical applications. For an analyst to properly optimize the ac response in cases where a coupled homogeneous chemical step is operative, a quantitative theoretical framework provides useful guidelines for recognizing the existence of the chemical step and for making the appropriate changes in solution composition to achieve the most favorable conditions for analysis.

Although a recent upsurge in activity is detectable (see Section IVD), the applications of ac polarographic theory for systems with coupled chemical reactions remain rather sparse. At this point in time the development of theory leads its application by a wide margin. However, if the history of the development of dc polarography can be taken as a reasonable precedent, one must conclude that the theory in question will eventually find wide use in each of the three contexts described above.

1. First-Order Processes Coupled to a Single Charge-Transfer Step

a. Fundamental Harmonic Response

From a formal mathematical viewpoint, the theory for fundamental harmonic ac polarographic behavior with coupled first-order chemical reactions had been developed to a fairly complete state by the mid-1960's.[7] However, there remained room for refinement, generalization, and more detailed scrutiny of the theoretical predictions. These latter ends have been the concern of the most recent publications in this area.

McCord and Smith[46] presented general equations for the fundamental harmonic ac polarographic response which encompasses mechanisms involving any number or type of *first-order* chemical steps coupled to a single charge-transfer step. The theory is general with regard to the status of the charge transfer step (Nernstian and non-Nernstian behavior are treated). It employs a rigorous solution for the expanding plane boundary value problem which is the model for the dropping mercury electrode one normally employs in precise analysis of dc polarographic data.[47] The spherical diffusion effects which are neglected can sometimes prove to be important in ac polarography, particularly with metal ion-metal amalgam redox systems.[7] In the latter instance a spherical correction term can be introduced.[48] Other approximations in the formulations are the normally minor ones attending the assumptions that kt > 5 (k = first-order rate constant, t=time) and that certain diffusion coefficients are equal. Theoretical expressions for the ac polarographic response with any particular mechanism in this category is obtainable with the aid of coefficients found in the corresponding surface concentration expressions. The relevant coefficients have been tabulated for numerous mechanisms.[7] This general theory was utilized to obtain mathematical expressions for the fundamental harmonic current with mechanisms involving single-step preceding[49] and following[50] chemical reactions–i.e., reaction schemes R1 and R2.

$$Y \underset{k_2}{\overset{k_1}{\rightleftharpoons}} O + ne \rightleftharpoons R \quad \text{(preceding reaction)} \qquad \text{(R1)}$$

$$O + ne \rightleftharpoons R \underset{k_1}{\overset{k_2}{\rightleftharpoons}} Y \quad \text{(following reaction)} \qquad \text{(R2)}$$

The predictions of the theory for mechanisms R1 and R2 were scrutinized in detail.[49,50] Some results are discussed below.

Sluyters-Rehbach and Sluyters[51] have independently formulated expressions for the fundamental harmonic response with mechanisms R1 and R2, as well as the so-called catalytic case represented by mechanism R3

$$\begin{tikzcd} O + ne & R \arrow[l, bend left, "k"] \end{tikzcd} \quad \text{(catalytic case)} \qquad \text{(R3)}$$

Their work differs from that of McCord and Smith by the use of an approximate solution of the expanding plane boundary value problem based on a steady-state diffusion-layer theory, in place of the more exact (but more complicated) solution espoused by McCord and Smith. Basically, the difference amounts to accounting for the dc polarization process at a dropping mercury electrode with a modification of the Nernst-type diffusion layer theory rather than with the rigorous Koutecky-Matsuda-Ayabe approach.[47] For the most part, the two levels of theory are in excellent agreement at a qualitative and semi-quantitative level. Quantitative differences between the rigorous and approximate theories have been carefully scrutinized.[51,52] In many instances these differences disappear, as they do for (a) the phase angle with any mechanism in this category, and (b) the current amplitude and phase angle with the catalytic mechanism where a stationary plane model is usually adequate, as first noted by Delmastro.[53] On the other hand, in the worst cases the approximate theory may be in error by as much as 20%. The simplicity of the more approximate model of Sluyters-Rehbach and Sluyters is very helpful when one must perform calculations without the aid of a digital computer facility or when one wishes to obtain analytical expressions for certain limiting cases. However, use of the approximate theory must be coupled with careful consideration of the attendant error in the theory—e.g., a mechanism cannot be rejected on the basis of a ± 10 to 20% deviation between experiment and theory for that mechanism. If digital computer aids are available, there is little to justify the sacrifice in theoretical precision and mechanistic resolution attending the use of the more approximate solution (the rigorous expanding plane theory already contains more than enough approximation). Even a small laboratory "mini-computer" (see section IIIB-3) can readily handle the most complex ac polarographic theory and little additional effort is required to utilize the most accurate expressions, particularly when available computer programs* can be utilized. Finally, it should be mentioned that very simple approximations to the Koutecky-Matsuda-Ayabe rigorous solution of the expanding plane problem are available[54] which introduce into the ac theory errors usually not exceeding 1 to 2%.[52]

Regardless of the quantitative accuracy of the particular theoretical derivation in question, one finds complete agreement regarding the concept that the ac polarographic response is notably sensitive to influences of coupled homogeneous chemical reactions. Of course, this was made apparent in the earliest theoretical work on the subject. The more recent contributions cited above have confirmed emphatically this idea, in addition to providing more detailed quantitative insights into the nature of the chemical reaction's effects and revealing useful approaches for data analysis. Figure 4 illustrates predicted effects of an irreversible following chemical reaction (mechanism R2) on the fundamental harmonic current amplitude–direct potential profile (conventional ac polarogram) and the phase angle cotangent–direct potential plot (phase angle polarogram).[50] For the conditions considered in Figure 4, the peak current magnitude would be approximately 16 microamps if there were no effect of the following chemical reaction ($k_f = 0$). Thus, even the ac polarogram for $k_f = 1 s^{-1}$ is already significantly attenuated by the follow-up reaction (see section IIC for an explanation of this observation). When k_f becomes sufficiently large the magnitude and shape of the ac polarogram become independent of k_f, as seen in Figure 4B. This limiting case, which is sterile from a kinetics measurement viewpoint, is reached when $k_f \gg \omega$. Consequently, by increasing the frequency a larger value of k_f is required to reach this limit [note that the rather low frequency of about 160 Hz ($\omega/2\pi$) was employed in Figure 4]. Figure 5 provides a similar illustration of the predicted effects of a preceding chemical reaction (mechanism R1).

Although Figures 4 and 5 deal with rather restricted sets of conditions, they are fairly representative and serve to illustrate the basis for the remarks at the beginning of this subsection. One may find disadvantages with the application of the ac polarographic method to measuring coupled chemical reaction rates, most notably because of complications due to non-Nernstian charge transfer.[49,50] However, it requires a substantial level of

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*FORTRAN programs for the fundamental and second harmonic ac polarographic response with mechanisms R1, R2, and R3 are available from this writer on request. The programs are written in the CDC 6400 FORTRAN version. Bond[55] has successfully modified them for use on the IBM 7044 computer.

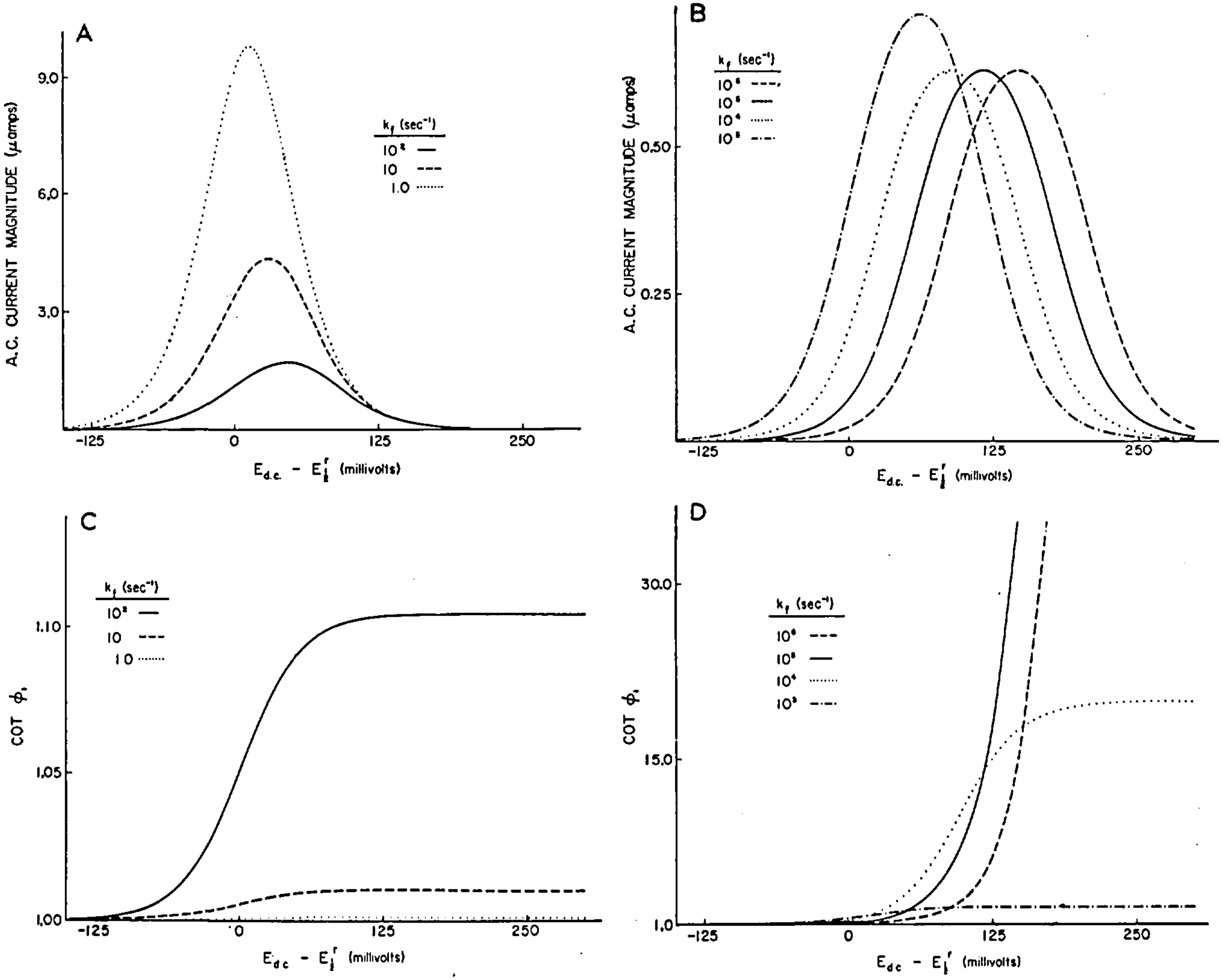


FIGURE 4. Calculated fundamental harmonic ac polarographic response versus direct potential for system with an irreversible first-order chemical reaction following Nernstian charge transfer. A,B = fundamental harmonic ac polarograms. C,D = fundamental harmonic cot Φ - E_{dc} response. Parameter values: k_f shown in Figure, t = 6.0 s, n = 1, T = 290°K, electrode area = 0.035 cm^2, ac amplitude = 5.0 mV, bulk concentration of oxidized form = 1.00 x 10^{-3} M, all diffusion coefficients = 1.00 x 10^{-5} cm · s^{-1}, frequency = 159 Hz. (Reprinted from reference 50 by courtesy of Elsevier Publishing Co.)

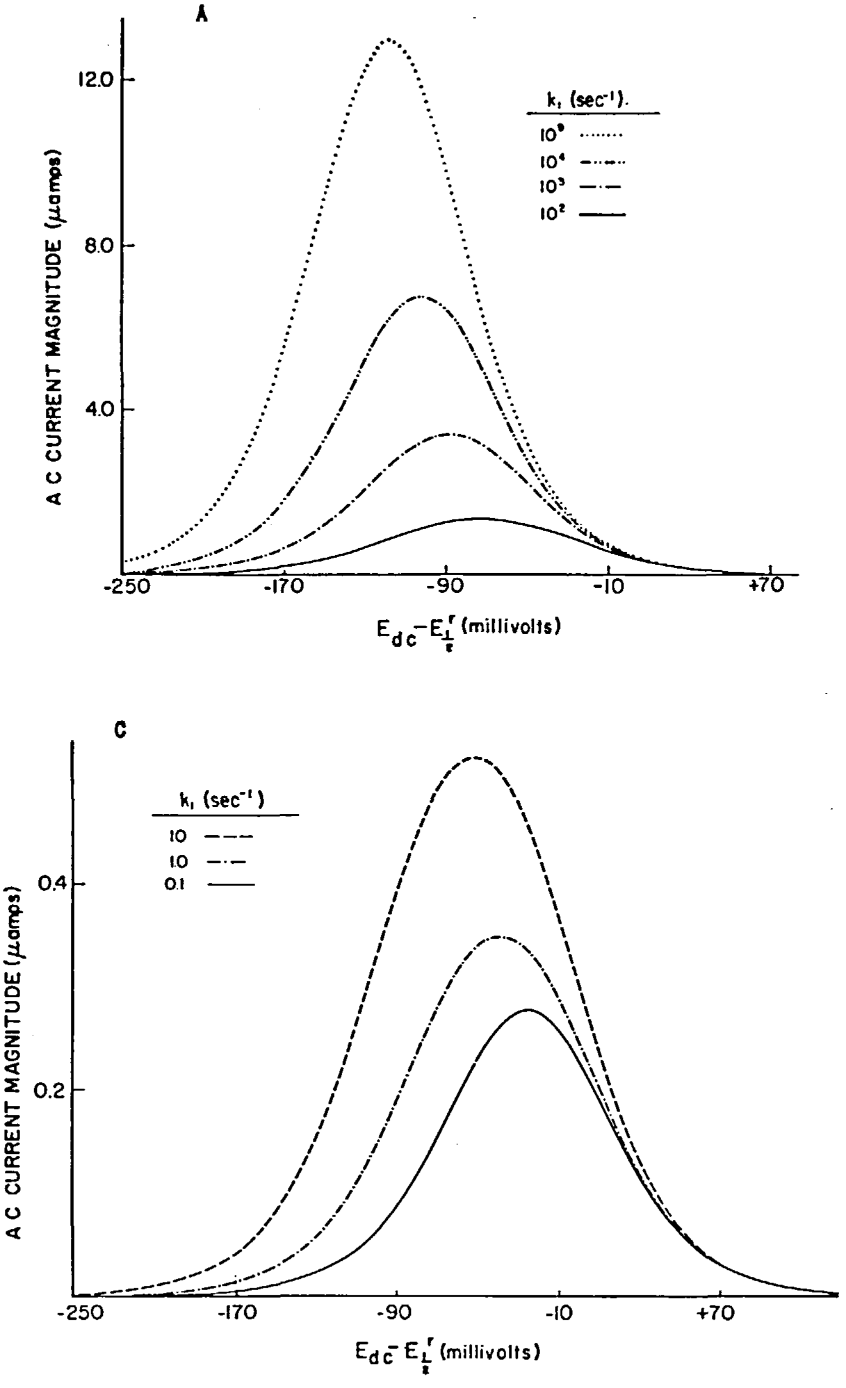


FIGURE 5. Calculated fundamental harmonic ac polarographic response versus direct potential for system with a first-order chemical reaction preceding Nernstian charge transfer. A,C = fundamental harmonic ac polarograms. B,D = fundamental harmonic cot Φ - E_{dc} response. Parameter values: k_1-values shown in Figure, k_1/k_2 = 1.00×10^{-2}, frequency = 100 Hz, other parameters same as Figure 4. (Reprinted from reference 49 by courtesy of the American Chemical Society.)

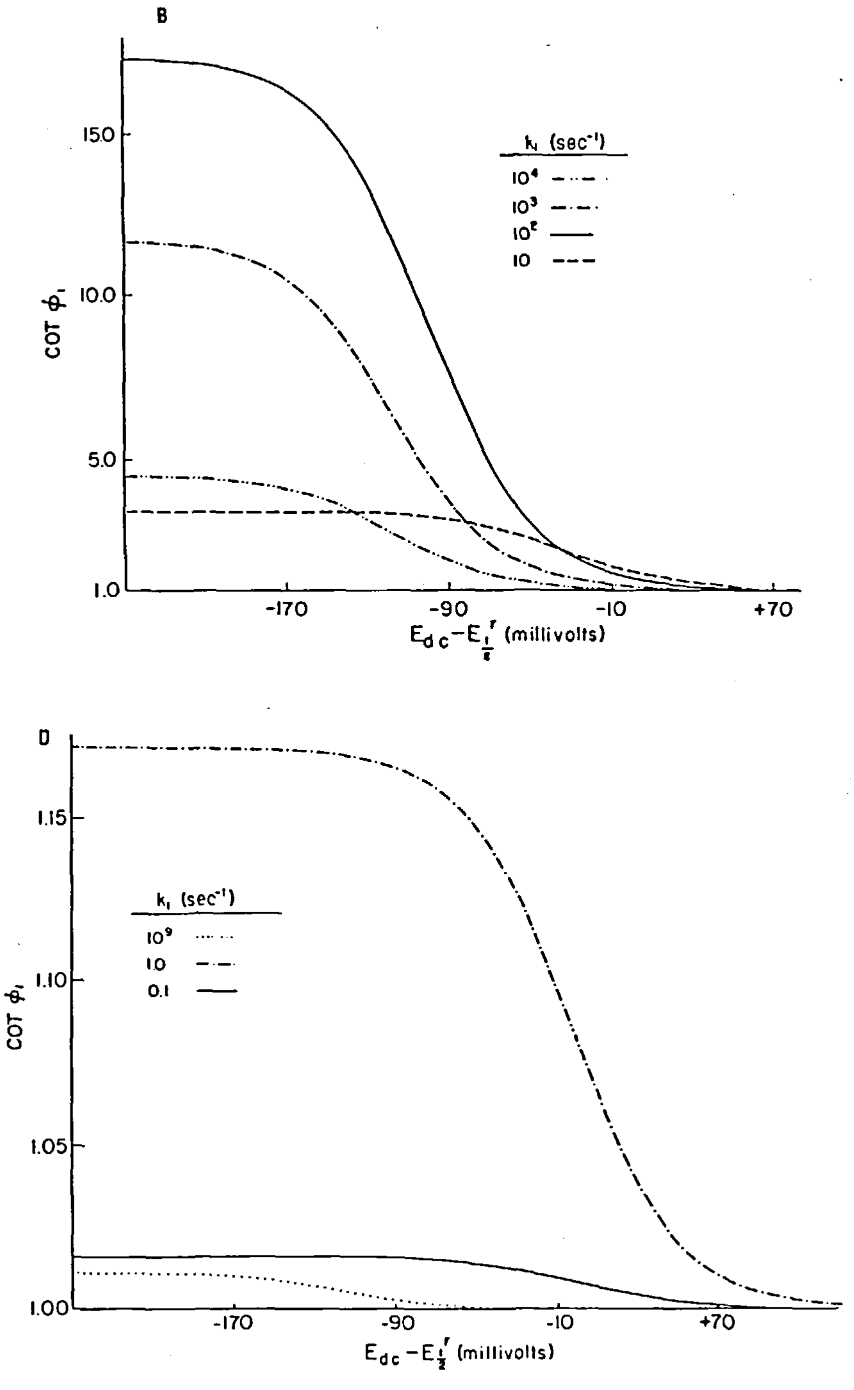


FIGURE 5. (see preceding page for caption).

myopia to fail to recognize that effects of coupled chemical reactions on the ac response can be large, can occasionally be employed advantageously, and certainly must be reckoned with, regardless of the context in which the ac polarographic method is employed.

b. Second Harmonic Response

The same theoretical framework employed to derive the "rate laws" for the fundamental harmonic current is readily extended to higher-order current components, such as the second harmonic.[7] McCord and Smith[56] have exploited this possibility for the case of second harmonic currents by presenting theoretical relationships for systems with first-order chemical reactions coupled to a single charge transfer step. This theory embodies the same level of rigor and generality as the corresponding general theory for the fundamental harmonic.[46] The predictions for mechanisms R1 and R2 have been scrutinized in detail.[57,58] The second harmonic response with mechanism R3 also has been examined for Nernstian conditions.[52] It is probably fair to say that the mathematical theory of second harmonic ac polarography for mechanisms involving coupled first-order chemical reactions is at the same level of development as the fundamental harmonic theory.

In the cases where theoretical predictions have been examined carefully,[57,58] one clearly finds that the second harmonic response is even more sensitive to kinetic manifestations of coupled chemical reactions than the fundamental harmonic, as was suggested in the early literature on the basis of qualitative arguments. This fact, combined with the often negligible contributions of the double-layer charging process, should make second harmonic measurements particularly appealing for the precise evaluation kinetic parameters. However, with a few notable exceptions to be discussed later, these long-recognized potentialities of second harmonic ac polarography have not been exploited on a scale worth noting. It is possible that many workers are discouraged by the non-routine and somewhat demanding nature of the experiment, a situation which instrumental advances promise to negate (see section III).

Figures 6 and 7 illustrate some calculated second harmonic observables with an irreversible follow-up chemical reaction and a preceding reaction, respectively. The conditions considered are comparable to the corresponding fundamental harmonic results illustrated in Figures 4 and 5. Conventional second harmonic ac polarograms (current magnitude vs. direct potential), phase angle polarograms (phase angle versus direct potential) and complex plane polarograms (imaginary or quadrature current versus real or inphase current) are represented in these Figures. Each type of polarogram is an accessible experimental observable with modern instrumentation (see section III). In Figure 7, the response for $k_1 = 10^{12} s^{-1}$ provides an example of the results expected when no chemical kinetic effect is existent. Given this frame of reference the profound effects of the coupled chemical reactions on the shape and magnitude of the various observables are quite evident. One should also note the very obvious differences in the nature of the second harmonic behavior between the two mechanistic schemes in question. This is simply one example of the normally excellent mechanistic resolution afforded by second harmonic measurements.

Although there is a tendency to become somewhat preoccupied with kinetic applications of these theoretical advances, one should not overlook possible applications of a thermodynamic nature. In particular, the theoretical predictions for second harmonic ac polarography reveal some remarkably powerful features of this technique with regard to measuring normally inaccessible standard potentials. One rather obvious example is implicit in Figure 6. Note in Figure 6 that regardless of the other effects of the irreversible follow-up chemical step, the minimum on the conventional second harmonic polarogram (Figures 6A, 6D) occurs precisely at the $E^r_{1/2}$ value (which is approximately the E°) as long as the minimum is discernible. Close inspection of the theory shows that for Nernstian behavior, the second harmonic minimum occurs at the $E^r_{1/2}$ value, provided $k/\omega \lesssim 3$. Taking $\omega = 10^5 s^{-1}$ as a very conservative estimate of the highest frequency one might employ, one concludes that the parameter $E^r_{1/2}$ is directly measurable from the second harmonic minimum with Nernstian systems, even with irreversible follow-up reactions characterized by half-lives of the order of a few microseconds. Under these conditions the dc polarographic half-wave potential and the fundamental harmonic ac peak potential are far removed from the $E^r_{1/2}$ value (by 176/n and 84/n mil-

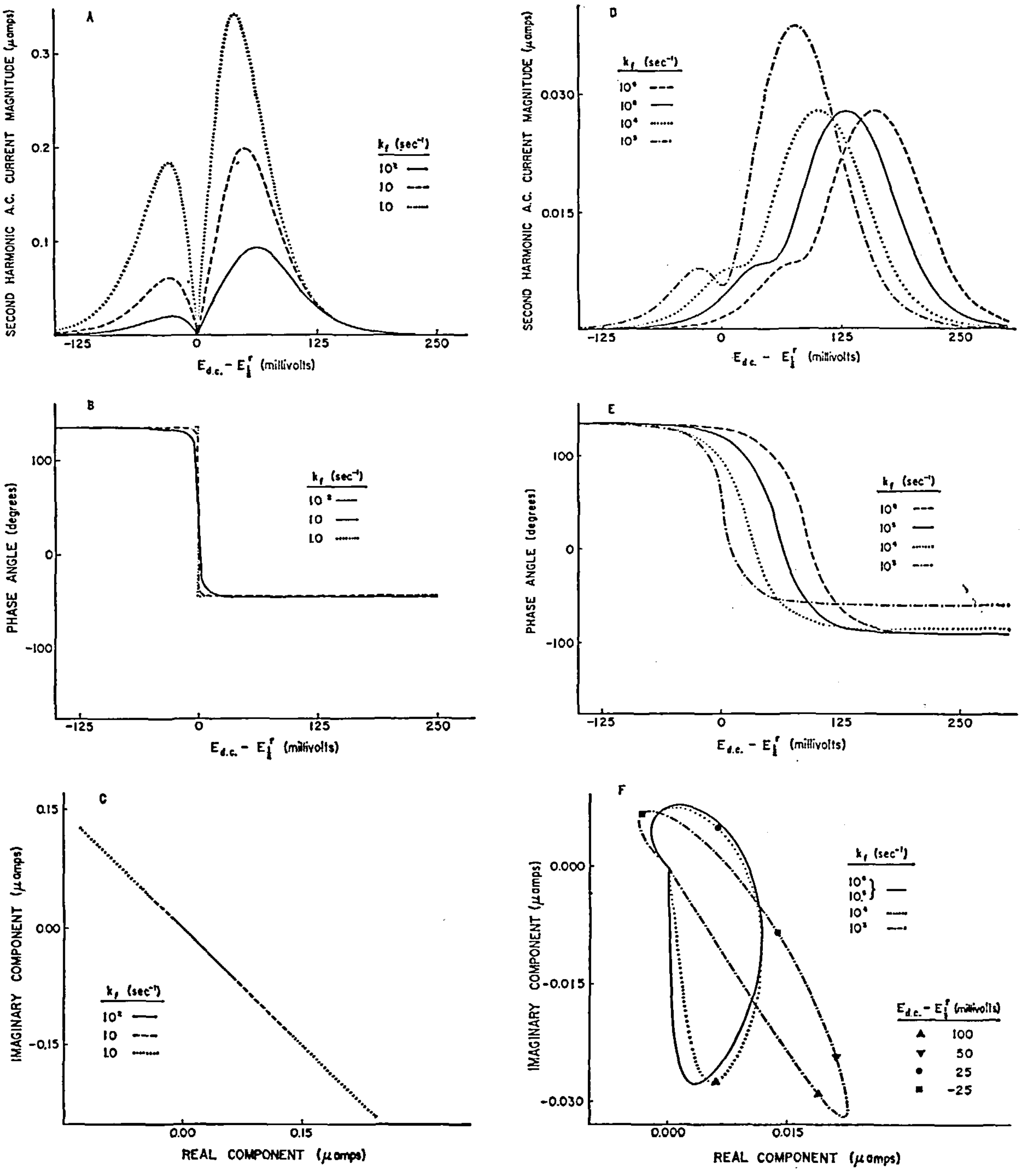


FIGURE 6. Calculated second harmonic ac polarographic response versus direct potential for system with an irreversible first-order chemical reaction following Nernstian charge transfer. A,D = second harmonic current amplitude polarograms. B,E = second harmonic phase angle polarograms. C,F = second harmonic complex plane polarograms. Parameter values: same as Figure 4. (Reprinted from reference 58 by courtesy of the American Chemical Society.)

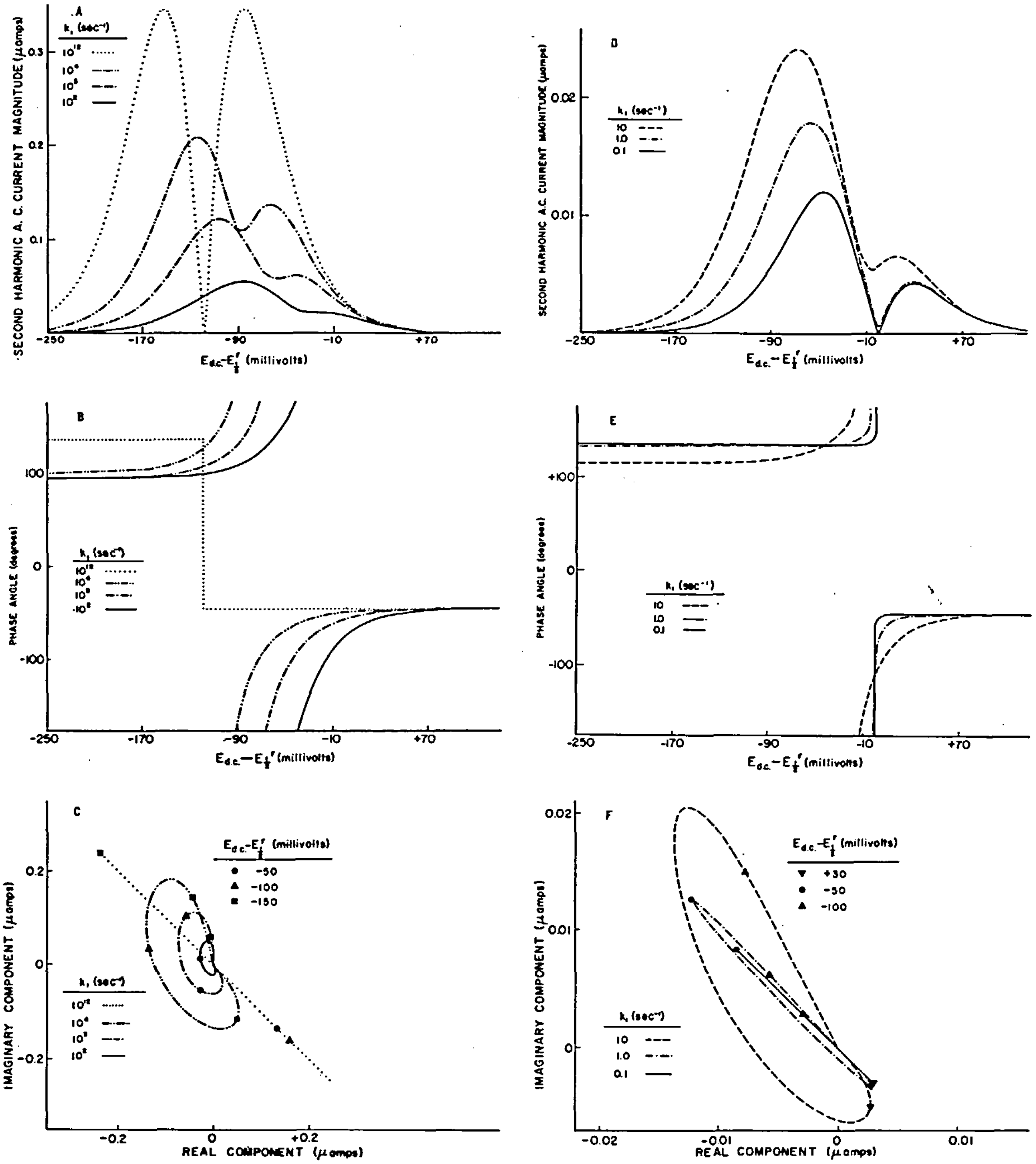


FIGURE 7. Calculated second harmonic ac polarographic response versus direct potential for system with a first-order chemical reaction preceding Nernstian charge transfer. A,C = second harmonic current amplitude polarograms. B,E = second harmonic phase angle polarograms. C,F = second harmonic complex plane polarograms. Parameter values: same as Figure 5. (Reprinted from reference 57 by courtesy of Elsevier Publishing Co.)

livolts,* respectively, for a drop life of 5 seconds with $k = 10^5 s^{-1}$ and $T = 298°K$). The situation is less simple, but still quite favorable for estimating thermodynamically significant potentials in cases where non-Nernstian behavior exists or where reversible follow-up or preceding chemical reactions are operative. One of the interesting observations one makes upon scanning theoretical predictions for second harmonic behavior with various mechanisms is that the existence of a minimum characterized by a null or near-null current (e.g., $\leqslant$ 20% of largest second harmonic peak) is apparently a guarantee that the minimum is "pointing out" a thermodynamically significant potential such as $E^r_{1/2}$ or

$$E^r_{\frac{1}{2}} + \frac{RT}{nF} \ln \left(\frac{1 + K}{K}\right),$$

where K represents the equilibrium constant of a coupled chemical reaction. This is a rather unique result because here is a case where simply the existence of a particular type of observable (a near-zero minimum on the second harmonic polarogram) appears to be a sufficient condition to allow one to take that observable as indicating a purely thermodynamic quantity. When kinetically induced perturbations ensue, the minimum either disappears or loses its near-null character. The same cannot be said for the dc polarographic half-wave potential and the fundamental harmonic ac peak potential, whose existences are obviously not sufficient to rule out kinetic perturbations. Considering the upsurge in use of the fundamental harmonic peak potential for obtaining E°s, stability constants, etc. (see section IVD-1), the rather remarkable possibilities of second harmonic ac polarography for this purpose should not be overlooked for long.

Many of the advances in fundamental and second harmonic ac polarographic theory outlined above have successfully passed experimental scrutiny. Section IV describes some of these experimental tests.

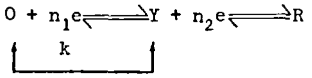
2. *First-Order Processes Coupled to Multi-Step Charge Transfer*

Until the late 1960's, ac polarographic theory for systems involving multi-step charge transfer had been almost non-existent. Only the so-called "EE Mechanism" (mechanism R4)

$$O + n_1e \rightleftharpoons Y + n_2e \rightleftharpoons R \qquad (R4)$$

had been examined in any detail.[7] However, very recently, workers have developed theoretical expressions for fundamental harmonic ac polarographic currents for two additional mechanisms (mechanisms R5 and R6).

$$O + n_1e \rightleftharpoons Y \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Z + n_2e \rightleftharpoons R \qquad (R5)$$



(R6)

$$O + n_1e \rightleftharpoons Y + n_2e \rightleftharpoons R$$

A theory for mechanism R5, the well-known ECE mechanism, was presented by Sobel and Smith.[59-61] It accounts for kinetic contributions of all relevant rate processes within the framework of the expanding plane model for the dropping mercury electrode. These authors also presented the theory for mechanism R6 for the special case of Nernstian heterogeneous charge transfer.[60] This theory was extended to encompass non-Nernstian behavior by deLevie, Kreuser, and Moreira.[62]

It is not the object of the present discussion to outline in any detail the predictions of the theory for Mechanisms R5 and R6. The complexity of the electrode reaction mechanisms in question gives rise to an enormous variety of types of predicted behavior whose discussion would require an inappropriate devotion of space to this topic. A few particularly novel predictions are mentioned in a different context in section IIC-3. Instead, we only wish to emphasize one important general conclusion obtained upon inspecting the theoretical derivations for mechanisms R5 and R6. This is that these developments tend to confirm that future advances of ac polarographic theory for the class of mechanisms under consideration will depend simply on the motivation of workers in the field, rather than on an ability to surmount difficult mathematical hurdles. Although algebraically quite cumbersome, theoretical derivations of the fundamental or second harmonic ac response are quite straightforward and can be accomplished with established derivational approaches, regardless of the number of heterogeneous electron transfer and first-order homogeneous chemical steps one wishes to invoke.

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*There is an error on this estimate in Reference 58.

3. Systems with Second-or-Higher-Order Chemical Reactions Coupled to the Charge Transfer Step.

An almost totally neglected area of ac polarographic theory involves mechanisms with higher-than-first-order chemical reactions coupled to charge transfer. This is not altogether surprising because such processes give rise to a boundary value problem with non-linear partial differential equations whose analytical solution is almost invariably quite difficult to formulate. In 1951 Gerischer[63] published a very elegant derivation for a coupled preceding chemical reaction of any order which assumed that the ac response was measured at the equilibrium potential (i.e., that dc polarization did not exist). His method for linearizing the ac part of the boundary value problem appears to be quite general. However, Gerischer's efforts did not encompass a key problem for conventional ac polarographic conditions, which is to account for effects of dc polarization with the mechanistic schemes in question.

Since 1951, the literature has shown no new developments in this area. However, some unpublished efforts to extend the Gerischer theory to encompass ac polarographic conditions have been concluded successfully and will be mentioned here to establish that the situation is *not* hopeless. Booman, Delmastro, and Smith[64] have derived expressions for the ac polarographic response with mechanisms involving irreversible dimerization and disproportionation following charge transfer (mechanisms R7 and R8).

$$O + ne \rightleftharpoons R \rightleftharpoons 1/2R_2 \qquad \text{(R7)}$$

$$2R \longrightarrow O + Y$$

$$O + ne \rightleftharpoons R \qquad \text{(R8)}$$

The results of these studies indicate that development of ac polarographic theory for systems with coupled second or higher-order reactions is tractable using modern computational tools. The derivational scheme employed for mechanisms R7 and R8 employs the Gerischer approach to linearize and subsequently solve the mathematical problem associated with the ac perturbation, while the dc polarization process is accounted for with the aid of recently popularized numerical methods[65-67] for handling non-linear partial differential equations. From a purely formal viewpoint, the mathematical relationships are quite analogous to those found for first-order cases. For example, the phase angle expression for mechanism R7 can be obtained from the corresponding relationship for the case of an irreversible first-order follow-up reaction[50] simply by replacing the quantity k_1/ω by $2k_2(\bar{C}_R)_{x=0}/\omega$, where ω is the angular frequency, k_1 and k_2 are the first- and second-order rate constants, respectively, and $(\bar{C}_R)_{x=0}$ is the dc component of the surface concentration of species R. This fact can be shown with relative ease. The major difficulty arises in mathematically describing the quantity $(\bar{C}_R)_{x=0}$, which is determined by the nature of the dc polarization process. This latter problem must be handled by numerical methods so that a completely analytical solution for the ac polarographic response is not possible. Consequently, one must offer a FORTRAN computer program, or the like, as the only generally useful form of the "rate law," a situation which is not uncommon in electrochemical kinetics.

Examination of the theoretical predictions for mechanisms R7 and R8 reveals effects which should be very useful for detecting the existence of higher-order coupled chemical reactions. For example, the phase angle is predicted to depend on the bulk concentration of the electroactive species initially present in the solution and on time (i.e., on mercury column height for the case of the dropping mercury electrode). Such behavior does not occur with first-order coupled chemical reactions. Similarly, the normally concentration-independent quantity $I(\omega t)/C_0^*$ [$I(\omega t)$ is the magnitude of the alternating current, C_0^* is the initial bulk concentration of Species O] also exhibits a concentration dependence with mechanisms R7 and R8. These effects are quite substantial as illustrated in Figures 8 and 9.

4. Systems with Simultaneous Effects of Adsorption and Coupled Homogeneous Chemical Reactions

The rather high level of sophistication which has been achieved recently in the development of theoretical electrochemical rate laws is epitomized in a paper by Sluyters-Rehbach and Sluyters[68] which considers simultaneous effects of reactant adsorption and coupled homogeneous chemical reactions on the ac response. The authors were concerned primarily with the manner whereby adsorption-induced coupling of faradaic and non-faradaic processes altered ac polarographic be-

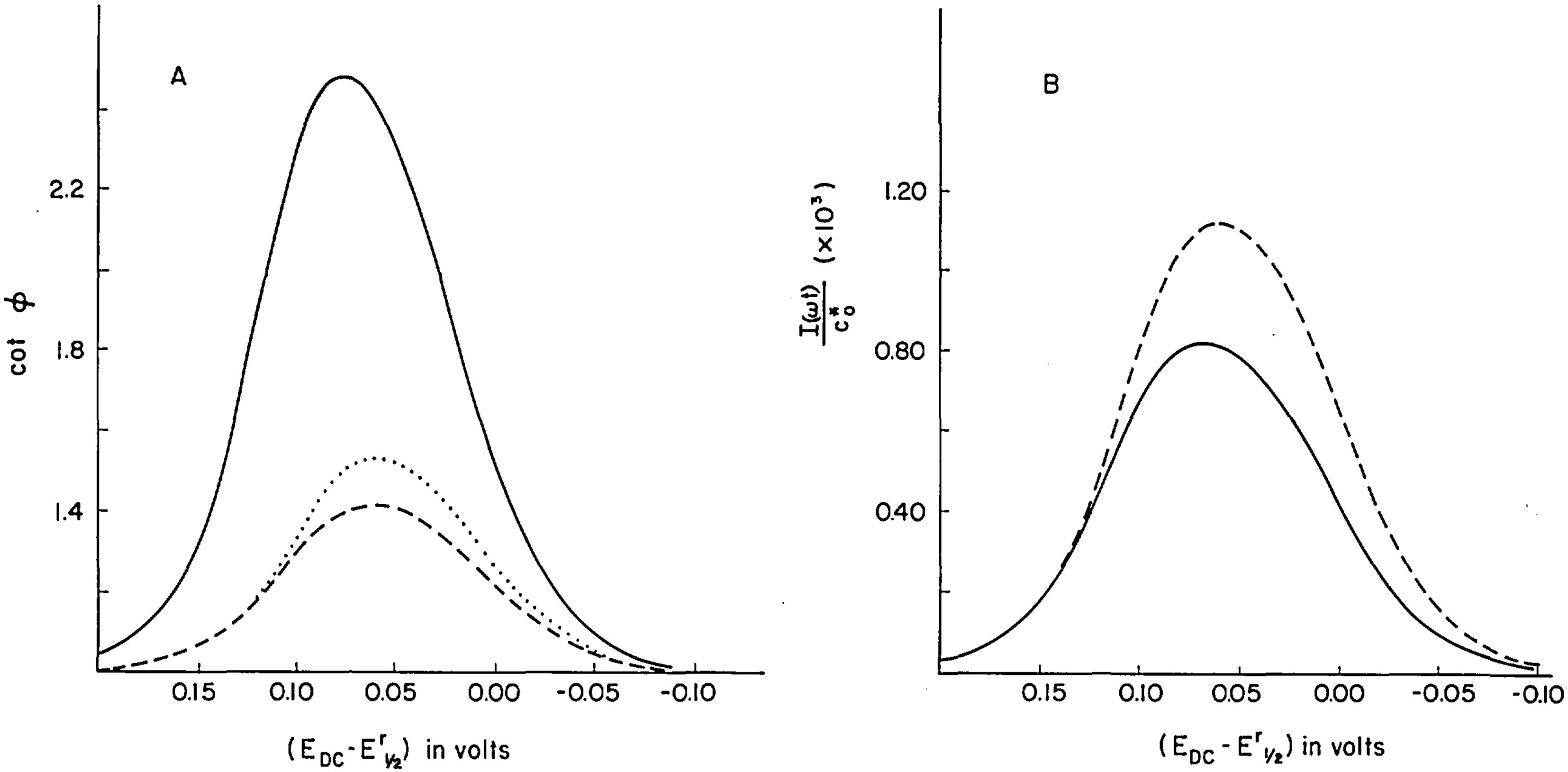

FIGURE 8. Calculated fundamental harmonic ac polarographic response versus direct potential for system with irreversible dimerization following Nernstian charge transfer. A - fundamental harmonic cot Φ - E_{dc} response. B - fundamental harmonic $I(\omega t)/C_o^*$ - E_{dc} response. Parameter values: all parameters same as Figure 4 except frequency = 150 Hz, chemical rate constant = 1.0×10^7 l · $mole^{-1}$ s^{-1}, and ---- $C_o^* = 5.0 \times 10^{-3}$ *M*, t = 6.0 sec. ---- $C_o^* = 1.0 \times 10^{-3}$ *M*, t = 6.0 sec. ······ $C_o^* = 1.0 \times 10^{-3}$ *M*, 3.0 sec.

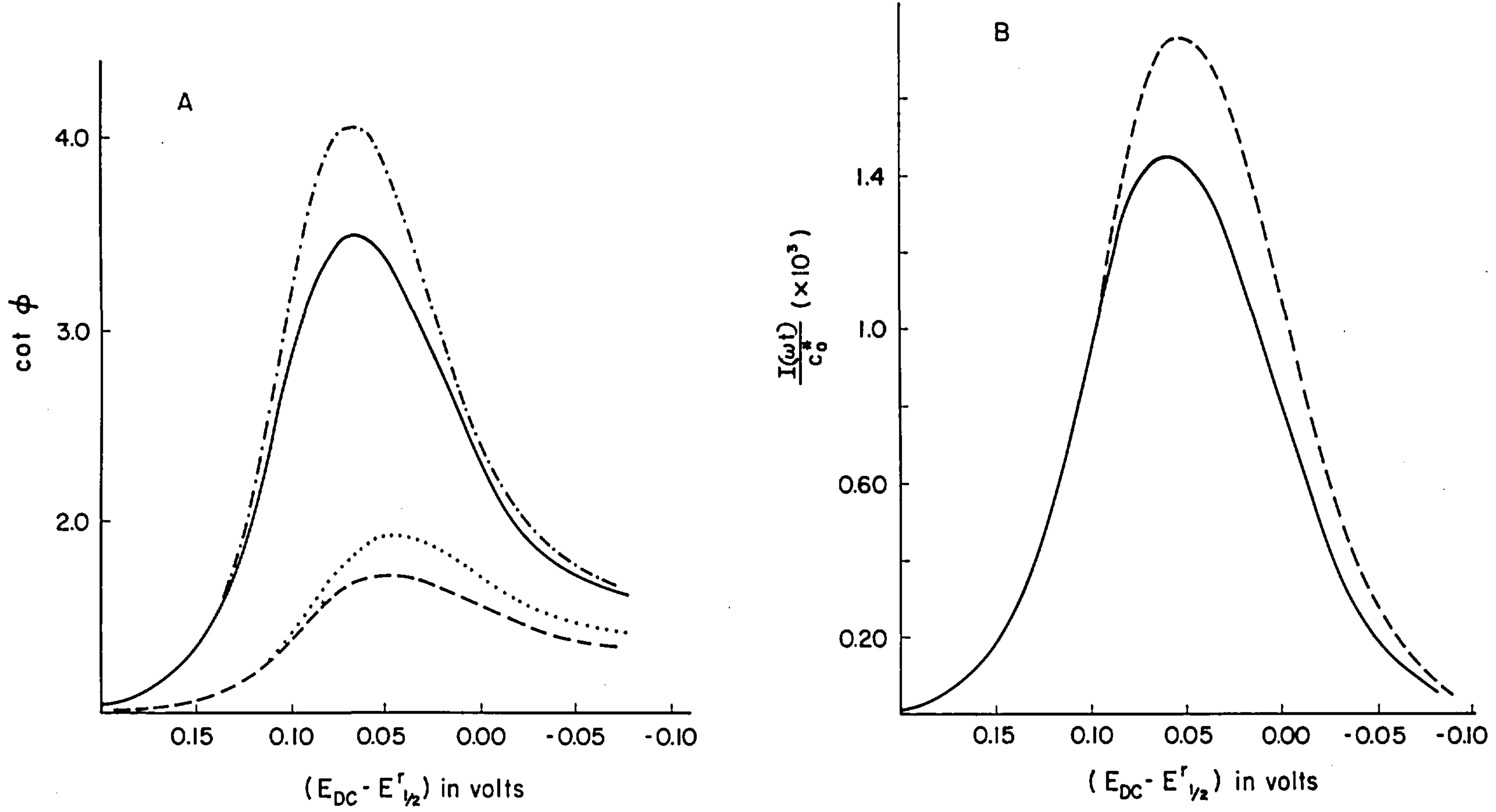

FIGURE 9. Calculated fundamental harmonic ac polarographic response versus direct potential for system with irreversible disproportionation following Nernstian charge transfer. Notation and parameter values same as Figure 8.

havior with mechanisms R1, R2, and R3. The authors did not attempt to formulate a completely general and rigorous theory. Their treatment was simplified by invoking the following assumptions or approximations: (a) Nernstian behavior prevails, (b) a stationary plane electrode model adequately describes mass transport, (c) the process occurs at the equilibrium potential, and (d) simultaneous adsorption of all three species does not occur (mechanisms R1 and R2). With regard to item (d), the authors considered two possibilities: (a) adsorption of Species O and R, independent of Species Y, and (b) adsorption of Species Y, independent of Species O and R.

Despite these simplifications it is fair to say that Sluyters–Rehbach and Sluyters have provided a successful and useful examination of a type of mechanism which would have been considered intractable a few short years ago. Furthermore, scrutiny of the derivation leads to the conclusion that the simplifying assumptions were invoked for convenience in discussing the basic characteristics of the problem, not by mathematical intractability. It appears that a quite rigorous extension of the equations is readily achievable. Consequently, we view this treatment of Sluyters-Rehbach and Sluyters as implicitly establishing the ability to theoretically formulate ac polarographic rate laws which account for combined complications due to charge transfer, adsorption, and coupled chemical reactions. This category encompasses a majority of conceivable mechanisms. It is this latter message conveyed by the efforts of Sluyters-Rehbach and Sluyters which I consider to be of general importance and wish to emphasize in the present discussion.

Among the detailed predictions of the theory in question, two main points are worth mentioning. First of all, the results of the derivation rather profoundly reaffirm the fact that success in deriving an electrochemical rate law does not guarantee that it can be usefully applied to experimental results. Specifically, one encounters in the cases considered the well-known practical problem of an observable whose behavior is described by too many independent parameters. Sluyters-Rehbach and Sluyters determined that seven independent parameters would be required in general to describe the frequency dependence of the electrode admittance with mechanisms R1 and R2, despite the simplifications invoked. Mechanism R3 requires six independent parameters. Complete quantitative characterization of such systems from ac data alone is normally quite impractical. This work provides one of the most impressive of numerous examples that can be forwarded to emphasize that electrochemical kineticists cannot in general rely on a single technique. With systems as complex as those under consideration, the only realistic hope of quantitative characterization of the relevant rate parameters is that sufficient *independent* measurements can be performed to generate as many or (preferably) more independent equations than parameters to be evaluated. Of course, if one is fortunate, a system under investigation might correspond to one of the limiting cases considered by Sluyters-Rehbach and Sluyters which follow relatively simple mathematical relationships. Most appealing and likely to be encountered is the case of weak adsorption. In this instance it is readily shown[68] that the second-generation approach for separating faradaic and non-faradaic components will be successful. The faradaic component will obey the simpler rate laws for mechanisms R1, R2, and R3 which ignore adsorption. The only evidence of reactant adsorption will be found in the fact that the double-layer capacity is not the same in the presence and absence of the faradaic process, just as in the case of weak adsorption with the simpler mechanism considered in section IIA-1.

5. Double-Layer Effects on Homogeneous Chemical Reaction Rates

At this point in time, a discussion of the theory for mechanisms with chemical reactions coupled to charge transfer is not complete without some mention of recent noteworthy progress in accounting for double-layer effects on the chemical reaction rate. The problem of double-layer effects on homogeneous chemical rate parameters derived from electrochemical techniques is important in the context of any electrochemical relaxation technique, including ac polarography. The problem arises because when a chemical equilibrium is perturbed by an electrode process, the perturbation is effective in a small region near the electrode known as the "reaction layer," part of which encompasses the diffuse double-layer. One need not possess much insight into the subject of chemical kinetics to conclude that with ionic homogeneous rate processes, the electrically anomalous environment provided by the diffuse double layer will influence chemical equilibria and kinetics. Consequently, one must consider the possibility that a chemical rate parameter calculated from electrochemical data may not accurately reflect the true homogeneous rate, due to double-layer effects. It has been recognized for some time that under conditions where the reaction layer thickness, μ, greatly exceeds the thickness of the δ diffuse double layer, double-layer effects on the chemical rate constants are negligible and electrochemical results reliably reflect homogeneous chemical reaction rates (assuming that other sources of error are avoided). In a *majority of cases the latter conditions are realized* in electrochemical measurements. The double-layer thickness, given by[69]

$$\delta = \frac{3.04 \times 10^{-8}}{z\sqrt{c}} \tag{10}$$

for an aqueous solution of a symmetrical electrolyte with ionic charge z and ionic concentration c at 25°C is of the order of 1 to 10Å under normal electrochemical conditions (e.g., ~2.5 Å for a 1.5 *M* univalent electrolyte). In contrast, the reaction-layer thickness which is calculable from expressions such as (for mechanism R1)

$$\mu = \sqrt{D_o/k_2} \tag{11}$$

normally exceeds a few hundred Ångstroms. However, with certain very rapid processes, such as some protolytic reactions in aqueous media, one finds that $\delta \approx u$ and electrochemically deduced apparent chemical rate parameters can deviate significantly from the true homogeneous value. Failure to recognize this fact led to one of the most embarrassing episodes in electrochemical kinetics in which erroneous rate data were published for a variety of protolytic reactions. The stature of electrochemical relaxation techniques as a means of measuring chemical reaction rates has never fully recovered from this setback in the eyes of non-electrochemists, despite the fact that over a decade of progress and clarification has elapsed and the problem is now virtually solved.

The inhomogeneity introduced by the diffuse double layer can perturb the apparent rate of a chemical reaction through the following specific mechanisms: (a) alteration of the stationary ion concentrations from the bulk values due to the different electrical potential in the diffuse double layer, (b) acceleration or inhibition of ionic mass transfer due to the potential gradient in the diffuse double layer, (c) alteration of rate and equilibrium relations due to dielectric saturation, and (d) enhancement of dissociation rates by the electric field (Second Wien Effect). A rigorous theoretical accounting for these combined effects on the apparent chemical reaction rate presents an almost overwhelming task. Consequently, for a significant period little progress was made and little hope was held for the prospect of obtaining a practical solution to this problem. However, as so often happens in scientific endeavors, a fresh outlook has led to an elegantly simple and practical technique whereby a global correction for the sum of all double-layer effects on the chemical reaction rate can be implemented. Rather than a brute force theoretical attack, Nürnberg et al.[70] (see Reference 70 for complete bibliography) and Schroeder and Shain[69] independently arrived at a semi-empirical approach for obtaining chemical rate constants, corrected for double-layer influences. A series of relatively sound, semi-quantitative theoretical arguments, *which do not require explicit calculation of the position-dependence of the rate and equilibrium constants in the double layer*, led these workers to a simple graphical scheme for effecting the desired corrections. The technique's only apparent restriction is that $\mu \geq 4\delta$. The approach can be best illustrated with the aid of a specific mechanism. For example, consider the process

$$\begin{gathered} HA \underset{k_b}{\overset{k_f}{\rightleftharpoons}} H^+ + A^- \\ H^+ + e \rightleftharpoons 1/2H_2 \end{gathered} \tag{R9}$$

For mechanism R9 one performs a series of experiments at constant ionic strength, but at different pH values (different A^- concentrations, C_{A^-}). Thus, one is varying the chemical reaction rate, $k_bC_{A^-}$, and the reaction-layer thickness is changed relative to the double-layer dimension. Apparent rate constants, (e.g., $k_{f,a}$) are calculated in the usual manner from the appropriate electrochemical rate law for each experiment and a plot of $k_{f,a}/C_{A^-}^{1/2}$ vs. $C_{A^-}^{-1/2}$ is generated. The semi-quantitative theory[69] leads one to expect this plot to be linear and to have a slope equal to the true homogeneous rate constant, k_f. Tests of these ideas confirm expectations as illustrated in Figure 10. Homogeneous protolytic reaction rates thus obtained are in good agreement with those generated from conventional chemical relaxation methods. The work of Nürnberg and co-workers has been particularly extensive and convincing with regard to this scheme's validity. Most recently, Nürnberg and Wolff have carried out an approximate, but detailed, theoretical examination of the various double-layer perturbations on chemical reaction rates. Their work provides a more solid theoretical foundation for the graphical correction described above. They also conclude that the dissociation field effect (Second Wien Effect) is normally the dominant double-layer effect.[70]

As a result of these efforts, measurements of homogeneous chemical reaction rates by ac polarography and other electrochemical approaches can be considered to be on solid footing, even for the most rapid reactions, in solution.

Some Recently Recognized Effects of the DC Polarization Process on the AC Polarographic Wave

During the early development of theoretical insights into the ac polarographic response, an interesting sequence of events led to a rather retarded view of the role of the dc polarization process which endured for well over a decade. Two quite understandable factors which dominated pioneering work in ac measurements led to this conceptual miscarriage. First, the European school's preoccupation with ac measurements at the equilibrium-direct potential led them to devote little attention to the question of dc polarization effects. Second, there was a preoccupation with rapid electrode processes so that even when consideration was given to the existence of dc polarization (originally by the Australian school), workers were content to assume that the dc process was diffusion-controlled (reversible). Thus, on the basis of no consideration or a simplistic consideration of the dc process, a number of qualitative and quantitative theoretical concepts regarding the response of the faradaic impedance were formulated and widely accepted. Some of these ideas become readily apparent upon inspection of the classical expression for the faradaic impedance for the case of measurements *at the equilibrium potential* with a simple electrode reaction involving rate control by diffusion and/or charge transfer (mechanism R10).

$$O + ne \rightleftharpoons R \qquad \text{(R10)}$$

The expressions may be written

$$r_s = \frac{RT}{nF}\left\{\frac{1}{I_a^o} + \frac{1}{nF\sqrt{2\omega}}\left[\frac{1}{C_O D_O^{1/2}} + \frac{1}{C_R D_R^{1/2}}\right]\right\} \qquad (12)$$

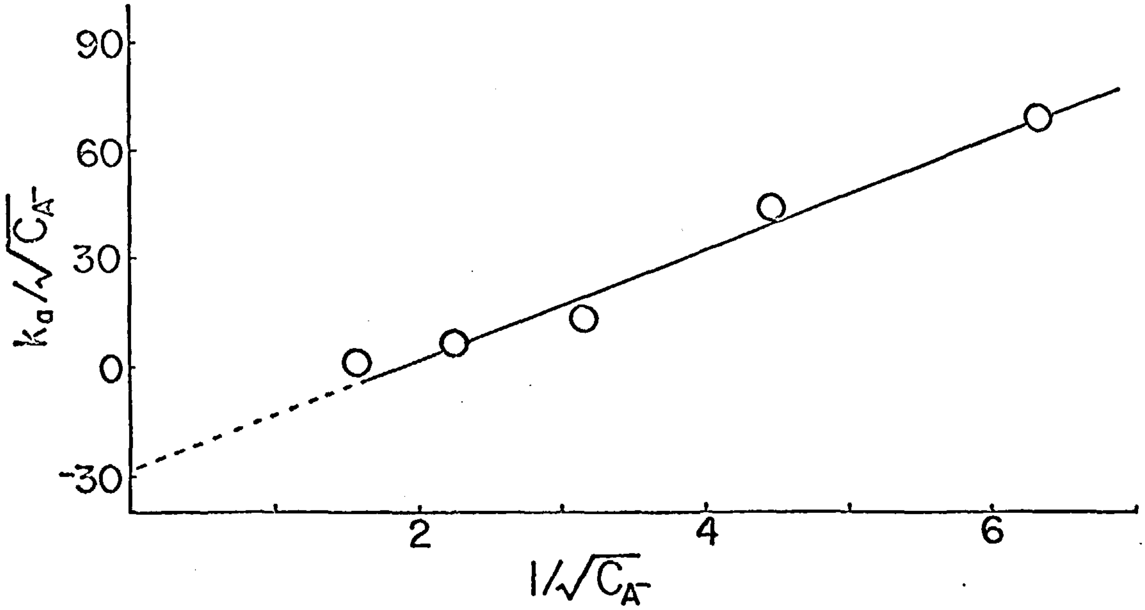

FIGURE 10. Graphical correction for double-layer effects on homogeneous chemical reaction kinetics. Units are $k_a/\sqrt{C_{A^-}}$-(x 10^{-5}) $\ell^{-1/2}$/mole · s^{-1} vs. $1/\sqrt{C_{A^-}}$-($\ell^{1/2}$ mole$^{-1/2}$). (Reprinted from reference 69 by courtesy of the American Chemical Society.)

$$\frac{1}{\omega C_s} = \frac{RT}{nF}\left\{\frac{1}{nF\sqrt{2\omega}}\left[\frac{1}{C_O D_O^{1/2}} + \frac{1}{C_R D_R^{1/2}}\right]\right\} \qquad (13)$$

$$I_a^0 = nFk_s C_O^{1-\alpha} C_R^{\alpha} \qquad (14)$$

where

r_s and $1/\omega C_s$ are the *series* resistive and capacitive components of the faradaic impedance, $I_a°$ is the so-called "exchange current density," k_s is the heterogeneous charge-transfer rate constant at the potential E° (standard rate constant), α is the charge-transfer coefficient, ω is the angular frequency, C_O and C_R are the *bulk concentrations* of Species O and R, respectively, D_O and D_R are the corresponding diffusion coefficients, and the usual significances are assigned to R, T, n, and F. Inspection of Equations 12 to 14 and similar relationships for more complex mechanistic schemes leads to the following conclusions (the "classical concepts" of the faradaic impedance):

a. As k_s becomes very small, the impedance approaches infinity–i.e., irreversible processes yield no ac current;

b. Because all terms in Equations 13 and 14 are constant for a given experiment, the faradaic impedance is time-independent;

c. The faradaic impedance behaves like some combination of simple passive RC circuit elements because the phase angle is predicted to be in the first quadrant;

d. The faradaic impedance is separable into individual components such as the "charge transfer resistance," r_{CT} ($r_{CT}=RT/nFI_a°$, the "mass transfer" or "Warburg impedance,"

$$Z_W\Big(Z_W = r_W + \frac{1}{\omega C_W}\ ;\ r_W = \frac{1}{\omega C_W}$$

$$= \frac{RT}{n^2F^2\sqrt{2\omega}}\left[\frac{1}{C_O D_O^{1/2}} + \frac{1}{C_R D_R^{1/2}}\right]\Big) \quad ,$$

and other components which arise in mechanisms more complex than the one considered by Equations 12 to 14;

e. The only relevant time scale in the ac experiment is that associated with the ac perturbation–i.e. $2\pi/\omega$; and

f. Because Equations 12 to 14 are obtained for normal experimental conditions, regardless of the geometrical model employed for the electrode, effects of electrode growth or geometry are negligible.

While these concepts are completely rigorous and useful for measurements in absence of dc polarization, the widespread tendency to apply the same ideas to the normal ac polarographic experiment where dc polarization exists led to numerous oversights.

It was recognized quite early that with Nernstian behavior in the dc sense, Equations 12 to 14 can be adapted to ac polarographic conditions by replacing the bulk concentration terms, C_O and C_R, by the mean surface concentrations (dc concentration components), $\bar{C}_{O_{x=0}}$ and $\bar{C}_{R_{x=0}}$ However, the profound implications of this transformation were not widely recognized until the early 1960s. Despite the restriction of Nernstian dc behavior, careful consideration of the implications attending the replacement of C_O and C_R by $\bar{C}_{O_{x=0}}$ and $\bar{C}_{R_{x=0}}$ is sufficient to allow one to recognize the general inapplicability of the foregoing simple concepts (items a to f) under normal ac polarographic conditions. To reach this conclusion, one must simply recognize that when dc polarization exists, the magnitudes of the concentration terms, $\bar{C}_{O_{x=0}}$ and $\bar{C}_{R_{x=0}}$, are governed by the various rate processes which are important in the dc sense–i.e., the rate laws of dc polarography apply. For example, (1) since electrode geometry and growth are significant influences in the dc experiment and effect $\bar{C}_{O_{x=0}}$ and $\bar{C}_{R_{x=0}}$, ac measurements with dc polarization will be subject to such effects, and (2) for many mechanisms $\bar{C}_{O_{x=0}}$ and $\bar{C}_{R_{x=0}}$ will be time-dependent and, consequently, the ac response may exhibit time-dependence (dependence on the mercury-column height with a dropping mercury electrode). Clearly, kinetic-mechanistic features of the electrode reaction which are important on the dc time scale will influence the ac response regardless of their relevance in the ac time domain. These foregoing complications introduced by dc polarization were well-documented by the mid-1960s.[7] The viewpoint that conventional ac polarography is a technique with a dual personality was advanced.[7] It is a technique in which two time scales are important, the dc time scale (e.g., mercury drop life) and the ac (period of the alternating potential). Furthermore, the duality applies in another sense in that the experiment possesses features of techniques utilizing large amplitude (the direct potential) and small amplitude (the alternating potential) perturbations. Figures 4 and 6 (above) provide useful examples of these ideas. In both cases the ac response is notably attenuated by the follow-up chemical reaction, even when $k \ll \omega$–i.e., when the reaction is kinetically inoperative in the ac sense. Under these conditions the rather significant effect arises due to the chemical reaction's influence on $\bar{C}_{O_{x=0}}$ and $C_{R_{x=0}}$. In cases such as these, the ac process may be looked upon mainly as a sensitive probe into the dc process, at least from a kinetic viewpoint. Incidentally, careful studies show that complications attending this duality of the ac polarographic experiment are more than offset by gains in information content.

The recognition of time-dependence, electrode geometry, and growth effects and the duality of the conventional ac polarographic experiment turned out to be somewhat of a prelude to the recognition of some even more novel effects of dc polarization. In the last three years, several newly recognized consequences of dc polarization (among other things)* have been theoretically and experimentally established which force one to greatly liberalize concepts regarding the nature of the faradaic impedance under ac polarographic conditions.

1. Coupling of the Various Components of the Faradaic Impedance

The recent attention accorded the subject of coupling between interfacial impedance components has not been limited to the faradaic-non-faradaic coupling question raised by Delahay. DeLevie and co-workers[27,71] have focused on the question of separability of components of the faradaic impedance alone, specifically, the interfacial and mass-transfer impedances. They have demonstrated quite conclusively for a variety of mechanisms (mechanisms R1, R2, R3, R6, and R10, as well as mechanisms involving passivation and adsorption)[27,71] that separability of interfacial and mass transfer impedances is an erroneous concept under normal ac polarographic conditions. DeLevie et al. argue that these components are coupled in the most intimate sense–i.e., that the characteristics of the interfacial impedance can in general influence the magnitude of the mass transfer impedance and vice versa. That this viewpoint is necessarily correct becomes rather obvious if one considers once again the predictions of Equations 12 to 14 when modified to account for dc polarization. It suffices to focus on the resistive component which consists of the charge-transfer resistance which, for this case, is written

$$r_{CT} = \frac{RT}{n^2F^2k_s(\bar{C}_{O_{x=0}})^{1-\alpha}(\bar{C}_{R_{x=0}})^{\alpha}} \tag{15}$$

and the mass-transfer resistance given by

$$r_W = \frac{RT}{n^2F^2\sqrt{2\omega}\left[\frac{1}{\bar{C}_{O_{x=0}}D_O^{1/2}} + \frac{1}{\bar{C}_{R_{x=0}}D_R^{1/2}}\right]} \tag{16}$$

The origin of coupling between r_{CT} and r_W is found in the surface concentration terms, $C_{O_{x=0}}$ and $C_{R_{x=0}}$ which are common to both impedance components. Because both mass transfer and charge transfer combine to determine the surface concentrations, it is evident from Equations 15 and 16 that these impedances influence each other. Even an effect as mundane as an electrode geometry contribution, which one intuitively tends to associate with the mass-transfer impedance, must show up in r_{CT} as well as r_W via the surface concentrations. The fact that Equations 15 and 16 are strictly applicable only for Nernstian dc behavior does not invalidate this rationale. Modification of these expressions to account for non-Nernstian dc behavior or *any* other mechanistic complication does not alter the key point which is the appearance of $\bar{C}_{O_{x=0}}$ and $\bar{C}_{R_{x=0}}$ in both the interfacial and mass-transfer impedances. Specific consideration of more complex situations leads to more interesting and impressive results. For example, deLevie et al.[27,71] demonstrate for certain rather anomalous electrode reactions (e.g., cases involving unusual potential dependences of the heterogeneous charge transfer rate–see section IIC-3) that the charge transfer resistance influences not only the magnitude of the mass-transfer impedance, but also its *sign*.

This work, together with the efforts concerning faradaic-non-faradaic separability, should impress on investigators that the separability of interfacial

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*The reader should carefully note that all phenomena discussed in this section depend on the existence of factors in addition to dc polarization. On the other hand, the common denominator and a necessary condition for all effects discussed is dc polarization.

impedance components is an idea whose operational validity is questionable and should be implemented only with great caution. Hopefully, the field of electrochemical kinetics has matured to the point where the separability concepts are neither necessary for data analysis nor required as a "pedagogical crutch."

2. AC Polarography and Irreversible Processes

The view that irreversible electrode reactions do not give rise to an ac polarographic wave was among the earliest conclusions reached regarding characteristics of the ac polarographic response. It grew out of pioneering experimental studies which failed to detect a measurable response with such systems and was reinforced by theoretical results of the type illustrated in Equations 12 to 14. Here again, workers were led astray by failure to recognize the inapplicability of classical faradaic impedance theory to ac polarographic conditions as well as by the low sensitivity of the first instruments. In some recent reports, Timmer, Sluyters-Rehbach, and Sluyters[72] and Smith and McCord[73] demonstrated that this long-accepted outlook is incorrect. It was concluded that irreversible processes in general give rise to small but measurable ac polarographic waves (including higher harmonic polarograms) which are predicted to exhibit characteristic and useful properties, many of which have been experimentally verified (see section IVB-4). Equations describing the fundamental and second harmonic ac polarographic response have been derived for electrode processes which are irreversible by virtue of slow heterogeneous charge transfer [72,73] and chemical decomposition of the electrode reaction product.[73] A typical predicted fundamental and second harmonic ac polarogram with an irreversible process is illustrated in Figure 11 (faradaic currents only).

These studies lead one to conclude that an observable faradaic ac polarographic response should be associated with the rising or falling (i.e., retrograde currents) portion of a dc polarogram, regardless of the degree of reversibility of the electrode reaction. Failure to detect a faradaic ac response under such conditions probably reflects inadequate instrument sensitivity (particularly inability to minimize double-layer charging current contributions), rather than the absence of a faradaic response.

3. Limitations on AC Polarographic Phase Angles

The phase angle of the faradaic alternating current relative to the applied potential is sensitive, convenient, and diagnostically useful for electrochemical kinetic-mechanistic studies. Consequently, attention has been focused on its behavior since the advent of small-amplitude ac measurements. Prior to about 1967, examples of valid theoretical studies which predicted values of phase angle (Φ) outside the first quadrant (outside the range $0 \leqslant \Phi \leqslant 90°$) were quite rare as was experimental evidence of such behavior. The rare exceptions were cases involving the prediction or observation of "inductive" or fourth quadrant behavior ($-90° \leqslant \Phi \leqslant 0°$). As a result, second and third quadrant behavior (negative faradaic admittance) was viewed as definitely anomalous, if not suspect. However, in the last three to four years a rash of papers has appeared dealing with such "anomalous" ac polarographic phase angles. Theoretical arguments have been presented which predict such behavior for a variety of mechanisms,[27,59-62,71,74-79] and convincing experimental verification has accompanied some of this work.

The most carefully scrutinized source of anomalous ac polarographic phase responses is an unusual potential dependence of the heterogeneous rate constant.[27,71,74,76-79] For example, deLevie and co-workers[27,71,74,76] and Timmer, Sluyters-Rehbach, and Sluyters[77,78] have shown that when one removes the usual assumptions regarding $\partial K/\partial E$ for electrode reactions,* the prediction that the faradaic impedance may be either positive or negative is obtained. Such results are predicted, for example, if one assumes that the rate constant for reduction *decreases* as the direct potential is made increasingly *negative*. Such behavior can arise when an unfavorable double-layer transition, such as desorption of a species which catalyzes an electrode reaction, accompanies the variation of potential. The less subtle phenomena associated with classical passivation[71,75,79] offer an alternative possibility. Anomalous phase angles

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*In accord with classical absolute rate theory and much experimental data, it is usually assumed that the reduction rate constant, k, increases exponentially as the electrode potential, E, is made more negative.

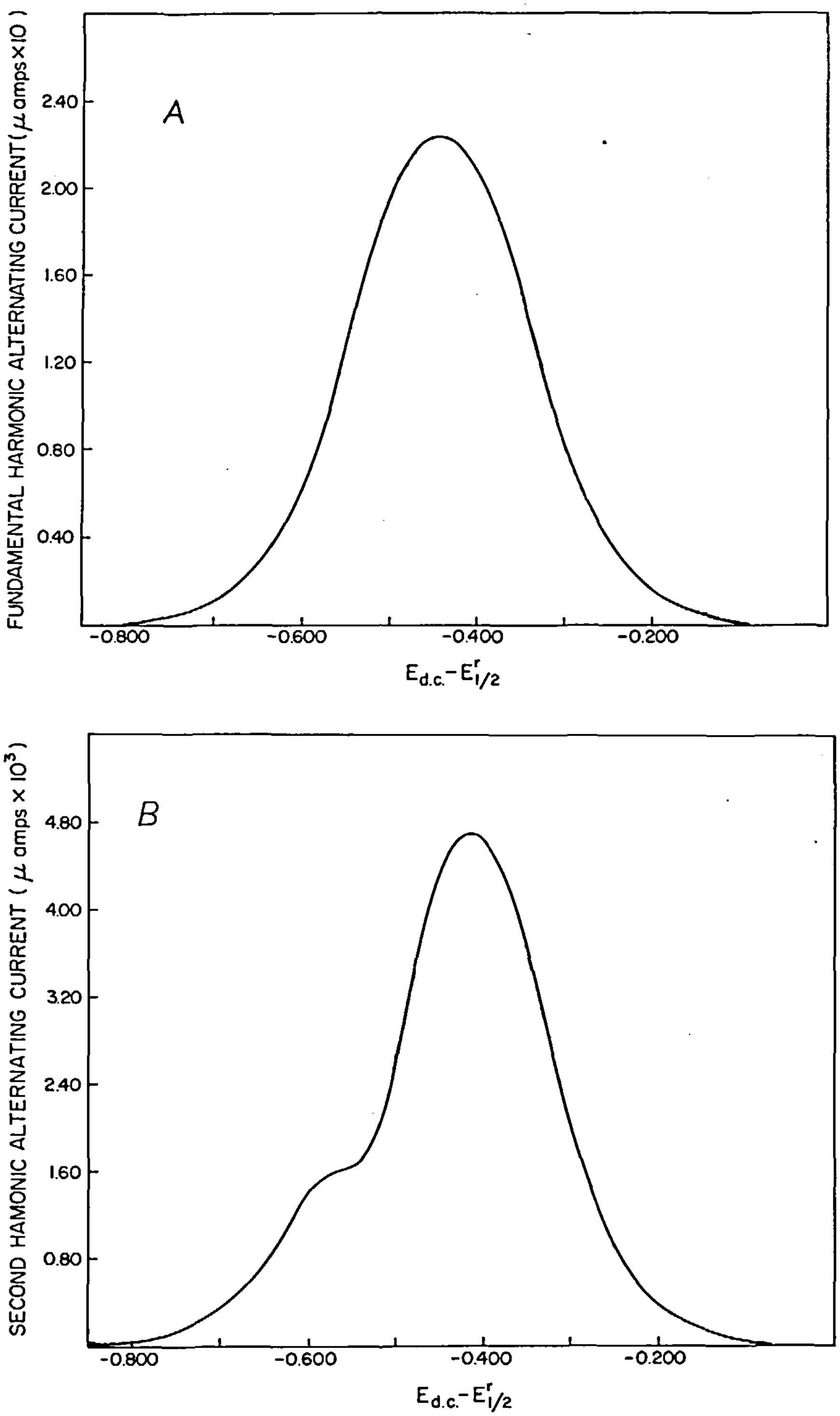

FIGURE 11. Calculated fundamental and second harmonic ac polarographic waves for a system with irreversible heterogeneous charge transfer. A – fundamental harmonic current amplitude polarogram. B – second harmonic current amplitude polarogram. Parameter values: k_s = 1.00 x 10^{-6} cm · s^{-1}, α = 0.500, t = 10.0 s, frequency = 15.9 Hz, all diffusion coefficients = 1.00 x 10^{-5} cm · s^{-1}, bulk concentration of oxidized form = 1.00 x 10^{-3} *M*, ac amplitude = 5.00 mV, electrode area = 0.035 cm^2, T = 298°K, n = 1.

originating in unusual heterogeneous charge-transfer behavior can be predicted in the context of any mechanistic scheme, even the simplest (mechanism R10), provided that the heterogeneous charge-transfer process is at least partially rate-controlling. Retrograde dc polarographic currents often accompany such systems.[74,77,78]

Under appropriate conditions, mechanisms R5 and R6 also are predicted to yield anomalous phase angles.[59-62] An extrapolation of these conclusions strongly suggests that electrode processes involving chemical reactions coupled to multi-step charge transfer may be a frequent source of abnormal phase angles. An interesting aspect of the work on mechanisms R5 and R6 is that it established the possible existence of unusual phase angles without kinetic involvement of the heterogeneous charge-transfer step. Mechanisms R5 and R6 are predicted to give rise to such behavior under strictly Nernstian conditions. In fact, in both cases it was shown that sufficiently slow charge transfer will eliminate the possibility of observing phase angles outside the first quadrant.[59,61,62]

The topic of anomalous faradaic phase angles is another case where details of the theoretical predictions are of less concern to this review than the general significance of the findings which is more than simply academic or theoretical. The establishment that negative faradaic admittances are definitely theoretically admissible is important in almost any experimental context, even if one does not intend to apply quantitative theoretical concepts to data (e.g., in routine analysis). This development is particularly timely because of the rapidly expanding use of phase-sensitive detectors (i.e., "lock-in amplifiers") in ac polarography (see section IIIB-1). Unlike the full-wave rectifiers commonly employed in older instruments, whose output manifests only the absolute magnitude of the alternating current, the phase-sensitive detector produces an output signal related to the amplitude and phase of the faradaic current.[7] In particular, a phase-sensitive detector will yield a negative output in response to a negative faradaic admittance. Thus, if it were not for the theoretical advances just enumerated and if reports of negative faradaic admittances were nearly non-existent, an ac polarographer observing a negative response from the output of a phase-sensitive detector might be inclined to question the fidelity of his instrument. A considerable waste of time while looking for a non-existent electronics problem might be the result.

Another important general consideration and common denominator underlying the effects under consideration becomes evident when one searches for a rationale to the fact that abnormal ac polarographic phase angles were almost completely overlooked for two decades. Why did so much time elapse before it was finally generally realized they are not particularly uncommon? Partial responsibility is found in the fact that phase-sensitive detection did not enjoy widespread popularity in ac polarography until recently, when broad-band phase-sensitive detectors became avaliable at reasonable cost. Consequently, for a long while the majority of experiments performed with dc polarization were incapable of sensing a negative faradaic admittance, even if it existed. However, once again it appears that the oversight in question arose in large measure from inadequate attention to effects of dc polarization. Because most of the early quantitative theoretical and experimental work was preoccupied with ac measurements at the equilibrium direct potential, no predictions or observations of negative faradaic admittances were forthcoming. The reason why unusual faradaic phase angles are not associated with ac measurements at the equilibrium potential may be found in the relation which describes power dissipation in a *pure* ac process;

$$P = E_{ac} I_{ac} \cos \Phi \qquad (17)$$

where P is power dissipation, E_{ac} is the amplitude of the alternating potential, I_{ac} is the alternating current amplitude, and Φ is the phase angle between the current and potential. Equation 17 indicates that *power dissipation* (P positive) corresponds to $-90^\circ \leq \Phi \geq 90^\circ$ (Φ in first or fourth quadrant) whereas *power gain* is realized if Φ is in the second or third quadrant. For the case of ac measurements *confined to the thermodynamic equilibrium direct potential*, where only alternating current flows, values of Φ in the second or third quadrants would represent a situation where the cell is a net source of electrical energy. This is difficult to reconcile with thermodynamic principles because an obvious ac energy source does not exist at the equilibrium potential and, consequently, phase angles outside the first and fourth quadrants seem to be precluded. A minor flaw in this argument is found in the possibility that an electrode process may exhibit an abnormally nonlinear faradaic admittance which will produce a response with substantial harmonic content. Under such conditions Equation 17 does not accurately represent total power dissipation in the cell. However, such events are unlikely, so that chances of second or third quadrant phase angles arising in measurements at the equilibrium direct potential are at least very remote, an observation which is supported by all theoretical and experimental precedent. On the other hand, as soon as one allows for the exsistence of dc polarization, the foregoing line of argument leads to no restrictions for the fundamental harmonic phase angle. With dc polarization, Equation 17 must be replaced by (again ignoring higher harmonics)

$$P = E_{dc}\, i_{dc} + E_{ac}\, i_{ac} \cos \Phi \qquad (18)$$

where E_{dc} and I_{dc} are the direct potential and current, respectively, and the remaining terms are defined as in Equation 17. When Equation 18 is applicable, the requirement that P must be positive clearly does not restrict the ac term, $E_{ac}\ I_{ac} \cos \Phi$, to positive values because dc power dissipation ($E_{dc}\ I_{dc}$) can make up for power gain in the ac process. Thus, as with so many other aspects of the ac response discussed earlier, "all bets are off" when dc polarization exists. In terms of this general qualitative line of argument, any phase angle appears admissible with dc polarization. Although rather simplistic and incompletely developed, the foregoing arguments in terms of Equations 17 and 18 seem to be supported by the facts that theoretical and experimental demonstrations of faradaic processes which imply net power gain in the ac term (second and third quadrant phase angles and electrochemical oscillators[76]) all involve processes in which dc polarization occurs. Thus, it does not appear that the role of the dc process is overemphasized by this discussion.

4. *Second Harmonic AC Polarograms with Quasi-Reversible Processes*

A final note which emphasizes that one should not take lightly the influences of dc polarization is provided in a paper[80] dealing with second harmonic ac polarography of simple electrode reactions controlled by diffusion and charge transfer– i.e., quasi-reversible processes (mechanism R10). The work in question did little more than remove the assumption of Nernstian behavior in the dc sense which characterized earlier theoretical treatments of the second harmonic response. Despite this seemingly minor generalization of earlier models, substantial deviations from the accepted characteristics of the second harmonic polarogram were deduced for situations where the dc process is non-Nernstian. Contrary to the prevailing view that the quasi-reversible second harmonic ac polarogram (current amplitude polarogram) would exhibit two peaks, polarograms ranging from those showing a single peak with a shoulder (e.g., Figure 11) to those with as many as four peaks were predicted. These extremely complex polarograms, such as shown in Figure 12, arose when conditions corresponding to quasi-reversible dc polarographic behavior were invoked. Furthermore, the calculations suggested that the assumption of Nernstian dc behavior could be applied to data analysis with general validity only if $k_s \geq 10^{-1}$ cm-S^{-1}. This is well above the value of 10^{-2} cm-S^{-1} which is sufficient to validate a Nernstian assumption in dc or fundamental harmonic ac polarography. The difference arises because of the enhanced sensitivity of the second harmonic response to kinetic effects and it provides further basis for caution and rigor in treating dc polarization effects.

D. General Implications of Theoretical Advances

There is a good possibility that the theoretical developments enumerated above may cause future workers to view the last 3½ years as a high point in the elucidation of basic principles of ac polarography. It was a period in which one witnessed the elimination of certain incorrect, progress-inhibiting concepts and the unraveling of some previously confusing problems of long-standing. Hopefully, on the basis of the foregoing remarks and some independent reflections the reader will appreciate that clarification of matters such as the separability of interfacial impedance components, the true nature of the double-layer capacitance, the ac polarographic response with irreversible processes, the limitations on ac polarographic phase angles, etc. must benefit the informed user of ac polarography. This statement should hold true regardless of whether one's application of ac polarography is analytical or physical chemical in nature or whether one's interest in the theory is qualitative or quantitative.

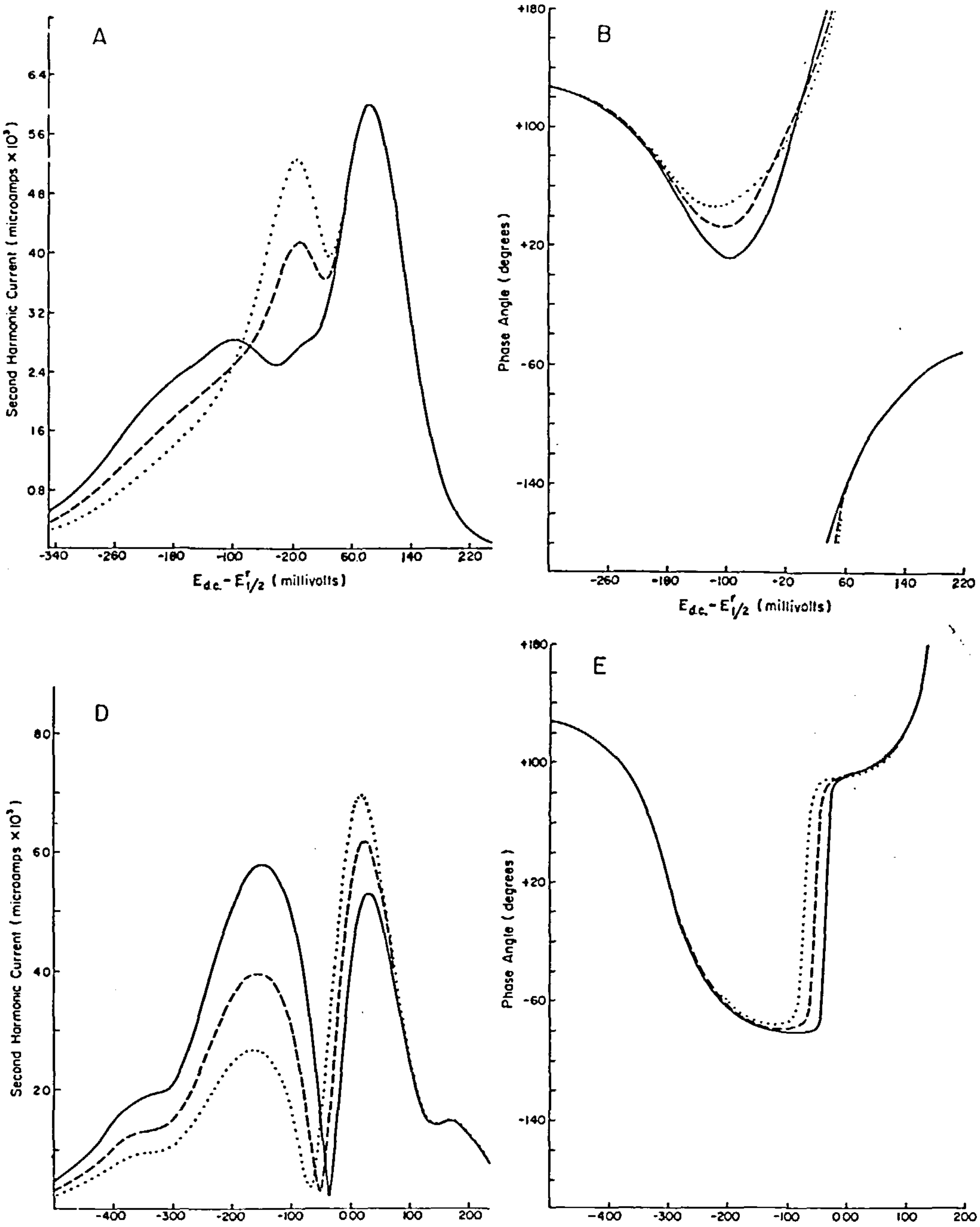

FIGURE 12. Calculated second harmonic ac polarographic response versus direct potential with a system exhibiting quasi-reversible dc behavior. A,D = second harmonic current amplitude polarograms. B,E = second harmonic phase angle polarograms..C,F = second harmonic complex plane polarograms (see next page). Parameter values: $k_s = 3.00 \times 10^{-3}$ cm · s^{-1}; $a = 0.400$; t = 3.00 s (——), t = 6.00 s (— —), and t = 12.0 s (••••••); frequency = 15.9 Hz (A,B,C) and 1590 Hz (D,E,F), other parameters same as Figure 11 except C–(E_{dc}-$E^r_{1/2}$) = -220 mV (□), -100 mV (△), 20.0 mV (○), 100 mV (○), 180 mV (△). F–(E_{dc}-$E^r_{1/2}$) = -340 mV (□), -220 mV (□), -100 mV (△), 20 mV (○), 100 mV (○), 180 mV (△). (Reprinted from reference 80 by courtesy of the American Chemical Society.)

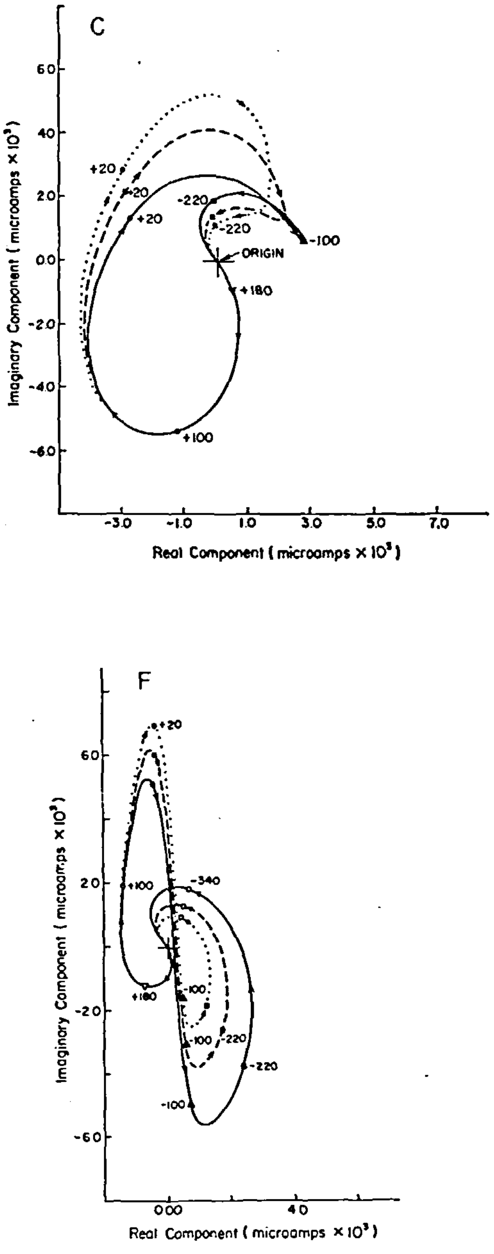

FIGURE 12(continued)

Upon surveying progress described above and remaining theoretical problems, this writer is led to conclude that the mathematical framework supporting the ac polarographic experiment has reached a level of full maturity. That is, although there remain numerous mechanisms whose ac polarographic rate laws are underived, the paths to effecting the necessary solutions are well-marked in the sense that existing mathematical tools should suffice. The latter statement is validated primarily by advances in computer-supported numerical methods for solving electrochemical boundary-value problems[38,65-67,81] which appear certain to succeed even when everything else fails.

III. INSTRUMENTATION

The field of ac polarographic instrumentation is in the midst of probably its most exciting and progressive period, a status it shares with many other areas of chemical instrumentation. We are witnessing an era of transformation brought on by advances in the electronic art whose final outcome is neither in sight nor confidently foreseeable. One can identify a number of factors which share responsibility for this situation, but the availability of small laboratory computers ("minicomputers") for on-line experiment control, data acquisition and data analysis, along with related advances in digital electronics, is clearly preeminent in this regard. Certain advances in analog electronics hold a poor, but not insignificant, second place. In a very real sense the present review is poorly timed from the viewpoint of surveying and evaluating advances in ac polarographic instrumentation because it is written at a time of flux with regard to accepted concepts and methodology and the "dust will not clear" for some time to come. One can envision numerous very promising and revolutionary experimental concepts made possible by the minicomputer. Many have not been implemented and evaluated at the time of this writing. The success level realized by the untried concepts will ultimately determine whether or not some of the advances reported below are merely modest preludes to bigger and better things and whether others are merely anticlimaxes of a soon-to-be-obsolete era. The situation is sufficiently uncertain and rapidly moving that there is a good possibility that the instrumentation section of this review might even be quite obsolete before it is published. Because of this state of affairs the present section will be characterized by greater selectivity in choice of topics to review than the previous one. With the exception of an attempt to clarify an apparent controversy regarding potentiostats and an effort to reveal the basis for the above analysis of the status of ac polarographic instrumentation, greater brevity will characterize coverage of the topics selected.

A. Impedance Bridges

Since their advent, the vast majority of quantitative kinetic measurements using small amplitude sinusoidal techniques have been effected using the classical impedance bridge approach. Although a survey of the most recent literature shows that the more automated methods involving direct measurement of the alternating current are gradually supplanting the bridge technique, one still finds considerable attention given to improving impedance bridges for electrochemical measurements.[82-85] An analysis of the present state of the art reveals little basis for recommending the impedance bridge approach for measurements at frequencies below about 10 kHz. In this realm instrumentation which characterizes the ac response by alternating current measurement matches bridge techniques with regard to accuracy and provides the advantage of convenient adaptation to various automated data acquisition methods.[7,39,86,87] On the other hand, for frequencies significantly above 10 kHz, most schemes involving current measurements run into difficulty, particularly with regard to accurate potential control,[39] whereas bridge techniques offer the possibility of meaningful measurements up to 1 MHz.[8,83] This clearcut advantage of the bridge approach at high frequencies may be challenged soon by the application of novel, computer-enabled data-analysis techniques to alternating-current data (see section IIIB-4). However, for the moment the impedance bridge continues to offer the most appealing path to accurate measurement of the fundamental harmonic ac response at very high frequencies.

A paper by Armstrong, Race, and Thirsk[83] is recommended as a particularly useful survey of modern impedance bridge concepts, error sources, etc. Implicit in these authors' remarks is the concept that, for accurate measurements of the interfacial impedance over a wide frequency range, careful attention to cell design (particularly the dropping mercury electrode capillary) is as important as taking the appropriate precautions regarding the electronic aspects of the bridge (grounding, detectors, etc.). Tessary, Delahay, and Holub[88] emphatically concur with this observation and provide particularly impressive supporting data. Although advanced within the context of impedance bridge measurements, these reiterations of the importance of cell design (the concept is not new) and the attending experimental demonstrations are relevant to all approaches to interfacial admittance measurements. One must recognize that good data cannot be obtained from a poorly designed cell, regardless of the precision and data-handling power of one's instrument.

B. AC Polarographs

The instrument which provides direct automatic readout of the alternating current magnitude (or some component thereof)—the ac polarograph—has long been the favored approach to utilizing faradaic admittance data for analytical purposes. As stated earlier, this approach is now becoming widely favored for the more demanding task of quantitative electrochemical kinetic studies. The circuits comprising the modern ac polarograph may be divided into four categories: (a) signal sources; (b) signal-conditioning networks; (c) the potentiostat; and (d) the readout device. The signal sources normally consist of an initial direct voltage source, a ramp generator to provide the direct potential sweep, and a sinusoidal oscillator. Signal-conditioning networks are composed of various amplifiers, filters, sample-and-hold circuits, etc. which modify the nature of the cell-current signal so that one obtains a signal proportional to the cell-current component of interest (e.g., fundamental harmonic, second harmonic, etc.) whose magnitude and format (ac, dc) are compatible with the readout device, usually a recorder. The central and most critical component of the polarograph is the potentiostat, whose ultimate goal is to control *changes* of the potential across the electrical double layer of the working electrode in response to changes of the potential provided by the signal source. That is, a 10 millivolt sinusoidal potential from a sinusoidal oscillator should be converted to a *10 millivolt* sinusoidal potential across the electrical double layer of the working electrode. In the modern approach, this is usually attempted with the aid of an automatic feedback control network using a three-electrode cell configuration. The past three years have seen some progress in each area and much promise for the future is evident.

The vast majority of ac polarographs now in existence operate solely in the *analog signal domain*. That is, all information transmitted and manipulated in the polarograph is represented in terms of a continuously varying analog observable such as a voltage, current, displacement (as with a recorder pen), and the like. The alternative *digital* *signal domain* is the approach to information processing and transmission employed in modern digital computers, digital meters, etc. In the latter case information is handled in terms of discrete voltage levels within pulse trains or circuit combinations which represent digital numbers, usually in the binary number format. The reader who is unfamiliar with the distinction between analog and digital signal concepts is referred to an excellent discussion by Enke.[89] A short time ago it would have been unnecessary to acknowledge this distinction in a discussion of ac polarographs, because implementation of signal processing in the digital domain was virtually nonexistent and readers would have considered it implicit that the discussion dealt with analog signal processing. This is no longer the case, mainly because of the advent of the minicomputer and its increasingly widespread use in electrochemical laboratories. Consequently, in the forthcoming discussion an effort has been made to be specific regarding whether the remarks apply to digital or analog instrumentation.

1. Analog Signal Sources, Signal-Conditioning Devices, and Readout Devices

Analog units which normally support the potentiostat, the signal sources, signal-conditioning devices, and readout devices are considered in one category here because individually there is not a great deal to report. Although definite improvements continue to be realized and new commercial units have appeared, there are few, if any, truly dramatic or revolutionary developments.

Perhaps the most noteworthy advance in these categories has involved a significant increase in the use of phase-sensitive detectors (also known as "lock-in amplifiers") as signal-conditioning devices in ac polarography. Although phase-sensitive detectors have been available for many years, a combination of palatable cost and performance consistent with the more demanding needs of ac polarography has been realized only recently. This has stimulated a number of authors to publish their thoughts on various aspects of the use of phase-sensitive detectors in ac polarography[86,90-95] encompassing both fundamental and second harmonic measurements. In addition, most newly announced commercial ac polarographs are featuring phase-sensitive detection, so that the trend definitely appears to be toward routine use of this highly advantageous signal-conditioning device. It is probably this development more than any other which has enabled alternating current measurement techniques to provide a viable challenge to impedance bridge measurements for quantitative kinetic investigations. With the exception of a few specialized homemade units, most earlier ac polarographs were characterized by the ability to measure only the total magnitude of the alternating current. With this single observable, one cannot properly correct for non-faradaic effects and, consequently, at best one obtains semiquantitative kinetic data. On the other hand, as with impedance bridge measurements, phase-sensitive detection of the in-phase and quadrature components of the alternating current provides the information necessary for non-faradaic compensation (at least within the framework of the first- and second-generation approaches) and for convenient calculation of the faradaic phase angle. In addition, the phase-sensitive detector is highly frequency-selective[7] so that it very effectively minimizes the effects of electronic noise and unwanted harmonics (including dc) from the cell-current signal. In fact, it is generally recognized that the phase-sensitive detector (or lock-in amplifier) represents the most powerful concept in analog bandpass filters. Considering the foregoing advantages of phase-sensitive detection, the rejection of the double-layer charging current afforded by in-phase current detection and the wide availability of the device in question, this feature should be considered a necessary requirement when contemplating the acquisition of a new ac polarograph.

If one is willing to construct one's own circuits, quite inexpensive phase-sensitive detectors can be realized with the aid of operational amplifiers and circuit concepts given some time ago.[7] DeLevie and Husovsky[86] have described an instrument which provides quite precise automatic measurement of the electrode admittance and features an operational amplifier phase-sensitive detector. Figure 13 gives the circuit for a type of operational amplifier phase-sensitive detector which has been employed in this writer's laboratory for the past six years. Over this period it has proven to be quite reliable and precise for measurements up to approximately 20 kHz. It can be constructed for less than $200 (less than $100 if one can afford to sacrifice bandpass), a price so low that the concept of utilizing several such units in a single instrument is not economically infeasible. For example, Figure

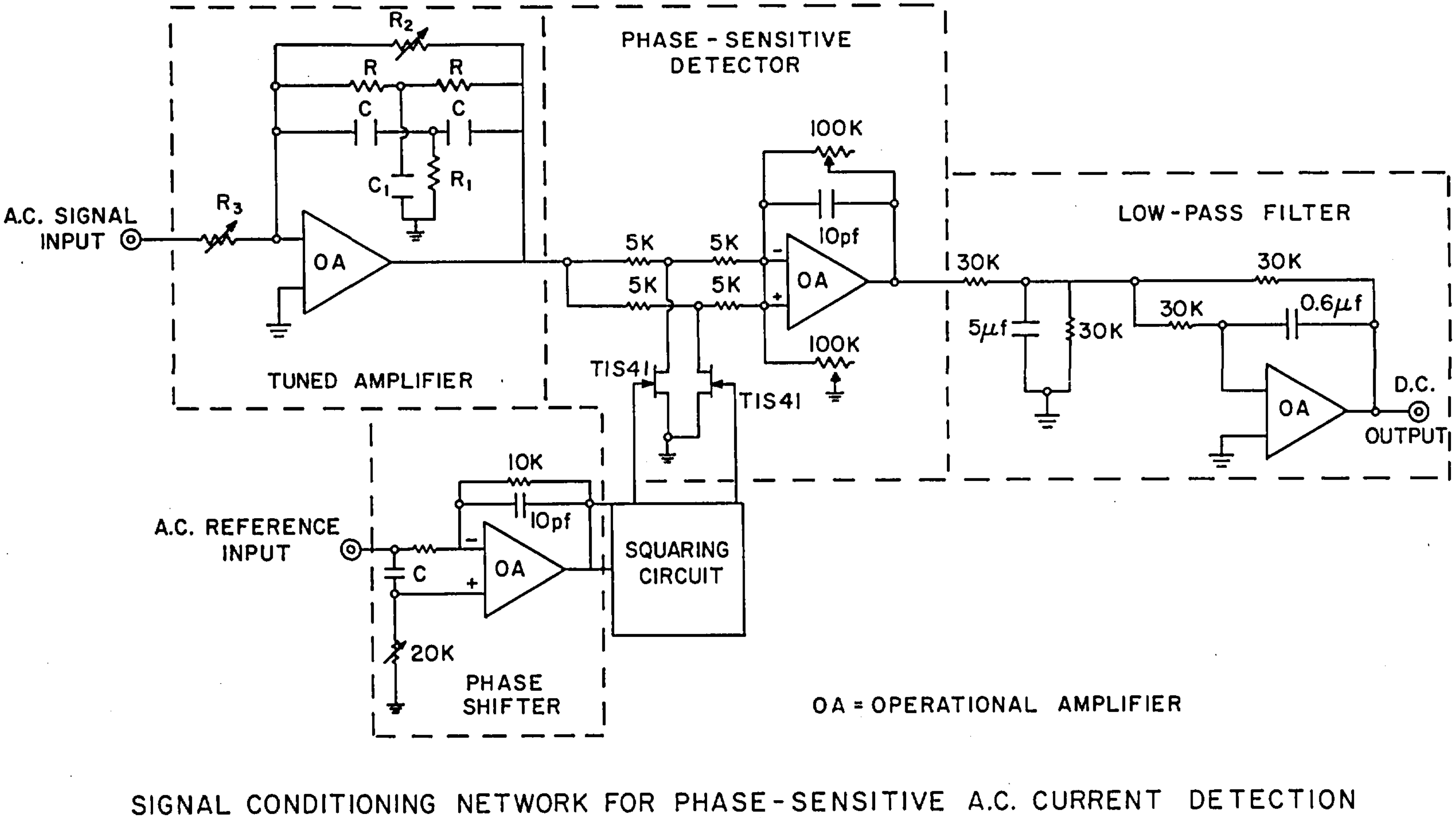

FIGURE 13. Signal-conditioning network for phase-sensitive ac signal detection (lock-in amplification). (Reprinted from reference 87 by courtesy of M. Dekker, Inc.)

14 gives a schematic of a recently described[93] signal conditioning network which provides for simultaneous measurement of the in-phase and quadrature components of the second harmonic alternating current. It is basically comprised of two detectors of the type shown in Figure 13, plus some additional units which aid in absolute phase calibration.[93] Even more profound examples of replacing redundancy in experimental manipulation* by redundancy in electronic circuits are described below (section IIIB-3).

Incidentally, the foregoing simple, inexpensive operational amplifier phase-sensitive detectors epitomize the benefits realized by those who subscribe to the operational amplifier approach to electrochemical instrumentation.[7] Such workers are enjoying the effects of another favorable jump in the cost-performance ratio characterizing operational amplifiers. One now can construct most of the circuits relevant to ac polarography[7] using amplifiers priced in the less-than-$10 category and obtain the same performance realized with $50 to $100 amplifiers 4 to 5 years ago. Alternatively, for the same financial investment as before, substantial improvement in performance can be realized, particularly with regard to bandpass. Benefits attending these cost reductions are particularly relevant to analytical applications where high performance and versatility are not required. In the latter context, available ultra-low-cost integrated circuit operational amplifiers now enable the construction of small inexpensive signal sources and signal-conditioning networks at a small fraction of the "conventional" prices.

2. Analog Potentiostats

The potentiostat is the most crucial and important electronic component in an ac polarograph or, for that matter, in any other controlled-potential electrochemical instrument. In a well-designed instrument, it is the potentiostat, cell-feedback-control network which ultimately determines the frequency limitations and accuracy of an ac polarograph. In the context of any electrochemical relaxation experiment, the demands on the control system amplifiers are quite severe because of the electrical characteristics of the electrochemical cell and, as a result, potentiostat performance seldom matches one's fondest desires, particularly with regard to frequency response. Because achieving the maximum possible potentiostat speed and accuracy is particularly important in kinetic investigations, electrochemists have devoted considerable time and effort to this problem since the early 1950s. The past three years have been no exception. What dramatically distinguishes this most recent period from its predecessors is the attention accorded the concept of positive feedback compensation of the ohmic potential drop (iR drop) in the solution. Although the concept dates back to the origins of modern potentiostats, only recently has it received widespread attention and reasonably successful utilization. Most recent publications dealing with potentiostats[39,69,86,96-102] have been concerned, at least in part, with this concept and numerous examples of its experimental utilization have been forthcoming.

For the reader whose interest in potentiostats has been only casual or nonexistent, further discussion will be facilitated by briefly and qualitatively reviewing the operations associated with feedback control of cell potential and positive feedback iR compensation. This is aided by referring to the potentiostat circuits shown in Figure 15. Figure 15A depicts one version of a "conventional" (without positive feedback iR compensation) operational amplifier potentiostat circuit which has been in common use for over a decade. In the ideal operation of this circuit the "control amplifier" (amplifier 1) responds to an input voltage e_{in} with an output e_o which induces current flow between the auxiliary and working electrodes. This current flow "polarizes" the working electrode (changes its potential relative to the solution and reference electrode). Amplifier 3 (the "current follower" amplifier) holds its input e_m at a virtual ground potential while producing an output voltage E_o proportional to the cell current ($E_o = iR_f$). Amplifier 2 senses the potential of the reference electrode e_f and delivers an output E_f which is equal (ideally) to e_f. If the feedback signal E_f is not equal to $-e_{in}$, the control amplifier adjusts e_o until the condition

$$e_f = E_f = -e_{in} \tag{19}$$

is realized. Ideally, the potentiostat responds sufficiently rapidly that the condition represented by Equation 19 is achieved on a much shorter time scale than that associated with the desired varia-

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*For example, measuring in-phase and quadrature current components in two sequential individual experiments with a single phase-sensitive dectector.

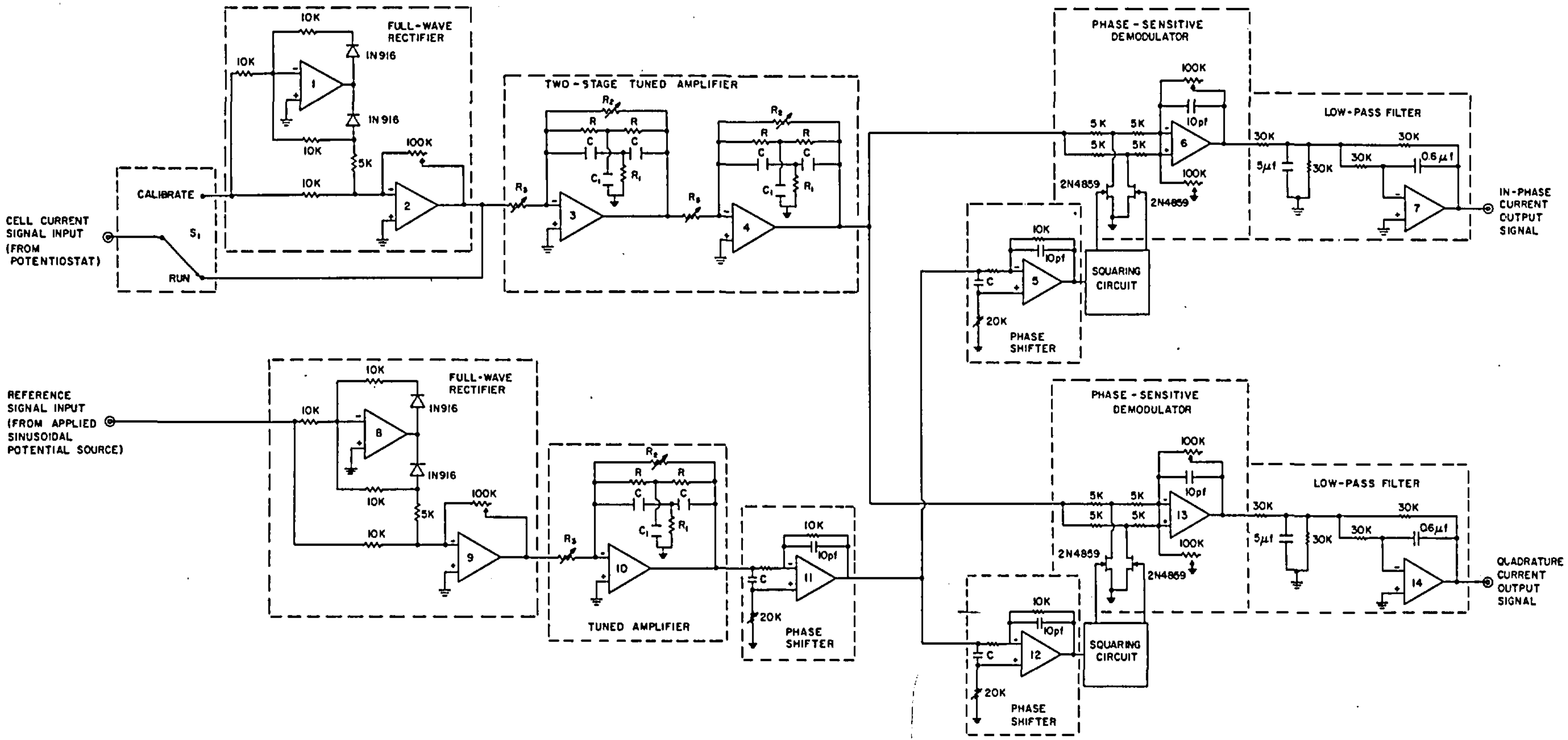

FIGURE 14. Signal-conditioning network for simultaneous in-phase and quadrature second harmonic current measurement. Amplifiers 1,2,8,9 = Burr-Brown Model 1510. Amplifiers 3,4,10 = Burr-Brown Model 1560. Amplifiers 5,11,12 = Burr-Brown Model 3057. Amplifiers 6,13 = Burr-Brown Model 3013. Amplifiers 7,14 = Burr-Brown Model 3119. S_1 = mode-control switch. (Reprinted from reference 93 by courtesy of the American Chemical Society.)

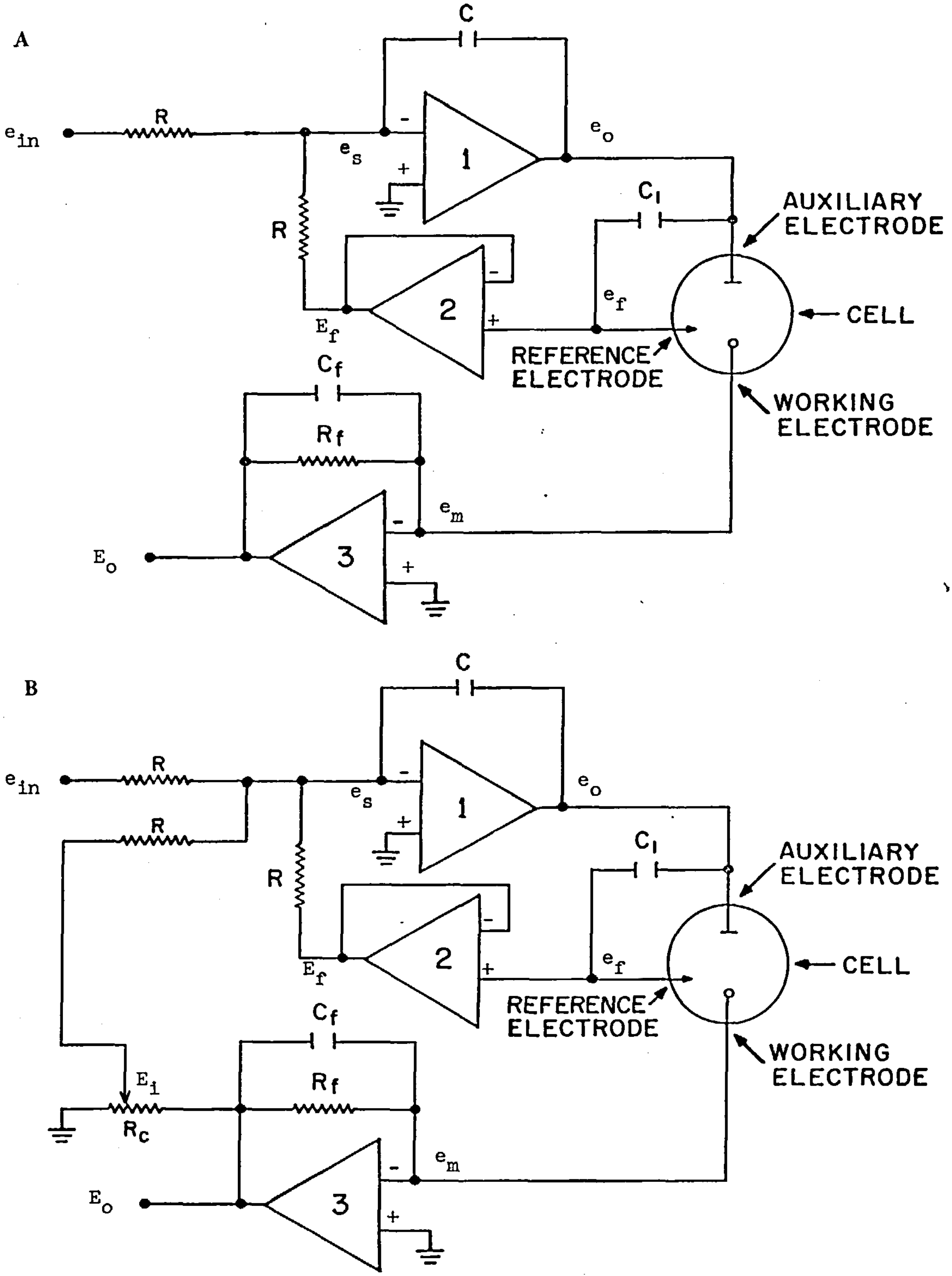

FIGURE 15. Potentiostats. A. "Conventional" operation amplifier potentiostat. B. Operational amplifier potentiostat with positive feedback iR compensation. Amplifier 1 - Control amplifier. Amplifier 2 - Voltage follower amplifier. Amplifier 3 - Current measuring amplifier (current follower). C,C_1 ,C_f - Network stabilizing capacitors.

tions of e_f. The question of why the potentiostat seeks the above described ideal state is not addressed here because it involves elementary, but lengthy, considerations which have been reviewed elsewhere and because it is not essential for the present discussion. The key point which the above remarks make apparent is that the circuit basically seeks to maintain the potential of the reference electrode e_f at the value $-e_{in}$ versus *the electronic ground. Only* if there is negligible resistance (iR drop) in the working electrode itself will the latter be at a virtual ground (i.e., shorted to the input to Amplifier 3); then the working electrode potential versus the reference electrode will be equal to $+e_{in}$, so that potential control is realized between these two electrodes. With conducting electrodes the latter situation, which is the best possible result obtainable from this circuit, is readily achieved. However, even this does not correspond to the electrochemist's primary goal of controlling *changes* of potential across the electrical double layer of the working electrode. A change of potential between the working and reference electrodes corresponds to a change of potential across the double layer of the working electrode only if the reference electrode is not polarized and the iR drop between these electrodes is negligible. Amplifier 2 prevents current flow of any consequence through its input, so reference electrode polarization and iR drop within the reference electrode compartment and in the mechanical boundary (e.g., frit) separating the reference and working electrode compartments (the major source of iR drop) are inconsequential. Nevertheless, a source of iR drop still exists between the working electrode and the point where the working- and reference-electrode compartments make contact. This source of residual iR drop, together with any iR drop in the working electrode itself, combines to make the circuit of Figure .15A imperfect with regard to the ultimate objective of the control circuit, even when the amplifiers are behaving ideally. Changes of potential across the double-layer will differ from changes of potential associated with e_{in} by the iR drop. This effect distorts the ac polarographic response and the attending correction is at best tedious and at worst too large for reasonably accurate correction. The circuit in Figure 15B depicts the possible solution to this problem referred to as positive feedback iR compensation. The circuit in Figure 15B differs from Figure 15A in that a fraction E_i of the current follower amplifier output E_o is returned to the summing junction of the control amplifier. The idea is that if the potentiometer R_c is adjusted so that E_i equals the effective cell iR drop, the effects of ohmic resistance will be eliminated (ideally). In principle, one is adding to the input signal e_{in} a voltage equal to the iR drop in the cell so that the net potential changes across the working electrode double layer are determined solely by e_{in}.

Upon comparing Figures 15A and 15B it becomes evident that the modification of the potentiostat required to implement positive feedback iR compensation is quite trivial from the viewpoint of wiring requirements, additional components required, etc. Similarly, the above-stated concept underlying the positive feedback operation may seem quite simple. However, introducing a second feedback path to the basic potentiostat (Figure 15A) is not at all trivial from a control system engineering viewpoint. A detailed quantitative description of the behavior of the circuit in Figure 15B and alternative circuits implementing positive feedback iR compensation is not at all simple [96-103] and even a qualitative understanding of certain aspects of the positive feedback operation can be elusive (e.g., is overcompensation possible?). Perhaps because of this one finds in the literature instances of apparent disagreement among workers regarding the limitations and advantages of positive feedback iR compensation. For example, on the basis of a mathematical analysis of the stability and accuracy characteristics of the circuit in Figure 15B, Brown, Smith, and Booman[96] concluded that the positive feedback scheme can completely compensate or even overcompensate for the ohmic resistance. Confirmatory dummy cell measurements were mentioned.[96] Brown and co-workers[39] also presented experimental ac polarographic results which supported the alleged ability to effect complete iR compensation and several subsequent papers from the same laboratory[48,93-95,104-106] have implemented this technique with apparent success in both fundamental and second harmonic ac polarography. In an elegant, independent study of similar nature, Koopman[100] reached the same conclusions. Bewick's[107] mathematical analysis of positive feedback potentiostats led to the conclusion that severe overcompensation is possible and he viewed this possibility as a decided disadvantage. At the same time, papers by Pilla et al.,[97] deLevie,[76] Wells,[101] and Will[99] state in one context or another that complete iR compensation and overcompensation cannot be realized in practice—i.e., the potentiostat-cell system will become oscillatory before these states are reached.

From a careful study of the papers in question and some discussions,[108] it appears that, for the most part, the seemingly diametric opposition of these viewpoints is more apparent than real. This statement is most easily defended by first recalling a few important general principles of linear automatic control theory. These concepts are best illustrated in the context of the generalized feedback control network depicted in Figure 16. Using the notation of Figure 16, we insert the following definitions:

$$G_c = \frac{m}{e} \tag{20}$$

$$G_s = \frac{c}{m} \tag{21}$$

$$G_h = \frac{b}{c} \tag{22}$$

$$e = r + b \tag{23}$$

where G_c, G_s, G_h are the so-called "transfer functions" of the controller, controlled system, feedback network, and summing junction, respectively. These transfer functions, describing the responses of the control-network components, may be treated as either frequency- or time-dependent quantities, depending on the domain of interest. When the frequency domain is used the transfer functions take on vectorial properties because they possess both phase and amplitude characteristics, and the complex variable formalism is normally used. When the time domain is of interest, mathematical manipulation in Laplace transform space is favored. For the present discussion, it is only necessary to keep in mind the complex frequency- or time-dependent properties attending these transfer functions. The block diagram of Figure 16 and the transfer function notation is readily applied to the potentiostats in Figure 15.[103] For example, the controller comprises amplifier 1 and its associated external components. The controlled system is the cell, and the feedback network is amplifier 2 in Figure 15A and amplifiers 2 and 3 and associated components in Figure 15B. The inputs to the control amplifier resistances R may be taken as the summing junction, and so on. In most control network design one is trying to control the ratio between the input signal r and the existing signal c so that this ratio (transfer function) is characterized by a simple constant (often unity). The transfer function relating c and r may be written

$$G_N = \frac{c}{r} \tag{24}$$

Algebraic combination of Equations 20 to 23 gives

$$G_N = \frac{c}{r} = \frac{G_s G_c}{1 - G_c G_s G_h} \tag{25}$$

The "ideal response" of a control network corresponds to the case where

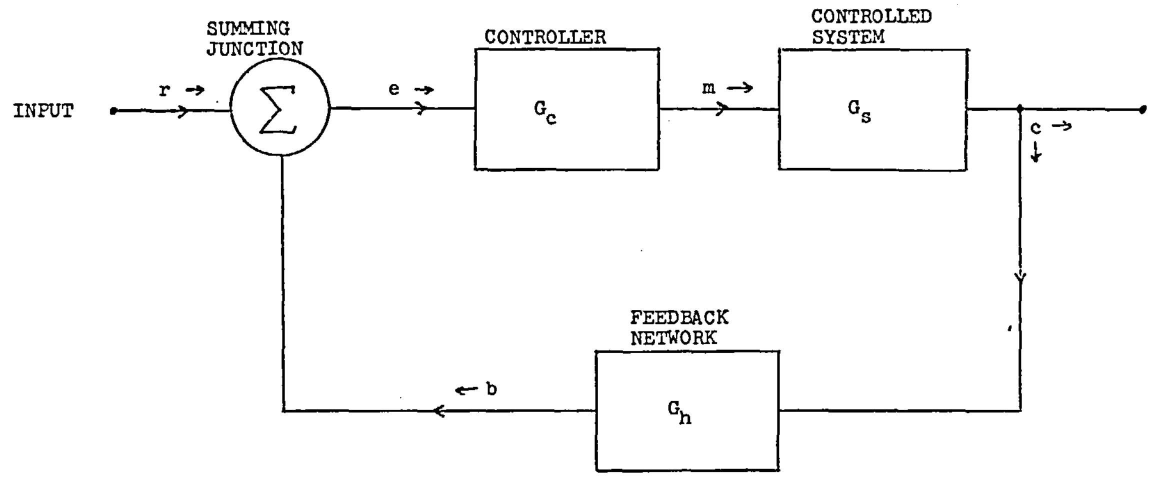

FIGURE 16. Block diagram of generalized feedback control network. r = input signal; e = error signal; m = manipulated variable; c = controlled variable; b = feedback signal; G_c = controller transfer function; G_s = controlled system transfer function; G_h = feedback network transfer function. (Reprinted from reference 103 by courtesy of Wiley-Interscience.)

$$G_cG_sG_h >> 1 \qquad (26)$$

and

$$G_N = (G_N)_I = G_h^{-1} \qquad (27)$$

The feedback network is usually designed so that under these conditions G_h is usually a simple constant, such as unity. Control network accuracy may be defined in several ways.[103] For the sake of illustration we will define % error as the relative deviation of the transfer function G_N from the ideal value, $(G_N)_I$. Algebraic combination of Equations 25 and 27 gives

$$\% \text{ error} = \frac{G_N-(G_N)_I}{(G_N)_I} \times 100 = \frac{100}{1 - G_cG_sG_h} \qquad (28)$$

The primary point of this exercise is to illustrate that the quantity $G_cG_sG_h$ is the key which determines the quality of control network response. This product of controller, controlled system, and feedback network transfer functions is usually referred to as the open-loop gain of the system and will be defined as G_{ol}:

$$G_{ol} = G_cG_sG_h \qquad (29)$$

The tendency of control networks toward instability and the key role played by G_{ol} in this characteristic also is obvious from the singularity in Equation 25 when

$$G_{ol} = 1 \qquad (30)$$

In terms of the complex variable representation of G_{ol}, the implication of the singularity is that if a frequency exists where the open loop gain has a magnitude of unity and no imaginary component, the system will undergo sustained oscillation at that frequency. To recognize the full significance of this singularity, one must also recall that all natural processes have finite rates so that all transfer functions will exhibit a "roll-off" (the magnitude of the transfer function decreases with increasing frequency) at sufficiently high frequencies, eventually approaching zero at infinite frequency. This is simply equivalent to saying that at sufficiently short times a process will have had inadequate time to respond at all to an input perturbation. Combining the foregoing facts leads to the following well-known qualitative conclusions which are basic to automatic control theory:

a. *All control networks are bandpass-limited.* Even if it behaves ideally at some frequencies (times) there will be some upper frequency (minimum time) beyond which a control network will fail to achieve the desired goal.

b. One faces with any control network the possibility that it will become oscillatory. Even though G_{ol} exhibits very favorable characteristics at frequencies of interest, Equation 30 may apply at some frequency far beyond this region and the system will be useless. Because G_{ol} is characterized by a magnitude and phase, the condition of Equation 30 can be avoided for a given network simply by designing the system so that the phase angle at the unity gain frequency has the appropriate properties. The rules for obtaining a stable system are quite simple for linear systems,[103] but their quantitative description is not essential here.

c. The response of any control network in general depends on all components and valid conclusions cannot be made by considering just a single component. Otherwise, one might conclude that just because a system is by itself naturally oscillatory that it cannot be controlled. The fallacy in the latter view is readily recognized by considering whether or not the position of a grandfather clock pendulum (oscillatory system) can be controlled by the arm (controller) and brain (feedback network) of a five-year-old. In any event, with a potentiostat-cell system one must consider the control amplifier, cell, and feedback network before valid conclusions can be reached.

d. Unless two control networks are made of components with identical transfer functions, quantitative or even qualitative conclusions regarding one network do not necessarily apply to another. For example, just because one potentiostat-cell system is unstable when attempting complete iR compensation does not mean that a system of different design will show the same characteristics.

The points made in items a to d are among the simplest and most frequently-repeated principles of automatic control. Nevertheless, these concepts appear to be an adequate basis to resolve the apparent controversy regarding the limitations of positive feedback iR compensation. Perusal of the literature statements dealing with the possibilities of achieving complete compensation or overcompensation leads this writer to the following conclusions: (1) those authors who deny the possibility of complete compensation or overcompensation are either defining complete compensation, for example, as achieving elimination of iR drop effects at *all* frequencies (or times) or their conclusions refer to a specific potentiostat-cell design; (2) the authors who allege that complete iR compensation or overcompensation is possible are defining these terms so that complete compensation is acknowledged even if it is achievable *only at a particular frequency of interest or within a limited frequency domain*–i.e., all authors in this group explicitly acknowledge that the ability to achieve any degree of compensation is bandwidth-limited. It appears that most authors are essentially correct when their remarks are analyzed within the original contexts. It is only when the conclusions are extrapolated beyond the contexts and definitions of the original articles that apparent disagreement arises. Thus, if one chooses to define "complete compensation" as the elimination of iR drop effects at all frequencies or times, then it is quite evident (item a, above) that complete compensation or overcompensation is physically unrealizable–as, in this sense, is any goal of automatic control systems. Such a viewpoint is not unrealistic to workers concerned with transient measurements (which may be coulostatic, potentiostatic, or galvanostatic) where instrument response over a broad frequency (time) domain is always relevant. On the other hand, if one defines complete iR compensation or overcompensation in terms of whether or not these are realizable within a limited domain of frequencies (or times), which is a useful operational definition for the ac polarographer, then the conclusion that these states are obtainable is readily shown on an empirical and theoretical basis for typical ac polarographic conditions. Of course, the last remark may not apply to a particular potentiostat-cell system which lacks the appropriate amplifier characteristics or stabilizing network (item d). Also, processes in which non-uniform current distributions give rise to substantial iR drop variations across the electrode are intractable.

There appear to be two critical points about utilizing positive feedback iR compensation which must be kept in mind: (a) the ohmic resistance to be compensated must be determined accurately; (b) an effort should be made to characterize the bandwidth limit of one's system. For analytical applications, where low frequencies (10 to 20 Hz) are recommended, it is probably safe to ignore the bandwidth limit with impunity, but only under such circumstances is this recommended. Finally, it is recommended that, when examining the literature in this field, one keep in mind items a to d stated above.

3. Applications of Minicomputers to ac Polarography

The utilization of the small laboratory digital computer (minicomputer) in an on-line capacity is presently perhaps the most ubiquitous topic in discussions of scientific measurements.[109] The minicomputer-induced revolution in scientific instrumentation has encompassed electrochemical measurements and it appears to be only a matter of time before the existence of a minicomputer as part of an ac polarograph is considered routine. Although publications dealing with various minicomputer applications to ac polarography[87,94,95,110] are relatively few to date, these accounts clearly herald a new era in the measurement of the faradaic admittance. They make it obvious that with a computerized ac polarograph the terms "time-consuming" and "tedious" will no longer be applicable to measurements of the faradaic admittance. It is this new development which makes the present state of ac polarographic instrumentation rather mobile and prone to obsolescence as pointed out earlier. The reader should not be deceived by the smallness of the number of reports which are presently available for discussion and should anticipate that the minicomputer revolution will prove to be one of the most significant events since the advent of ac measurements.

a. The Computerized Ac Polarograph

To provide some insights into the capabilities provided by an on-line computer system, let us examine first the possible make-up of a computerized ac polarograph. Figure 17 provides a schematic of a conventional ac polarograph interfaced to a minicomputer with its typical peripherals. The configuration represents an instrument in which the computer plays a role in data acquisition, data analysis, data readout, and experiment control. Arrows in Figure 17 show the directions of signal transmission and, thus, designate implicitly outputs and inputs. Units one normally finds with the non-computerized ac polarograph are the external analog signal sources, potentiostats, polarographic cell, analog signal-conditioning network, analog readout devices, and

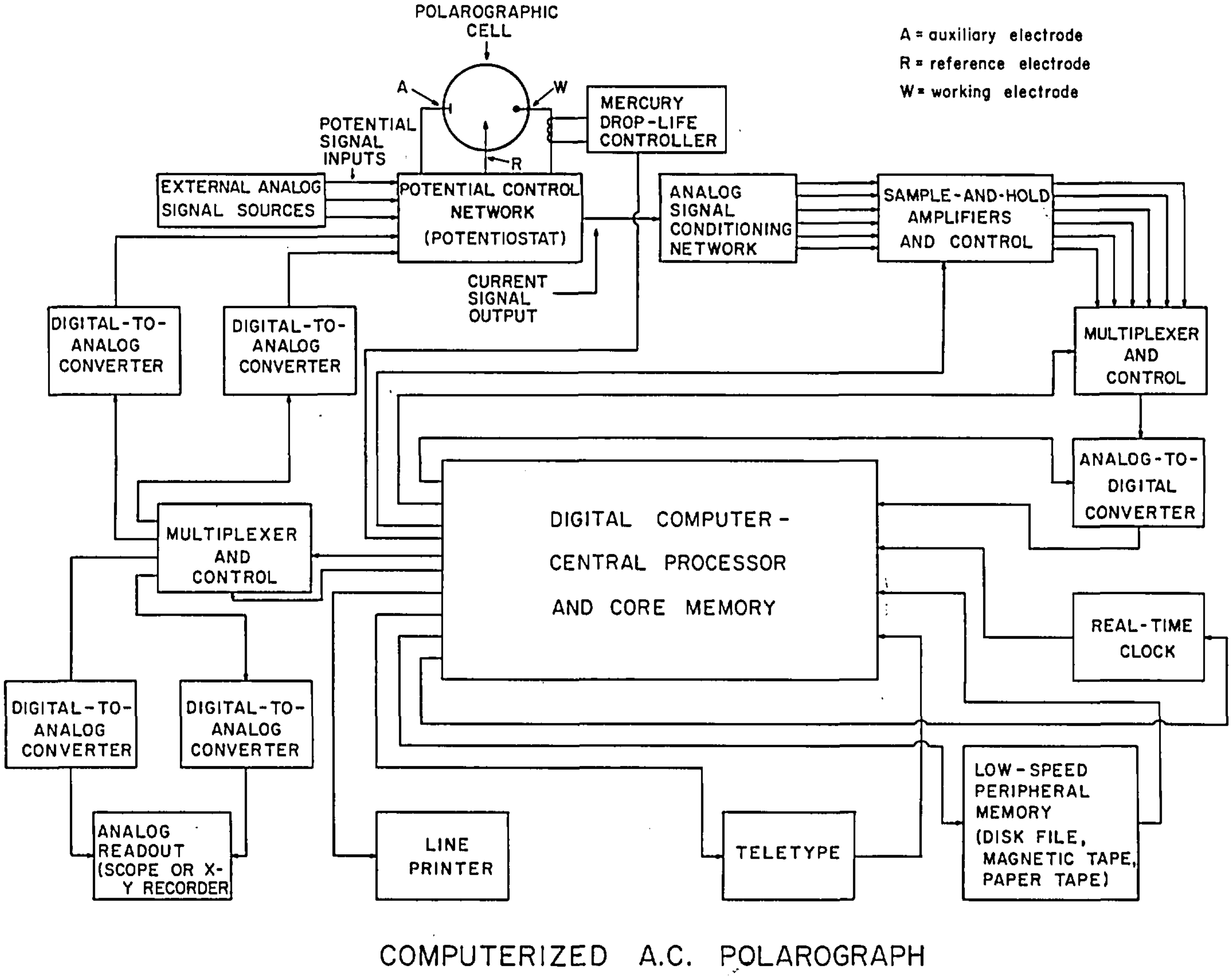

FIGURE 17. Computerized ac polarograph. (Reprinted from reference 87 by courtesy of M. Dekker, Inc.)

mercury drop-life controller. The remaining units shown in Figure 17 are among the devices normally provided by the computer vendor as part of the on-line computer system. Not all of the devices shown are necessary requirements for a computerized ac polarograph. and, on the other hand, Figure 17 does not show all of the possible peripherals, which may include card readers, digital incremental plotters, and others.

At this point a few remarks are appropriate regarding the function of the devices provided with the computer. The *sample-and-hold amplifiers* enable simultaneous analog sampling of an array of analog outputs. *Muliplexers* are simply computer-controlled switching arrays which allow rapid switching of device inputs between various signal channels. *Analog-to-digital* and *digital-to-analog* converters are the system's "translating" elements which enable communication between circuits operating in the analog and digital domains. The analog-to-digital converter translates the analog signals generated by the polarograph into the digital signal format which the computer understands. The inverse operation is performed by the digital-to-analog converters. Readout of information to the operator is provided in analog and digital form with the aid of the teletype, line printer, scope display and recorder. The teletype also permits the operator to input digital information to the computer and usually provides the main means of computer-operator interaction. Of course, the "command center" of the computerized ac polarograph is the *digital computer* with its *central processor* and *core memory*. This unit stores and implements the program for the experimental operation. In addition to its well-known arithmetic capabilities, the digital computer can control the peripheral hardware and the chemical instrument by generating appropriate driving signals, as depicted in Figure 17. The operation sequence can be timed with great precision by the *real-time clock*. All operations are performed with considerable speed, usually much faster than required by the conventional ac polarographic experiment. Thus, with a facility such as depicted in Figure 17, one can readily implement an experimental sequence of a moderately sophisticated type, involving operations such as (1) mechanical control of mercury drop life using computer-generated pulses which dislodge drops in accord with a preprogrammed timing arrangement; (2) computer generation of an incremental dc ramp in which the dc voltage changes to a new value at the beginning of the life of each successive mercury drop; (3) ac polarographic data acquisition effected at a precisely timed point in the life of each mercury drop; (4) real-time data readout provided in analog and digital form; (5) ensemble averaging of replicate measurements; and (6) data analysis involving complex arithmetic operations after an adequate data array has been generated, such as, for example, the invocation of a Sluyter-type second-generation compensation of non-faradaic effects, after data has been obtained at a sufficient number of frequencies.

b. Multiplexing Techniques in Ac Polarography

The reader's imagination will undoubtedly enable him to recognize various methods whereby the on-line computer can aid the *conventional* ac polarographic experiment. The use of the computer in this context certainly provides gains in experimental efficiency and fidelity adequate to justify the *non-trivial initial investment*. However, a much more exciting and potentially advantageous realm of computer utilization in ac polarography entails applications in which the nature of the ac polarographic experiment is altered so that better use is made of the computer's capabilities. All published accounts of on-line computer applications at the time of this writing are concerned with applications which fall in the latter category. All can be characterized as invoking multiplexing concepts in ac polarography.

In electronic operations, *multiplexing* refers to the transmission of more than one type of signal over a single line with subsequent separation and analysis of the "mixed" pieces of information at the receiver. Separation of the multiplexed data is usually based on the time and/or frequency characteristics of the information. In a sense, the first property of multiplexing (several types of information passed over one "line") always exists when the conventional ac polarographic experiment is performed. That is, the cell-current signal under ac polarographic conditions contains information of three types: (1) the dc response of the faradaic admittance (dc polarographic current), (2) the linear characteristics of the ac response of the faradaic admittance (fundamental harmonic current), and (3) non-linear characteristics of the faradaic admittance (higher harmonic currents). Normally, only one component of the current is monitored with a particular instrument. In fact, in the classical context, measurements of the dc, the fundamental harmonic, and the second harmonic currents are each viewed as separate techniques, requiring different instruments. Because the kinetic-mechanistic information contained in these various current harmonics is usually complementary, fundamental electrochemical studies are aided substantially if all three kinds of data are acquired. Rather than approaching these measurements as separate techniques, Glover and Smith[93] have utilized the minicomputer's multichannel data-handling capability to effect simultaneous measurement of the dc fundamental (total and quadrature), and second harmonic ac (in-phase and quadrature) polarographic currents. They refer to this technique as *"ac polarography in the harmonic multiplex mode."* A schematic of the instrument utilized for this purpose is given in Figure 18, while a portion of the signal conditioning network is shown in Figure 14. As one can see, the instrument basically involves expanding the analog signal conditioning network so that it "sorts out" all current components of interest before computerized data acquisition is effected. Sample-and-hold amplifiers enable the various current signals to be measured simultaneously once during each drop life. Real-time data readout is effected via the teletype. The latter operation includes printout of ac phase-angle data which the computer calculates from the two current components measured. The instrument also features the use of positive feedback iR compensation and subtractive polarography (note the two potentiostat-cell systems) to eliminate nonfaradaic effects.[39] The fidelity of this instrument concept and the self-consistency between the various current observables were established using model quasi-reversible electrode processes.[93] An alternative approach to harmonic multiplexing in ac polarography has been presented by Kojima and Fujiwara.[110] Their technique involves on-line computerized digital data acquisition at a sufficiently rapid rate so that the digital data points define the complex cell current waveform. Fourier analysis of the current waveform data is then invoked to obtain the fundamental and higher harmonic response data. In effect, these authors forego the use of analog signal-conditioning networks and let the digital computer carry out all of the signal analysis. Such digital signal conditioning is an important concept because of the obvious savings attending elimination of analog signal conditioning components (see section IIIB-4b). It has the disadvantage of requiring a high performance data acquisition system (particularly with regard to speed) whose cost is high relative to that of the system depicted in Figure 18. The computer system utilized by Glover and Smith[93] lacked the data acquisition speed needed to effect harmonic multiplexing in the Kujima-Fujiwara mode at reasonable frequencies, but it was more than adequate when aided by analog signal conditioning.

Ac polarography in the harmonic multiplex mode represents a relatively minor departure from the conventional ac polarographic experiment since it involves no alteration of the input signal and simply utilizes a larger than usual portion of the information provided by the cell-current signal. A single experiment still provides little detailed information regarding the frequency response characteristics of the faradaic admittance. In the context of harmonic multiplexing one is still required to perform repetitive experiments, each at a different frequency, until data have been obtained at sufficient frequency "points" to define the frequency response profile. This experimental repetition can be eliminated, in principle, simply by simultaneously applying more than one frequency component to the cell and measuring the desired response to each frequency. Huebert and Smith[95] have reported the successful implementation of this concept for *fundamental harmonic measurements* and refer to it as *"ac polarography in the frequency multiplex mode."* These authors tested and evaluated this concept with an instrument capable of analyzing the fundamental harmonic ac polarographic response to four discrete, simultaneously applied frequencies. The instrument schematic is illustrated in Figure 19. Here again, the technique involves separation of the various frequency components by analog signal conditioning procedures before the data are transmitted to the computer. Nonfaradaic compensation is effected with positive feedback iR compensation and subtractive ac polarography. Heterogeneous charge-transfer rate constants measured by the frequency multiplexing procedure were consistent with those obtained from conventional procedures.[95] Although the instrument in question was limited to detecting the fundamental harmonic response at 4 fre-

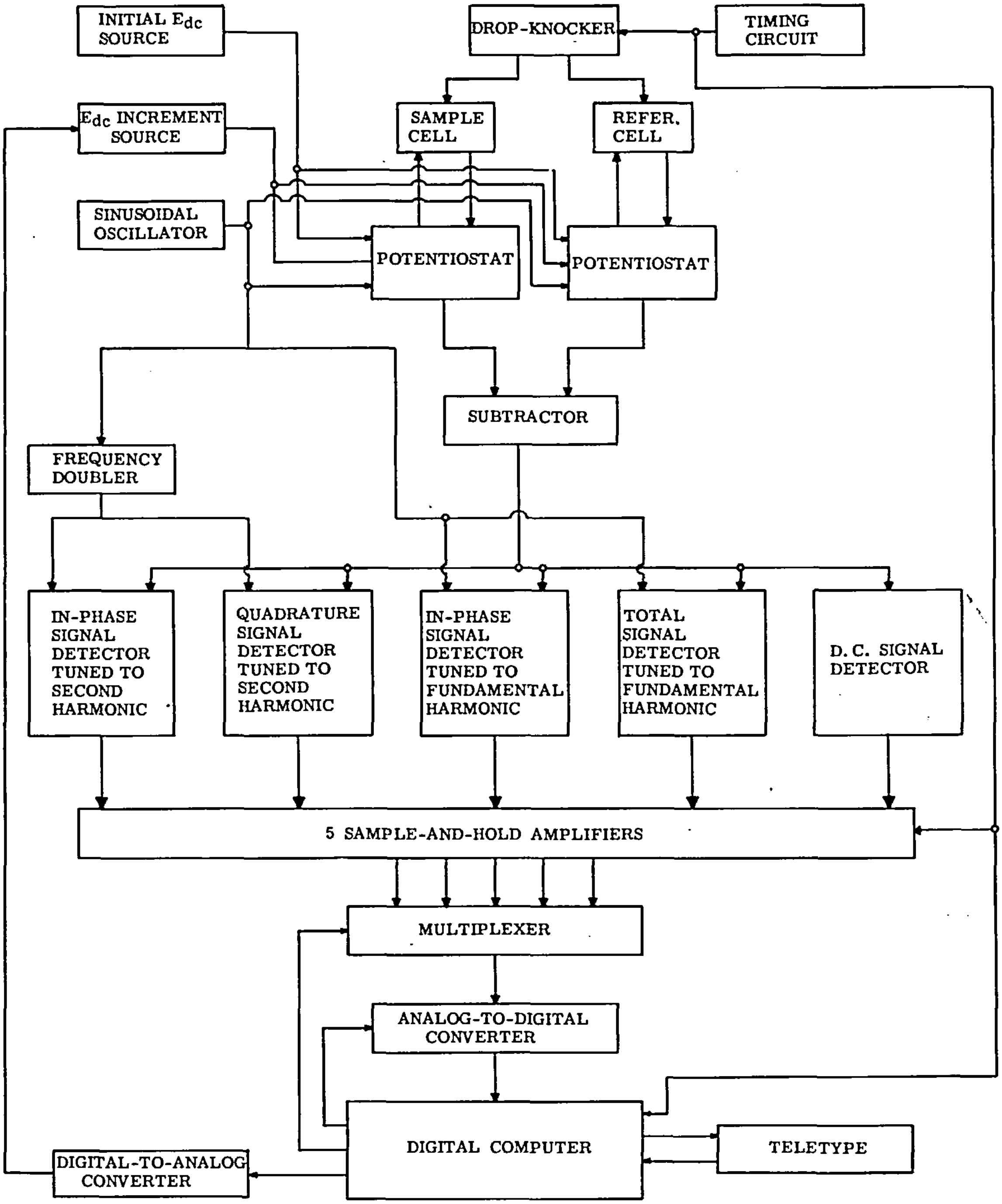

FIGURE 18. Block diagram of instrument for ac polarography in the harmonic multiplex mode. (Reprinted from reference 87 by courtesy of M. Dekker, Inc.)

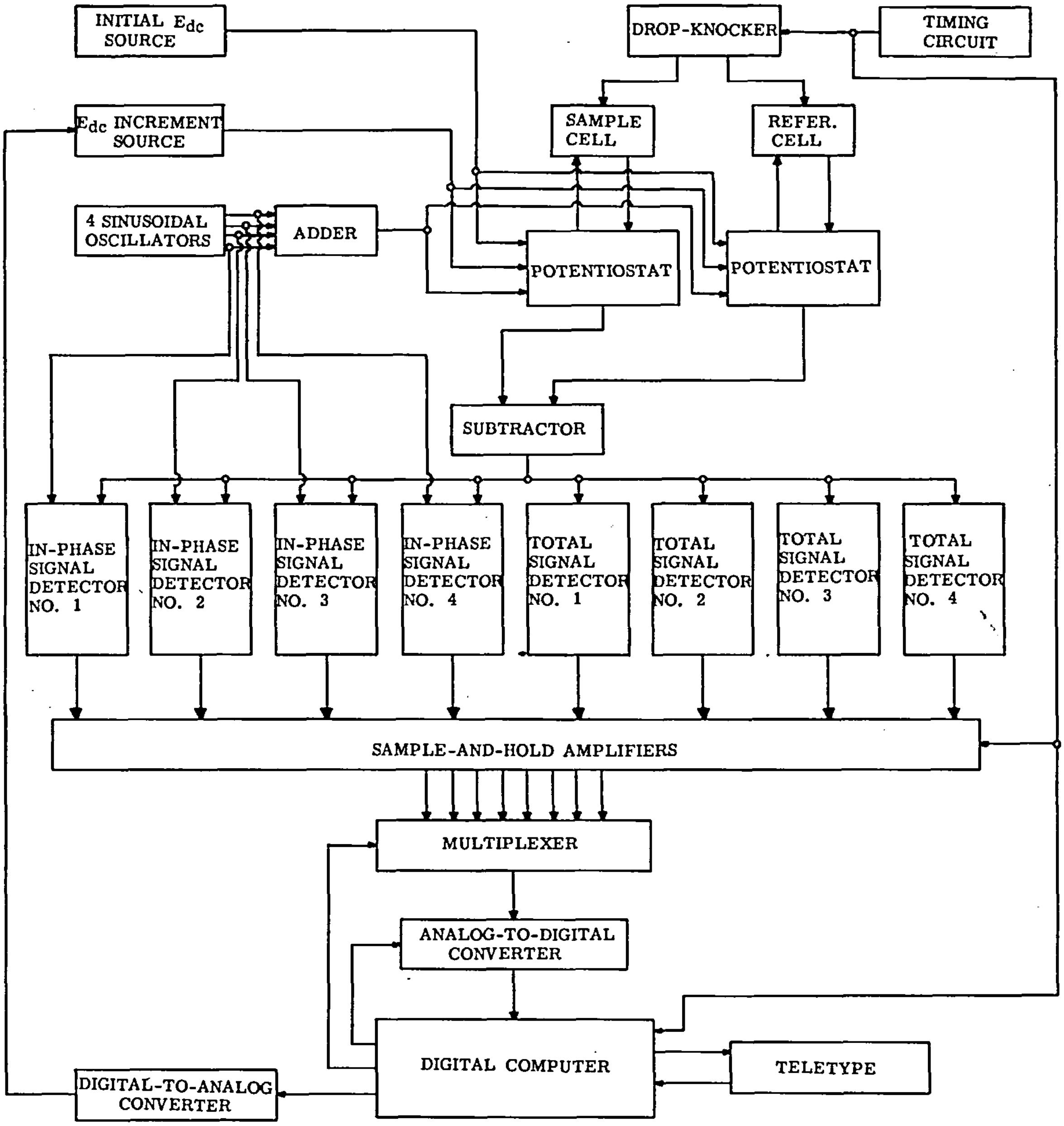

FIGURE 19. Block diagram of instrument for ac polarography in the frequency multiplex mode. (Reprinted from reference 87 by courtesy of M. Dekker, Inc.)

quencies at a time, experiments were performed with as many as 12 frequencies simultaneously applied. In the latter tests, the data at the four frequencies monitored were not significantly altered by the substantial increase in the number of applied frequency components, showing that the frequency multiplexing operation is readily expandable to more than four frequencies. Such experiments must be carried out using sufficiently small applied ac signal amplitudes and adequately tuned detectors to prevent error arising from current signals generated by faradaic non-linearity (higher harmonics and intermodulation components). Of course, digital Fourier analysis of the digitized cell current waveform represents an appealing alternative to the use of analog signal-conditioning circuits with ac polarography in the frequency multiplex mode.

4. *The Future of Computerized Faradaic Admittance Measurements*

The foregoing published applications of multiplex principles to ac polarography represent an exciting development to the experimentalist who is concerned with extensive use of faradaic admittance measurements. For example, ac polarography in the frequency multiplex mode brings within reach the concept of obtaining the frequency response of the faradaic admittance at a particular direct potential in a time period corresponding to the life of a single mercury drop. With this approach the generation of the faradaic admittance-direct potential-frequency profile of a particular electrode process probably can be achieved in the time normally required to run dc polarogram. This is a dramatic improvement over the time investment one must face in point-by-point impedance bridge measurements and results to date already have shown that the data obtainable with computerized multiplexing methods are no less precise than those obtainable with impedance bridges.[94,95] Despite these gains in information flux afforded by techniques reported to date, if one surveys the still untried concepts involving computerized faradaic admittance measurements, one concludes that workers have merely scratched the surface. Potentially more powerful and/or convenient possibilities exist which should be noted. The success realized in tests of the untried concepts mentioned below will determine the future evolution of faradaic admittance measurements. The reader should note in the forthcoming remarks that there exists a very real possibility that future computerized mutations of ac polarography may differ so much from their present day ancestor that generation of faradaic admittance data will be the only common denominator. If some of these anticipated mutations become widely used, then ac polarography as we know it may become extinct.

a. Fourier Transform Faradaic Admittance Measurements

The obvious extension of ac polarography in the frequency multiplex mode is to replace the input source which provides several discrete frequencies by a broad band signal source such as a white noise source or the like. Mathematical techniques known as cross-correlation and Fourier transformation provide the basis for converting the response of a system to a broad band input into the usual frequency response format.[111] The basic concept is that employed in Fourier transform infrared spectroscopy. The rather complex calculations associated with the Fourier transformation and cross-correlation can be accomplished in a fraction of a second with state-of-the-art minicomputer hardware.[112] Although such an experiment has not been reported, it is presently within the state of the art to perform an experiment using a small-amplitude white noise input to a polarographic cell in which data acquisition and analysis are effected in a few tenths of a second, yielding the frequency spectrum of the faradaic admittance. Ensemble averaging could be conveniently implemented to optimize precision.

An equally feasible alternative to the use of white noise or some other form of broad-band signal is a pulse or step function input. The transient response attending the application of a small amplitude potential step at an appropriate point in the life of a mercury drop (which is already polarized to the desired direct potential) can be converted to the frequency response of the faradaic admittance by Fourier transformation.[113] The operation is readily repeatable and, thus, one can also invoke the procedure of ensemble averaging. Because a step function or pulse is readily generated by the computer, an external signal source is unnecessary. Pilla[113] has advocated a technique of this type and has established its feasibility using an off-line computer to analyze manually digitized data from dummy cell measurements. Pilla also has pointed out that the ability to rapidly discern a frequency response profile makes it convenient to correct for non-ideality in potentiostat behavior so that the only requirement is that the potentiostat do something: that is the potentiostat must deliver an *adequate* perturbation, but not necessarily an accurate one. To those concerned with measurements of very rapid rate processes, the latter idea may be the most significant application of the Fourier transform concept. To those interested in solid electrode work, the prospect of obtaining the frequency response profile of the faradaic admittance with the aid of a small, brief perturbation might be viewed as equally significant because it affords the hope of circumventing problems such as progressive surface alteration due to trace impurities, electrode reaction products, etc., which often frustrate solid electrode measurements when long observation times are necessary.

The question of the relative advantages or disadvantages associated with the use of a broad band noise input versus a step function for the acquisition of faradaic admittance data is an interesting one. Time does not permit speculation and, in any event, empirical tests should ultimately clarify this matter. From a feasibility viewpoint both approaches appear quite sound and have enjoyed widespread success in measurements outside the realm of electrochemistry. The underlying mathematical framework assumes that the system response is linear. For this reason small amplitude perturbations must be employed to minimize effects of faradaic non-linearity and, consequently, one can obtain only the fundamental harmonic response by these techniques. Despite such unanswered questions and minor limitations, it appears that the day is near at hand when Fourier transform methods will be used to acquire, with great rapidity and high resolution, data on the faradaic admittance as a function of frequency using an instrument composed of a computer, a potentiostat and, perhaps, a signal generator.

b. Digital Signal Conditioning

We have mentioned the use of the Fourier transformation in obtaining faradaic admittance data in three contexts: (1) obtaining the fundamental and higher harmonic response with a pure sinusoidal input, (2) obtaining the fundamental harmonic response using a broad band signal input, and (3) obtaining the fundamental harmonic response using a step function input. In addition to the Fourier transformation operation itself, a noteworthy common denominator in these examples is the concept of digital signal conditioning. In each case the "raw" cell current waveform is digitized (necessarily at a rate at least twice that of the highest frequency of any significant component[111]) and "signal conditioning" is effected entirely by the digital computer so that a complex array of analog signal-conditioning circuits is avoided. Despite the requirement of fast analog-to-digital conversion and the attendant extra expense, there is much to recommend digital signal conditioning over the analog approach, even when the desired signal-conditioning steps are quite simple. Consequently, a few more words on the subject appear warranted.

First of all, the standard Fourier transformation discussed above is not the only approach to digital signal conditioning. *Any* well-known analog signal-conditioning operation can be duplicated by a sequence of digital operations if the signal waveform data are available in digital form. Computer programs have been written to digitally implement low-pass and high-pass filter actions of various types, tuned amplification, phase-sensitive detection, etc. Incidentally, analog phase-sensitive detection is nothing more than an attempt to effect a single point Fourier transformation in the analog domain. Thus, if one has a computerized ac polarograph with an adequate data-acquisition facility, the need for the usual complex analog signal-conditioning circuits disappears.

The main advantage of digital signal conditioning is not found in the elimination of the cost of analog circuits which, after all, are considerably less expensive than a minicomputer. The important advantage gained is in instrument reliability. The digital signal-conditioning transfer function is determined by a computer program which has fixed characteristics and does not "drift" like its analog counterpart. In an extensive analog signal-conditioning network such as depicted in Figures 18 and 19, drift problems can become annoying even though, individually, the amplifiers exhibit low drift. One simply faces a high probability that at least one of the many amplifiers will need "trimming," so all must be checked prior to a serious data acquisition run. For this reason alone this writer favors implementation of digital signal conditioning whenever possible. The above-mentioned concept of an ac polarograph comprising a potentiostat, a computer, and a signal source has much appeal.

c. Digital Potentiostats

When one considers applications of faradaic admittance measurements which are confined to low frequencies, as in analytical applications, another possibility arises in which the digital computer becomes essentially the entire instrument. The concept in question involves using the computer as the potentiostat, as well as the signal source, signal conditioning network, data acquisition device, etc. The use of digital computers as feedback control networks is well-known and is referred to as "direct digital control." In this operation the computer generates a control signal in response to an error signal which is the difference between a desired input level and an actual input level as observed at an analog-to-digital converter. The computer control network involves incremental control action, as opposed to the continuous action of the analog controller. However, when the necessary time scale for the control action is long relative to the period of one computer control cycle (read controlled variable level, calculate error signal, output control signal in response to error signal), then the incremental action of the digital controller approximates closely a continuous controller. The available computers are too slow to effect direct digital control at the speeds required for electrochemical kinetic studies by ac polarography, but low frequency control (10 to 20 Hz.) appears feasible. If it proves to be so, then we will someday see an ac polarograph comprised of simply a minicomputer and peripherals, the three-electrode cell and three wires leading from the electrodes to the computer!

IV. APPLICATIONS

By far the most voluminous contribution to the ac polarographic literature at the present time, as in the past, deals with various applications of the technique. At least two thirds of the relevant literature in the past 3½ years has involved applications of ac polarography and related techniques, rather than improvements in the theory and methodology. Thus, it is the applications category where a thorough review would involve considerable length and, consequently, the editorial directive to employ selectivity in discussing advances will be invoked with greatest force in this section. The survey of applications of ac polarography which follows is primarily confined to reports whose contents deal with a new area of application or are representative of a recent blossoming of an old, neglected area. A few papers which describe work characterized more by unusual elegance than by novelty also will be considered. However, the reader should realize that the following account falls far short of representing the volume of recent effort involving implementation of the ac polarographic method.

A. Analytical Applications

Application to analytical problems continues to be the area of greatest utilization of ac polarography and related techniques. On the basis of output over the past 3½ years, it appears that new analytical applications are being reported at a rate of about 20 papers per year. Metal ions continue to be the most popular substrate of concern to the analyst employing ac polarography, but the scope of the technique has been extended far beyond the area of metal-ion determination. From the literature one senses a definite general trend toward papers which describe determinations of particular substrates in "real-life situations" such as lead in gasoline,[114] sulfur in petroleum gases,[115] copper and lead in canned green peas,[116] drugs in pharmaceutical preparations,[117] etc. Such applications actually represent the majority of reports in contrast to earlier days when most papers dealt with the demonstration of analytical feasibility using ideal, simulated mixtures prepared in the laboratory. In this day of widespread concern of society with environmental problems, one must applaud such clear indications of maturity in this realm of ac polarographic applications.

1. Analysis of Biochemical Systems

Applications of ac polarography to the assay of biochemically important materials remain rare. However, there has recently been an upsurge of interest in the ac polarography of biological systems, particularly macromolecular types. To date many of the studies have been primarily phenomenological in nature and have not yielded specific analytical methods. For example, although details have not been worked out, the efforts of Palecek and Vetterl[118,119] and Berg and coworkers[120] clearly indicate that ac polarographic analysis of both synthetic and natural polynucleotides (including DNA and RNA) should be possible, particularly with regard to the estimation of percent denatured material in native samples. Some of this work is discussed below.

One interesting biological system in which analytical guidelines have been clearly formulated involves the ac polarographic determination of nonprotein sulfhydryl in rat liver and brain tissue.[121] Charles and Knevel developed a relatively straightforward method which was used to examine stress-induced physiological differences in nonprotein sulfhydryl levels in rat liver.

Despite the neglect, biochemical assays appear to be a promising field for implementation of ac polarography, at least if the infrequent publications in this area are representative. Most biological macromolecules will give an ac response of some type, either arising from adsorption-desorption effects (tensammetric processes) or faradaic processes. It seems quite possible that the papers mentioned here are harbingers of a future trend.

2. *Ac Polarographic Analysis Using Non-aqueous Solvents*

The utilization of non-aqueous solvent systems in analytical applications of ac polarography is another almost totally neglected possibility. The fraction of papers discussing ac polarographic analysis in such solvents is essentially infinitesimal. Historically, the primary reason for this state of affairs is found in the difficulties associated with the large ohmic resistance characterizing most conveniently usable non-aqueous solvents, particularly the abundant organic types. With classical instrumentation the distortion of the ac polarogram induced by the iR drops in such solvents is prohibitive. However, this difficulty has been negated for at least one half decade by potentiostats featuring positive feedback iR compensation. Ac polarograms which are virtually free from iR-drop distortion can be obtained routinely, even when one accentuates the ohmic resistance problem by combining an organic solvent with a dilute supporting electrolyte.[39] The elimination of iR-drop distortion, combined with the fact that many organic electrode reactions correspond to simple, reversible one-electron processes in aprotic organic solvents, leads in many instances to the realization of analytically ideal ac polarographic responses, as illustrated in Figure 20. In addition to useful ac polarograms, organic solvents provide other obvious advantages for the organic and organometallic substrates, such as favorable solubility properties and chemical inertness. These points have been emphasized by Woodson and Smith[40] in the context of ac polarographic analysis of pharmaceuticals. These authors surveyed the dc and ac polarographic (fundamental and second harmonic) responses of 24 pharmaceuticals in acetonitrile containing tetrabutylammonium perchlorate, and found 19 which yielded analytically useful ac polarograms This proportion of success is considerably higher than would have been realized for the same selection of compounds with an aqueous solvent system. In several cases drugs which yield no response in aqueous media produced "textbook" diffusion-controlled one-electron responses in acetonitrile. One example is reserpine whose fundamental and second harmonic ac polarograms in acetonitrile containing 0.001 *M* tetrabutylammonium perchlorate are shown in Figure 21.

Clearly, the use of organic solvents also can occasionally "streamline" an assay procedure by eliminating certain steps. For example, in determinations of organic species in many media it is necessary to effect an extraction with an organic solvent system. Because organic solvents now are suitable media for ac polarographic analysis, one can simply run the polarogram in the extract. Sugii and Kabasawa utilized this principle for the determination of anethole trithione in a pharmaceutical preparation with good success.[117]

An interesting application of a non-aqueous solvent system has been reported recently by Fleet and Jee[122] who developed a method for the ac polarographic determination of unsaturation. Their assay procedure is based on the fact that a wide range of olefins form electroactive addition compounds with mercuric acetate. The resulting organomercury compounds of 15 olefins were found to yield ac polarograms with comparable peak potentials, so that the observed ac response is a measure of total olefin concentration. The analytical response was investigated under a variety of conditions involving methanol-water mixtures and a medium containing 90 to 100% methanol and 0.1 *M* NaOH proved best.

3. *Uses of Rapid Ac Polarography*

"Rapid polarography," in either the dc or ac context, refers to the use of very short mechanically controlled mercury drop times. This modification of the standard dropping mercury electrode enables the use of high dc potential scan rates so that analytical results may be obtained with greater rapidity. Typically, a controlled drop time of the order of 0.2 seconds is used in conjunction with dc scan rates of up to 3 volts per minute. The associated ac polarographic "run times" are 20 to 30 seconds. The popularity of rapid ac polarography has increased recently, partly because some commercial instruments have provided this feature, but mainly because of an almost single-handed crusade by Bond and co-workers who have applied this measurement concept to

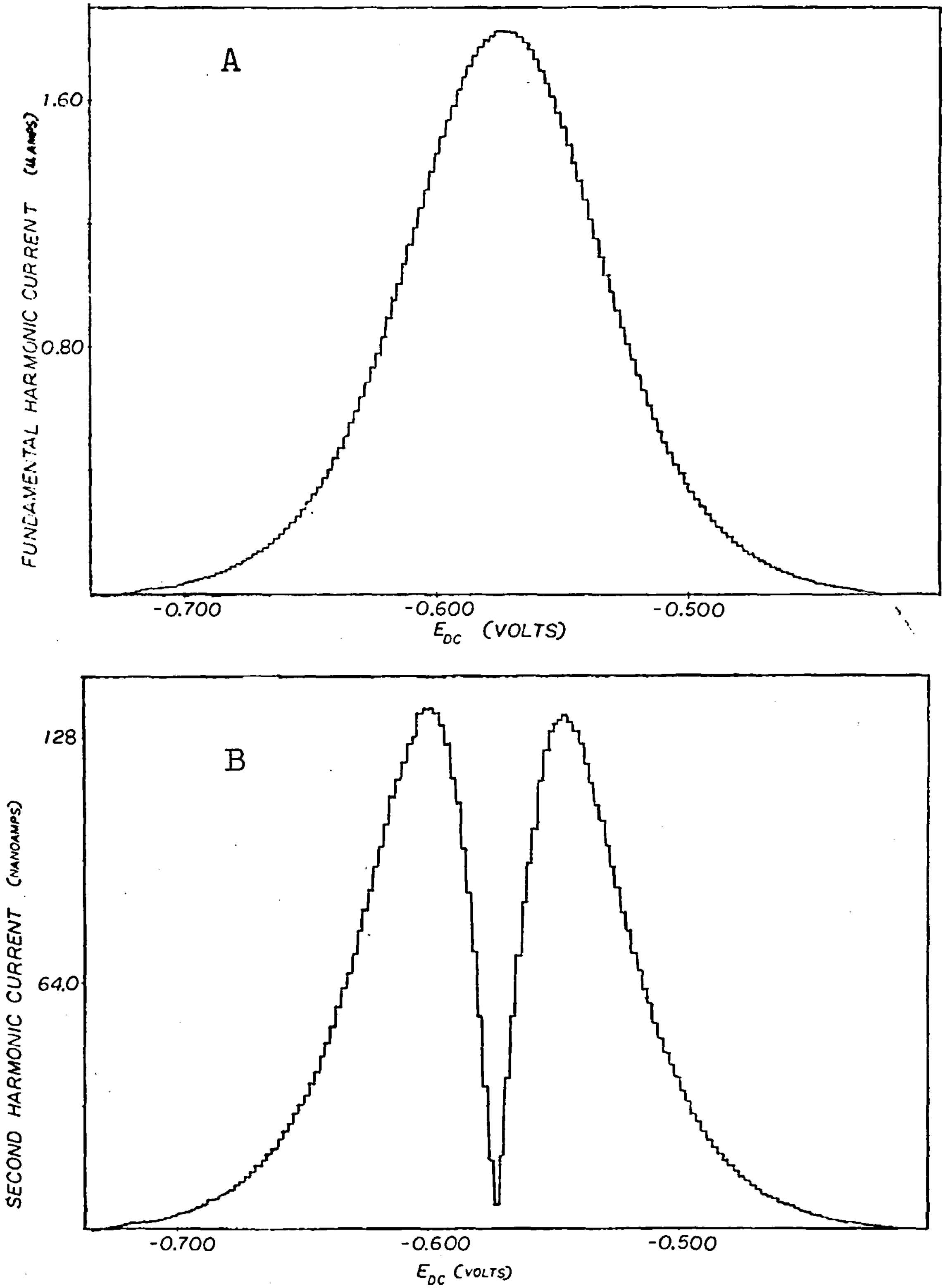

FIGURE 20. Ac polarograms of nitrobenzene in acetonitrile containing 0.0035 *M* tetraethylammonium perchlorate. System: 0.38 x 10^{-3} *M* nitrobenzene in acetonitrile containing 3.5 x 10^{-3} *M* tetraethylammonium perchlorate at 25°C. Applied: Sinusoidal potential of 23 Hz frequency and 10.0 mV peak-to-peak amplitude; dc scan rate of 25 mV/min. Measured: A - 23-Hz in-phase ac component employing sample-and-hold readout mode. (Reprinted from reference 39 by courtesy of the American Chemical Society.)

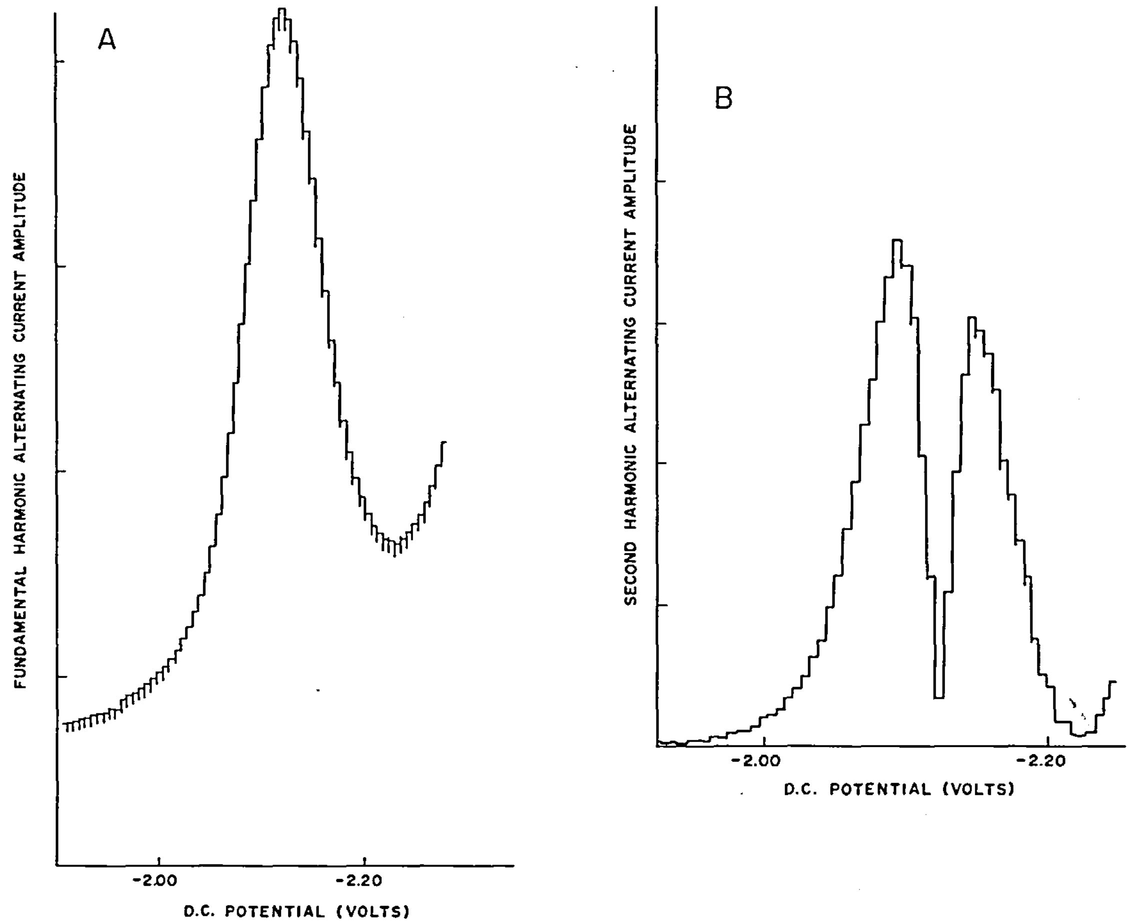

FIGURE 21. Fundamental and second harmonic ac polarograms of reserpine in acetonitrile containing 1.00×10^{-3} *M* tetrabutylammonium perchlorate. System: 3.76×10^{-5} *M* reserpine in acetonitrile containing 1.00×10^{-3} *M* tetrabutylammonium perchlorate at 25°C. Applied: Sinusoidal potential of 16 Hz frequency and 10 mV peak-to-peak amplitude; dc scan rate approximately 100 mV/min. Measured: A - 16=Hz total ac component employing sample-and-hold readout mode. B - 32=Hz total ac component employing sample-and-hold readout mode. (Reprinted from reference 40 by courtesy of the American Chemical Society.)

analysis[123-126] and the determination of stability constants (see section IVD-1). Bond and O'Donnell report one analytical application of rapid ac polarography where the quick analysis feature is more than just a convenient frill.[124] The investigation was addressed to the somewhat special problem of glass capillary degradation which occurs when polarography with a dropping mercury electrode is attempted in hydrofluoric acid solutions. The consequence is a prohibitively erratic mercury drop life. Because such solutions are potentially advantageous for polarographic determination of a variety of metals, particularly where mineralogical and metallurgical samples are involved, there has been some interest in solving this problem. The best previous suggestion was to utilize a somewhat expensive Teflon capillary. Bond and O'Donnell simply advocate using a regular glass capillary whose contact time with the HF solution is held to 30 seconds or less per analysis. This is accomplished by bringing the capillary into contact with the solution only after all solution steps are complete (including degassing and thermostating), obtaining the analytical data by rapid polarography, immediately removing the capillary from the HF solution, and rinsing it with a saturated sodium carbonate solution. This procedure permitted polarograms to be run in media containing up to 40% HF. With 5 to 15% HF, attack on the glass capillary was insignificant even after extended periods of use. The method was successfully applied to the metal ions Ce^{+2}, Tl^{+1}, Pb^{+2}, Sn^{+2}, Bi^{+3}, Mo^{+6}, and V^{+5}.

4. Ac Polarography at Stationary Mercury Electrodes

As long ago as the late 1950s, workers have suggested the use of stationary mercury electrodes (such as the hanging mercury drop electrode) in the ac polarographic determinations of amalgam-forming metals. The main advantage of the stationary mercury electrode lies in the application of the anodic stripping concept* to enhance the sensitivity for the purposes of trace analysis. Despite effective demonstrations of sensitivity enhancement attending the use of hanging mercury drop electrodes, few applications were forthcoming until recently. The publications since 1968 which report implementation of this concept[123-131] probably exceed in number all previous reports of this type. Bond and coworkers[123,126] have used ac polarographic detection of the anodic stripping wave at a hanging mercury drop to analyze for tin. Concentrations as low as 10^{-8} *M* were accessible using pre-electrolysis times of only three minutes. This sensitivity level was approximately ten times better than the same workers could achieve with the more conventional dc detection scheme. The method devised was applied to the quantitative determination of tin in a variety of geological samples, some with tin contents as low as ten parts per million.

Kodama and Noda[127] have introduced a simple, but effective, chemical "twist" to anodic stripping with ac detection to permit the determination of 10^{-6} *M* thallium in solutions containing large excesses of Pb^{+2}, Cd^{+2}, or In^{+3}. The response from these ions normally interferes with the thallium wave obtained on anodic stripping. Kodama and Noda eliminated this problem by masking the interfering ions with EDTA. From a solution containing EDTA reductions of Pb^{+2}, Cd^{+2}, and In^{+3} are so much more difficult than in non-complexing solutions that pre-electrolysis at about -0.80 volts vs. S.C.E. reduces only the thallium. The same authors have also shown that a mercury-film electrode on a platinum substrate (mercury plated platinum) can allow more effective concentration of the metals during the pre-electolysis step and, thus, a more sensitive response is obtained with ac polarographic detection of the anodic stripping wave.[128]

If one is interested in sensitivity records for ac polarography, I submit the report of Vasileva and Yustus[129] for consideration. These authors have claimed a detection limit of $5x10^{-10}$ *M* for antimony using phase-sensitive ac polarographic detection of the anodic stripping wave with a hanging mercury-drop electrode.

B. Measurement of Heterogeneous Charge-Transfer Rates

The application of ac polarography and related techniques to the measurement of heterogeneous charge-transfer rates continues to rank second to analytical applications in regard to numbers of reports. If productivity is used as the primary measure, the techniques in question have been by far the most successful class of electrochemical relaxation methods for the quantitative characterization of rates of rapid electrode processes. If anything, the gap in productivity between sinusoidal measurement approaches and the alternatives has widened in the last three years.

1. Heterogeneous Electron-Transfer Rates in Aprotic Organic Solvents

One of the most important and difficult challenges faced by electrochemical kineticists in recent years has involved measuring rate parameters for the rapid charge transfer steps which characterize the electrode reactions of aromatic and other highly conjugated organic and organometallic molecules in aprotic organic solvents. Reasons supporting the desirability of acquiring such rate data are quite compelling. Over a decade of mechanistically oriented studies have established that electrode processes in this category often involve simple one-electron processes leading in successive resolved steps from the neutral molecule to the anion radical and dianion (reduction) or the cation radical and dication (oxidation). In relatively inert aprotic solvents, these electrode reaction products are often either quite stable or undergo easily characterized follow-up chemical reactions. Consequently, the key preliminary step in acquiring rate data, that of

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*Anodic stripping refers to the sequence of operations involving concentration of the metal species in the mercury by cathodic pre-electrolysis, followed by an anodic direct-potential sweep during which the metals are "stripped" from the mercury by oxidation and the dc or ac polarographic wave attending the oxidation is detected.

establishing a mechanism and rate law, should involve little uncertainty in many instances, in contrast to the often difficult situation associated with organic and organometallic molecules in aqueous media. In addition to the favorable mechanistic feature, one has the rather substantial advantages associated with: (1) the availability of extensive homologous series of molecules whose rate data can be compared; and (2) the availability or obtainability of rather precise data regarding the molecular confirmation and electronic configuration of the various redox states *in solution*, thanks primarily to the magnetic resonance techniques. Considerations such as these lead one to conclude that electode processes involving organics and organometallics in aprotic solvents represent potentially one of the most fertile areas for obtaining data which might aid in better understanding the fundamental nature of the heterogeneous electron-transfer step. In no other area can one find large series of molecules whose electrochemical reactions are sufficiently simple to render mechanistic characterization trivial and the fidelity of the rate law employed in calculating the rate parameters unquestionable. When comparing such rates constants with predictions of fundamental theories for the heterogeneous electron-transfer rate process, the burden of proof will lie with the theory rather than the data. Despite considerations such as these which clearly establish the need for such rate data, difficulties of measurement have dramatically retarded this field of investigation for many years. The electrode reactions in question are extremely rapid in many instances and are characterized by rate constants which lie barely within the region of accessibility of existing electrochemical relaxation techniques. This problem is compounded by the already acknowledged difficulty associated with the high resistances of most systems containing aprotic organic solvents. The measurements are not impossible, as was shown in the early 1960s by Aten and Hoijtink[132] who used impedance bridge measurements, but the substantial demands upon the precision of measurement precision apparently discouraged most workers. However, the "activation energy" attending the experimental problems in this area appears to have been overcome. The time period relevant to this review has witnessed notable progress and the expectations regarding the utility of the data in question have been shown to be well-founded.

Probably the most extensive and significant study has been reported by Peover and Power[133], who obtained the heterogeneous charge transfer rate parameters attending the first reduction step (neutral molecule-anion radical redox couple) at mercury for a series of nitro compounds in dimethylformamide containing tetrabutylammonium iodide. Their measurements were carried out by the classical impedance bridge procedure Their results are given in Table 2. It is quite evident from these data that there is a marked dependence of the apparent value of k_s on the degree of delocalization of the molecular orbital for the odd electron, as indicated by the odd-electron coupling constant at the nitrogen atom, a_N. At the same time, the charge-transfer coefficient is relatively independent of molecular structure. A double-layer correction of the Frumkin type[7] yields "corrected" values of k_s which are significantly larger than the apparent values listed in Table 2, but the relative values are not substantially altered. The authors compared these data with predictions of the Marcus theory for a heterogeneous electron-transfer process whose *activation free energy comes from reorientation of the solvent molecules.*[134] A dielectric continuum model and the assumption that all molecules have the same pre-electrode state location predict that a plot of log k_s against the quantity $f(a_N)$ given by

$$f(a_N) = \Sigma(a_N Q_N)^2/r_{NO_2} + (1 - \Sigma a_N Q_N)^2/r_{ring} \quad (31)$$

should be a straight line whose slope is given by

$$\text{slope} = - Ne^2(D_{op}^{-1} - D_s^{-1})\ (18.42\ RT) \quad (32)$$

The notation of Equations 31 and 32 is as follows: N is Avogadro's number, D_{op} and D_s are the local optical and static dielectric constants, respectively, R is the ideal gas constant, T is the absolute temperature, e is the electronic charge, Q_N is the proportionality constant between charge density in the nitro group and the coupling constant a_N, and r_{NO^2} and r_{ring} are the average group radii for the nitro group and the benzene ring, respectively. The quantity representing the fraction of odd-electron charge on the nitrogen atom, $a_N Q_N$, was obtained from electron paramagnetic resonance spectroscopic data; and when this was combined with the electrochemical data of Table 2, the remarkably successful correlation

TABLE 2

Heterogeneous Charge-Transfer Rate Parameters for Some Nitro Compounds in Dimethylformamide Containing 0.1 M Tetrabutylammonium Iodide at 30°C

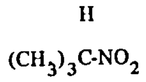
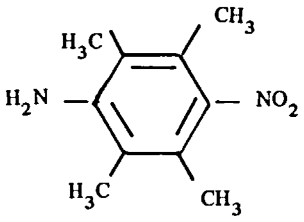
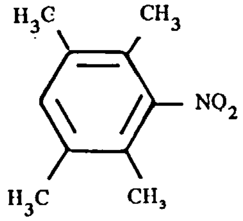
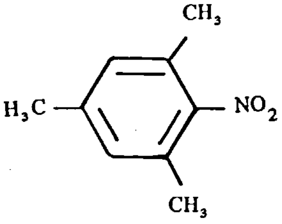
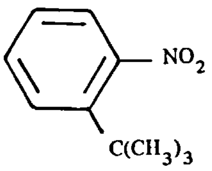
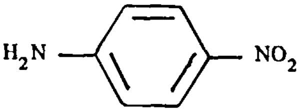
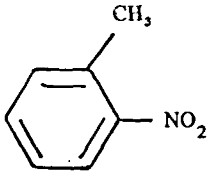
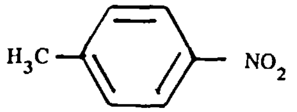
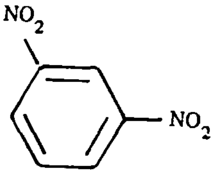
	Compound	$-E_{1/2}$ (V. vs. S.C.E.)	a_N [a]	α	k_s [b] $\text{cm} \cdot \text{s}^{-1}$
1.	$(\text{CH}_3)_2\text{C-NO}_2$	1.64	26	0.5	0.009
2.	 $\overset{\text{H}}{(\text{CH}_3)_3\text{C}}\text{-NO}_2$	1.64	26	0.5	0.0125
3.		1.52	20.65	0.51	0.128
4.		1.42	19.13	0.50	0.145
5.		1.38	15.95	0.50	0.28
6.		1.30	14.9	0.49	0.45

TABLE 2 (continued)

	Compound	$-E_{1/2}$ (V vs. S. C. E.)	a_N[a]	α[b]	k_s[b] (cm · s^{-1})
7.		1.37	11.49	0.51	1.21
8.		1.28	11.0	0.50	1.65
9.		1.14	10.06	0.54	2.7
10.		0.80	3.97	0.50	5

[a] a_N = coupling constant at the nitrogen atom.

[b] apparent rate constants uncorrected for double-layer effects.

shown in Figure 22 was obtained. Of course, this success establishes only a consistency between experiment and theory regarding the *relative* rate constants within the series of nitro compounds. Nevertheless, this investigation provides one of the most impressive examples of agreement between heterogeneous charge-transfer rate data and a fundamental theory for the corresponding process. The conclusion that solvent reorganization is the main source of the activation free energy appears sound and is further supported by the fact that $\alpha \simeq 0.5$ regardless of the molecular structure and the value of k_s. The latter observation is predicted bv the Marcus theory for a solvent-reorganization-controlled heterogenous charge-transfer step.

In a second relatively impressive experimental accomplishment, Dietz and Peover[135] presented heterogeneous charge-transfer rate data on the first reduction step for a series of stilbenes in dimethylformamide containing tetrabutylammonium iodide. Two planar aromatic hydrocarbons were included in this study for comparison. Some of the results obtained are given in Table 3. In this case a correlation is noted between the values of both k_s and α and the deviations from planarity of the neutral molecule (as measured by the angle θ given in Table 3). Sterically unhindered stilbenes behave much like the planar aromatic hydrocarbons, but notably smaller values of k_s *and* α are found for the more hindered species. Ambiguity in the interpretation of electron paramagnetic resonance data prevented a quantitative comparison with theory such as the one presented for the nitro compounds. However,

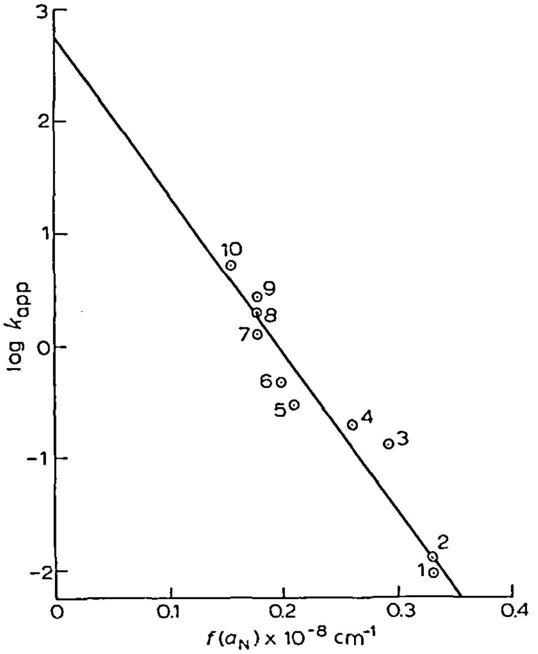


FIGURE 22. Dependence of experimental rate constants for electroreductions of nitro compounds on spin density at the nitrogen atom in nitroanion radicals with dimethylformamide solvent and a mercury electrode. $F(a_N)$ is given by Equation 31 and the solid line is of theoretical slope (Equation 32). Key as in Table 2. (Reprinted from reference 133 by courtesy of Elsevier Publishing Co.)

sound qualitative arguments were presented in favor of the concept that the rate differences arise because of effects of molecular conformation changes, rather than solvent reorganization. The authors argued that with the non-planar compounds the path to the activated complex involves the achievement of an orientation more planar than the conformation at the energy minimum. This contribution to the activation free energy is absent with compounds whose minimum energy conformation is planar and, consequently, the latter exhibit faster rates. The small values of α exhibited by the more hindered species also were used to support this idea by invoking the Marcus theory. According to Marcus,

$$\alpha = \frac{1}{2} + \frac{1}{2\lambda}\left[w^p - w^r - nF(E - E^{0'})\right] \qquad (33)$$

where λ is a reorganizational energy term which is equal to the standard free energy of activation at the formal potential $E^{0'}$ in absence of double-layer effects. The quantities w^r and w^p represent the reversible amounts of work required to bring the reactants (oxidized form) and the products, respectively, in their standard states, from the bulk of the solution into the configuration relative to the electrode surface required for charge transfer. Under the conditions associated with the stilbene study the overpotential is small, so that the quantity $nF(E\text{-}E^{\circ})$ is negligible. Thus, the observation that $\alpha < 1/2$ implies that $w^r > w^p$. This is compatible with the idea that greater work is required to achieve the relatively planar transition state when the initial state is the neutral reactant rather than the normally more planar anion radical.* These ideas, as presented by Dietz and Peover, appear to provide the best available rationale for the observations reported.

A molecule exhibiting a particularly profound apparent stereochemical effect on the heterogeneous electron-transfer rate has been studied recently by Huebert and Smith.[106] The molecule in question is cyclooctatetraene (COT), whose neutral form is known to be non-planar, while the anion radical, $COT^{\dot{-}}$, and dianion, COT^{2-}, are planar, or at least very nearly so. Using dc polarography, fundamental harmonic ac polarography in the frequency multiplex mode, and second harmonic ac polarography, these authors characterized the rates of the first and second electron transfers to COT, the first electron transfer to 1,3,5-cyclooctatriene, and the follow-up protonation of COT^{2-}. The solvent-supporting electrolyte system employed was dimethylformamide-0.1 M tetrabutylammonium perchlorate, in which the COT molecule exhibits three major polarographic waves. The underlying electrode reaction mechanism (see R11, p.315).

The rate data obtained for this reaction sequence are shown in Table 4. The key point of interest is that the rate parameters $k_{s,1}$ and α, that characterize the first electron transfer to COT, are significantly smaller than those for the second step. As in the case of the stilbene derivatives discussed above, the authors were led to conclude that a molecular conformation change leading to a relatively planar transition state is responsible for the anomalously low rate for the first reduction step, and the fact that $\alpha \ll 0.5$.

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*In the case of non-planar conjugated hydrocarbons one normally finds that the minimum-energy configuration of the anion radical tends to be more nearly planar than the neutral molecule, presumably because of an increase in appropriate bond orders resulting from the added electron.

TABLE 3

Heterogeneous Charge-Transfer Rate Parameters for Some Stilbenes and Planar Aromatic Hydrocarbons in Dimethylformamide Containing 0.1 *M* Tetrabutylammonium Iodide at 30°C

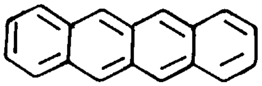
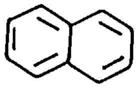
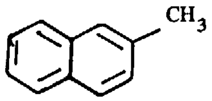
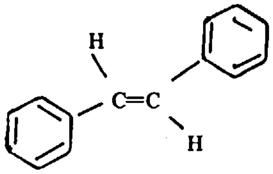
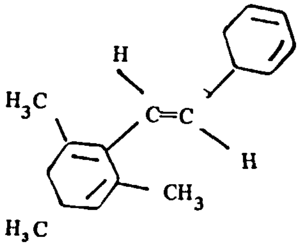
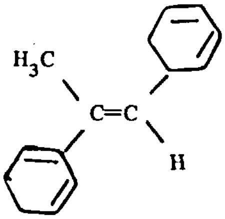
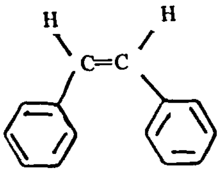
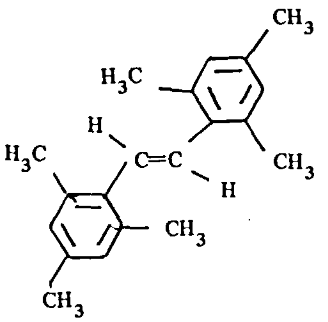
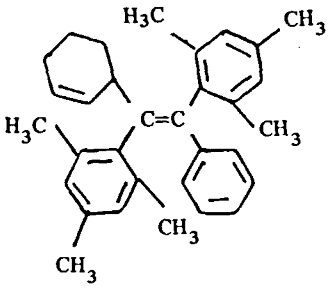
Compound	$-E_{1/2}$ (V. vs. S.C.E.)	θ^a (degrees)	α^b	k_s^b (cm·s^{-1})
	1.58	0	0.52	1.64
	2.49	0	0.56	1.00
	2.52	0	0.58	0.84
	2.15	0	0.58	1.22
	2.28	28-38	0.57	0.52
	2.26	35	0.45	0.43

TABLE 3 (continued)

Compound	$-E_{1/2}$ (V vs. S. C. E.)	θ^a (degrees)	α^b	k_s^b (cm · s^{-1})
	2.18	28	0.44	0.42
	2.46	54	0.46	0.18
	2.05	34.5	00.5	0.09

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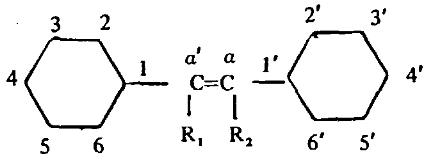
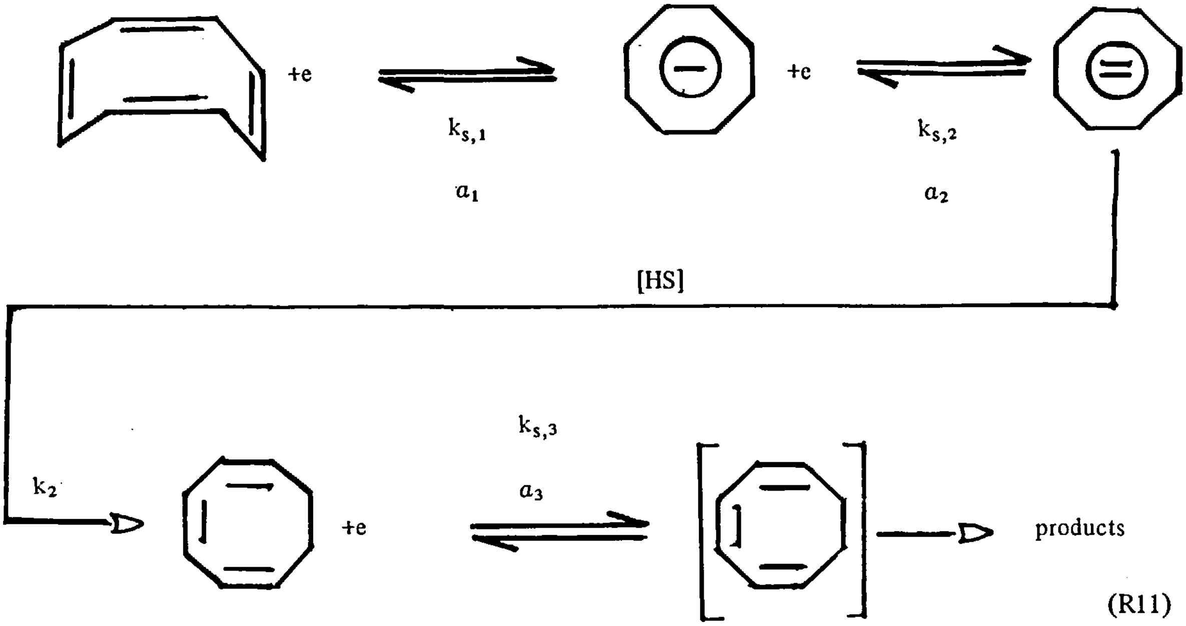
[a] θ = angle of twist about 1-α, 1-α' or α-R bonds where bond numbering system is defined by



[b] apparent rate constants uncorrected for double-layer effects.



(R11)

Another non-planar species, azobenzene, has had its heterogeneous charge-transfer rate parameters assessed in an aprotic solvent. Aylward, Garnett, and Sharp[136] used ac polarography to show that $k_s = 0.5$ cm•s^{-1} and $a = 0.37$ for the azobenzene-azobenzene anion radical redox couple in dimethylformamide containing 0.1 *M* tetraethylammonium perchlorate. Although the rate constant is not particularly small, the value of a is notably less than 0.5. Noting the fact that azobenzene is also non-planar, like the stilbenes and COT, one is tempted to speculate that this might be a common characteristic of molecules containing two or more π-bonded centers whose relative geometrical arrangement is non-planar.

Finally, as evidence that the automated faradaic admittance measurement procedures described earlier are beginning to pay dividends in the form of useful rate data, we submit without discussing their significance (let the reader have some fun!) the heterogeneous charge-transfer rate data shown in Tables 5 and 6. These results, which were obtained in this writer's laboratory,[137] were derived by measurement procedures which utilized exclusively automated compensation of non-faradaic influences and computerized data acquisition, data analysis, and experiment control. The data shown in Table 5 were obtained using ac polarography in the frequency multiplex mode. The time devoted to acquiring these results was relatively short and it was our experience that the rate-determining step in obtaining these rate parameters was found in the *chemical* manipulations (solvent and compound purification, etc.) and not in the actual electrochemical measurement, which contrasts dramatically to our experiences with the earlier approaches.

If the volume of data is any criterion, the results compiled in Tables 2 to 6 illustrate that the past few years have been relatively fruitful with regard to heterogeneous rate measurements in aprotic solvents.

2. *Measurements Based on Faradaic Non-linearity*

Prior to about 1968, the state of affairs regarding heterogeneous charge-transfer rate measurements using observables arising from faradaic non-linearity was rather muddled. Despite the obvious advantages of these techniques, which already have been discussed, the quality of the somewhat sparse rate data derived from these methods often seemed rather questionable, at best. Such data were often inconsistent with the results of more conventional techniques (e. g., fundamental harmonic measurements). In some cases the results seemed downright ridiculous–e. g., values of a very near zero or unity were indicated. Since 1968, the situation has been dramatically reversed. Sources of previous errors in data analysis have been revealed, such as the introduction of too many approximations into the rigorous theory in an effort to simplify calculations. Problems of measurement such as iR-drop distortion have been recognized and

TABLE 4

Heterogeneous Charge-Transfer Rate Parameters for Cyclooctatetraene in Dimethylformamide-Containing 0.1 M Tetrabutylammonium Perchlorate

Temp., °C	$k_{s,1}$ [c] cm·s^{-1}	α_1 [c]	$k_{s,2}$ [c] cm·s^{-1}	α_2 [c]	k_2 s-1	$k_{s,3}$ [c] cm·s^{-1}	α_3 [c]
15	a	a	$(1.2 \pm 0.2) \times 10^{-1}$	0.50 ± 0.03	4.7 ± 0.8	b	b
25	$(2.0\pm0.5)\times10^{-3}$	0.40 ± 0.03	$(1.5 \pm 0.1) \times 10^{-1}$	0.50 ± 0.03	8.0 ± 1.0	$(8.3 \pm 0.4) \times 10^{-2}$	0.50 ± 0.04
35	$(2.5\pm0.5)\times10^{-3}$	0.40 ± 0.03	$(1.7 \pm 0.3) \times 10^{-1}$	0.50 ± 0.03	65 ± 10	$(2.2 \pm 0.3) \times 10^{-1}$	0.50 ± 0.04

[a] Calculations precluded by polarographic maximum.
[b] Measurements necessary for calculations not performed.
[c] Apparent values uncorrected for double-layer effect.

TABLE 5

Heterogeneous Charge-Transfer Rate Parameters for Some Metal "Sandwich Compounds" in Acetonitrile Containing 0.3 M Tetrabutylammonium Hexafluorophosphate at 25°C.

Redox Couple[a]	k_s(cm·s^{-1})[b]	α[b]
Cp_2Co^+/Cp_2Co	0.92	0.52
Cp_2Co/Cp_2Co^-	0.28	0.50
$Cp(O\text{-}B_9)Co/Cp(O\text{-}B_9)Co^-$	1.00	0.50
$Cp(O\text{-}B_9)Co^-/Cp(O\text{-}B_9)Co^{-2}$	0.20	0.40
$(O\text{-}B_9)_2Co^-/(O\text{-}B_9)_2Co^{-2}$	0.82	0.48
$(O\text{-}B_9)_2Co^{-2}/(O\text{-}B_9)_2Co^{-3}$	0.37	0.48
$(O\text{-}B_9)_2Ni/(O\text{-}B_9)_2Ni^-$	0.43	0.50
$(O\text{-}B_9)_2Ni^-/(O\text{-}B_9)_2Ni^{-2}$	0.66	0.50
$(n\text{-}B_9)_2Ni^-/(n\text{-}B_9)_2Ni^{-2}$	1.60	0.47

[a] Cp = $C_5H_5^-$ (cyclopentadienide ion); O-B_9 = 1,2-$B_9C_2H_{11}$ (orthodicarbollide ion); n-B_9 = 1,7-$B_9C_2H_{11}$ (neodicarbollide ion).

[b] apparent values uncorrected for double-layer effects.

eliminated. As a result, the vast majority of recently published quantitative rate data based on measurements of faradaic non-linearity seem to exhibit excellent fidelity. Implicit in these successes has been the first really convincing experimental verification of many of the underlying theoretical approaches.

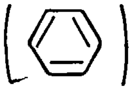
DeLeeuwe, Sluyters-Rehbach, and Sluyters have carefully reassessed procedures for data analysis used in faradaic rectification measurements and concluded that previous approaches were too approximate.[138] They advocate a numerical approach which uses the magnitude of the faradaic rectification signal and a method based on the measurement of the frequency where the rectification signal is zero (the zero-point method). In neither case do they compromise the rigor of the basic theory by introducing simplifying approximations. Their data-analysis concepts, along with some instrumental improvements, were applied to the kinetic characterizations of some relatively rapid electrode processes.[139] The measurements employed frequencies up to 16 MHz. These applications led

TABLE 6

Heterogeneous Charge-Transfer Rate Parameters for Some Silicon- and Germanium-Substituted Polyphenyls in Dimethylformamide Containing 0.1 M Tetrabutylammonium Perchlorate at 25°C

I. First Reduction Step

$R + e \rightleftharpoons R^-$

COMPOUND	$k_s(cm \cdot s^{-1})^a$	α^a
$(CH_3)_3Si$  $_2Si(CH_3)_3$	0.34 ± 0.02	0.63 b 0.03
$(CH_3)_3Si$  $_4Si(CH_3)_3$	0.64 ± 0.14	0.65 ± 0.05
$(CH_3)_3Ge$  $_2Ge(CH_3)_3$	0.28 ± 0.02	~0.5
$(CH_3)_3Ge$  $_3Ge(CH_3)_3$	0.30 ± 0.02	0.50 ± 0.05
$(CH_3)_3Ge$  $_4Ge(CH_3)_3$	0.38 ± 0.02	0.55 ± 0.05

II. Second Reduction Step

$R^- + e \rightleftharpoons R^{2-}$

COMPOUND	$k_s(cm \cdot s^{-1})^a\alpha$	α^a
$(CH_3)_3Ge$  $_3Ge(CH_3)_3$	0.67 ± 0.06	~0.5
$(CH_3)_3Ge$  $_4Ge(CH_3)_3$	0.38 ± 0.03	0.55 ± 0.05
$(CH_3)_3Si$  $_4Si(CH_3)_3$	0.62 ± 0.05	0.65 ± 0.05

[a]apparent values uncorrected for double-layer effects.

to the conclusion that the zero-point method is not as advantageous as the numerical method. The latter data analysis procedure led to the results shown in Table 7. The data on $Cd^{2+}/Cd(Hg)$ in 1 *M* $NaClO_4$ was in excellent agreement with measurements using more conventional procedures. The results for $Fe(C_2O_4)_3{}^{3-}/Fe(C_2O_4)_3{}^{4-}$ in 1 *M* $K_2C_2O_4$ + 0.05 *M* $H_2C_2O_4$ and $Cd^{2+}/Cd(Hg)$ in 1 *M* KCl were novel, for the rates for these systems are so large that quantitative estimates of them had been inaccessible until this report was published. However, the k_s value for the iron oxalate system had been "bracketed"by galvanostatic single-pulse and faradaic impedance

TABLE 7

Heterogeneous Charge-Transfer Rate Parameters Obtained by Faradaic Rectification Measurements Using Rigorous Numerical Data-Analysis Procedures[139]

Redox System	k_s(cm·s^{-1})^a	α^a
$Cd^{2+}/Cd(Hg)$ in 1 M $NaClO_4$ at 25°C	0.44 ± 0.03	0.32 ± 0.02
$Fe(C_2O_4)_3^{3-}/Fe(C_2O_4)_3^{4-}$ in 1 M $K_2C_2O_4$ + 0.05 M $H_2C_2O_4$ at 25°C	1.16 ± 0.04	0.86 ± 0.04
$Cd^{2+}/Cd(Hg)$ in 1 M KCl at 25°C	4.1 ± 0.5	0.75 ± 0.03

^{a}apparent values uncorrected for double-layer effects.

measurements which had led to the conclusion that k_s is between 1 and 3 cm· s^{-1}. Finally, we call attention to the favorable faradaic rectification data obtained for the Hg_2^{2+}/Hg system by DeLeeuwe and co-workers,[21] which we have already discussed in section II-A1. This system, which exhibited specific adsorption, along with the other problems attending faradaic rectification measurements, probably represents the greatest challenge which has been overcome by using observations related to faradaic non-linearity.

Randles and Whitehouse,[140] McCord and Smith,[48,105] and Glover and Smith[93,94] have presented papers describing quantitative measurements of heterogeneous charge-transfer rate constants using second harmonic ac polarography. The results have established the applicability of second harmonic current amplitude and phase angle measurements to this type of measurement. The systems included in these investigatons were: V^{3+}/V^{2+} in 0.01 M $(NH_4)_2SO_4$ + 0.2 M $HClO_4$ + 1 M and 5 M $NaClO_4$,[140] $Cr(CN)_6^{3-}/Cr(CN)_6^{4-}$ in 1 M KCN[48,94] $Cd^{2+}/Cd(Hg)$ in 1 M Na_2SO_4,[48,93,94] and $Zn^{2+}/Zn(Hg)$ in 1.0 M KCl + 0.001 M HCl.[105] In each case the rate parameters obtained from the second harmonic data were consistent with previously or simultaneously[94] obtained fundamental harmonic ac measurements. Excellent agreement between second harmonic theory for quasi-reversible processes and experiment was realized, as illustrated in Figures 23 and 24. The long-standing theoretical allegation that the second harmonic response is very sensitive to the value of α can now be considered quantitatively verified as a result of these studies. Because of the latter property of second harmonic measurements, Randles and Whitehouse are convinced that α can be obtained with three-significant-figure precision and recommend this measurement scheme for detecting small changes in α.

From the data mentioned above, it appears that the difficulties with rate measurements based on manifestations of faradaic non-linearity are essentially overcome and techniques such as *faradaic rectification measurements, second harmonic* ac polarography, intermodulation polarography, etc. may be applied with confidence. The only sour note is that the successes enumerated here were realized by implementing the theoretical "rate laws" with complete rigor. This implies the necessity of using relationships that are very cumbersome algebraically. At best, one is faced with using graphical procedures (numerically calculated sets of working curves) to obtain first estimates of the rate parameters followed by trial-and-error numerical fitting of theory and experimental data until the best set of parameters is obtained. To implement such procedures with reasonable efficiency requires digital computer aids. It simply appears that the observables arising from faradaic non-linearity are too sensitive to permit the general application of approximations which simplify data analysis. DeLeeuwe et al.[138] have made this point most convincingly.

3. Systems Exhibiting Heterogeneous Charge-Transfer Rates with Unusual Dependences on Potential

Because the environment in which the heterogeneous charge transfer step proceeds is within the electrical double layer, one naturally finds an abundance of so-called "double-layer effects" on the associated rate parameters. Double-layer effect origins range from the relatively mild "electrostatic" effects encompassed in the classical Frumkin correction to much more profound events such as anion-induced specific adsorption of metal cations. When particularly profound changes in double-layer structure accompany variations in the applied direct potential, heterogeneous charge-transfer rates can exhibit rather unusual dependences on potential, as noted earlier (section IIC-2). Normally, reduction rates increase

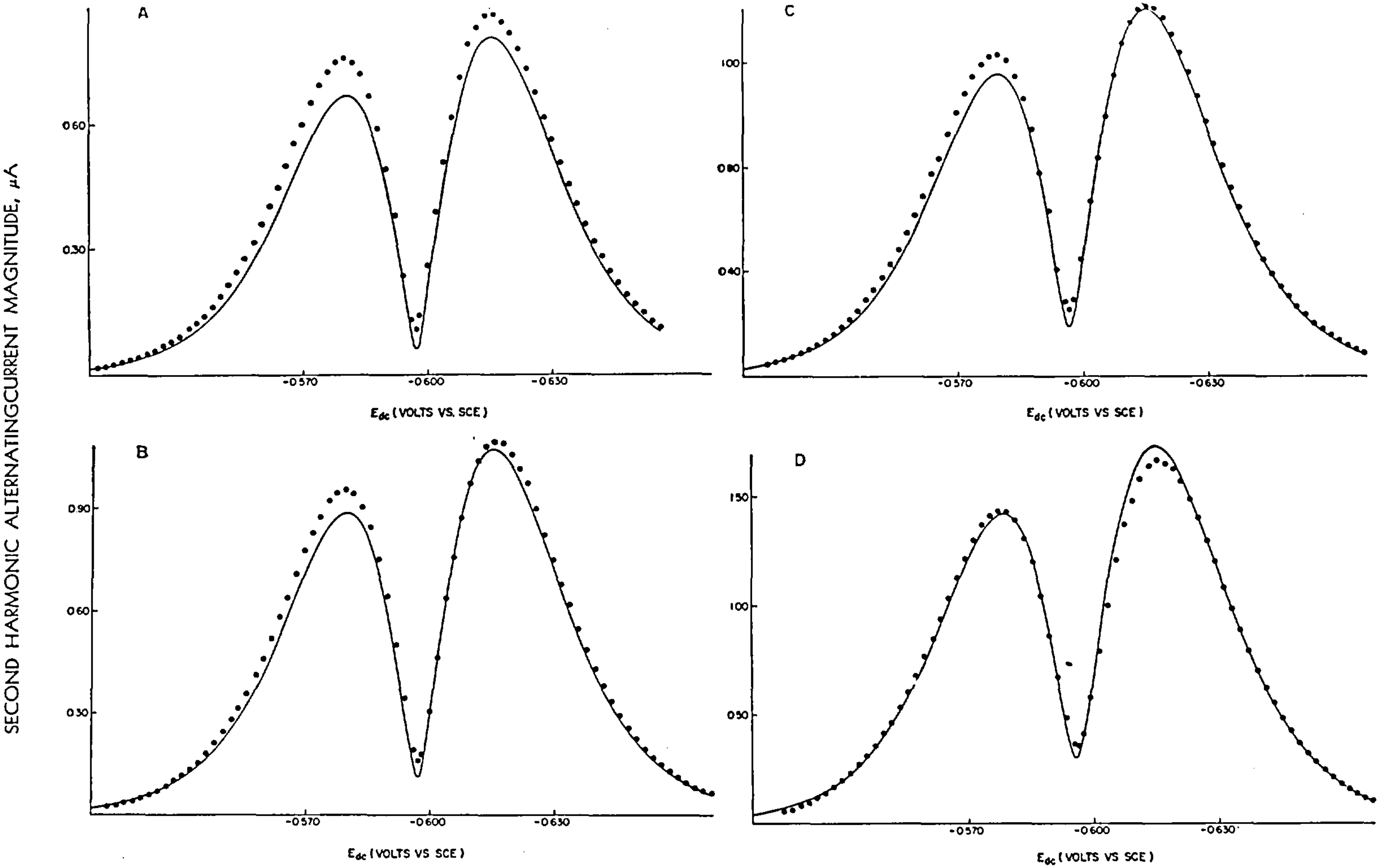


FIGURE 23. Second harmonic ac polarographic current–direct potential results for $Cd^{2+}/Cd(Hg)$ system. System: 2.00 x 10^{-3} *M* Cd^{+2} *in* 1.00 *M* Na_2SO_4. *Applied:* D.C. *scan rate* 10.0 *mV/min,* 10.0 *mV* peak-to-peak *sine wave*, frequencies listed below. Measured: Second harmonic faradaic component at end of mechanically controlled drop life. Readout aided by sample-and-hold circuitry. —— Theoretical second harmonic polarograms for $\alpha = 0.30$, $k_s = 0.15$ cm · s^{-1}, $D_R = 1.60 \times 10^{-5}$ cm^2 s^{-1}, t = 5.40 s, A = 0.0130 cm^2, T = 25.0°C, ΔE = 5.00 mV, n = 2, $C_O{}^* = 2.00 \times 10^{-3}$ *M*, and appropriate ω-value. ○ Observed second harmonic currents. A. Applied frequency = 23.0 Hz. B. Applied frequency = 46.0 Hz. C. Applied frequency = 83.0 Hz. D. Applied frequency = 166.0 Hz. E. Applied frequency = 332.0 Hz. F. Applied frequency = 555.0 Hz. G. Applied frequency = 1110.0 Hz. H. Applied frequency = 2220.0 Hz. (Reprinted from reference 48 by courtesy of the American Chemical Society.)

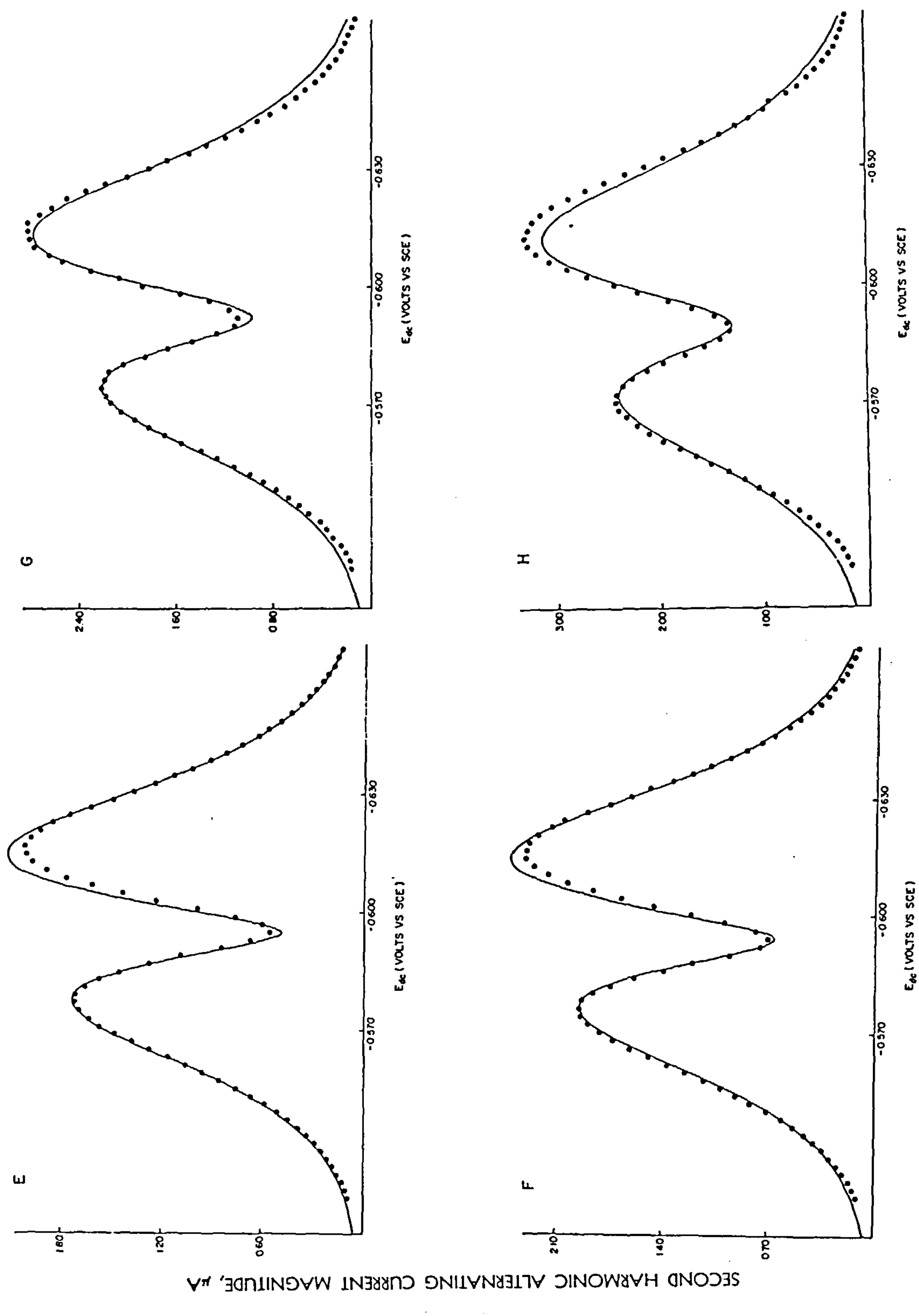


FIGURE 23 (see preceding page for caption).

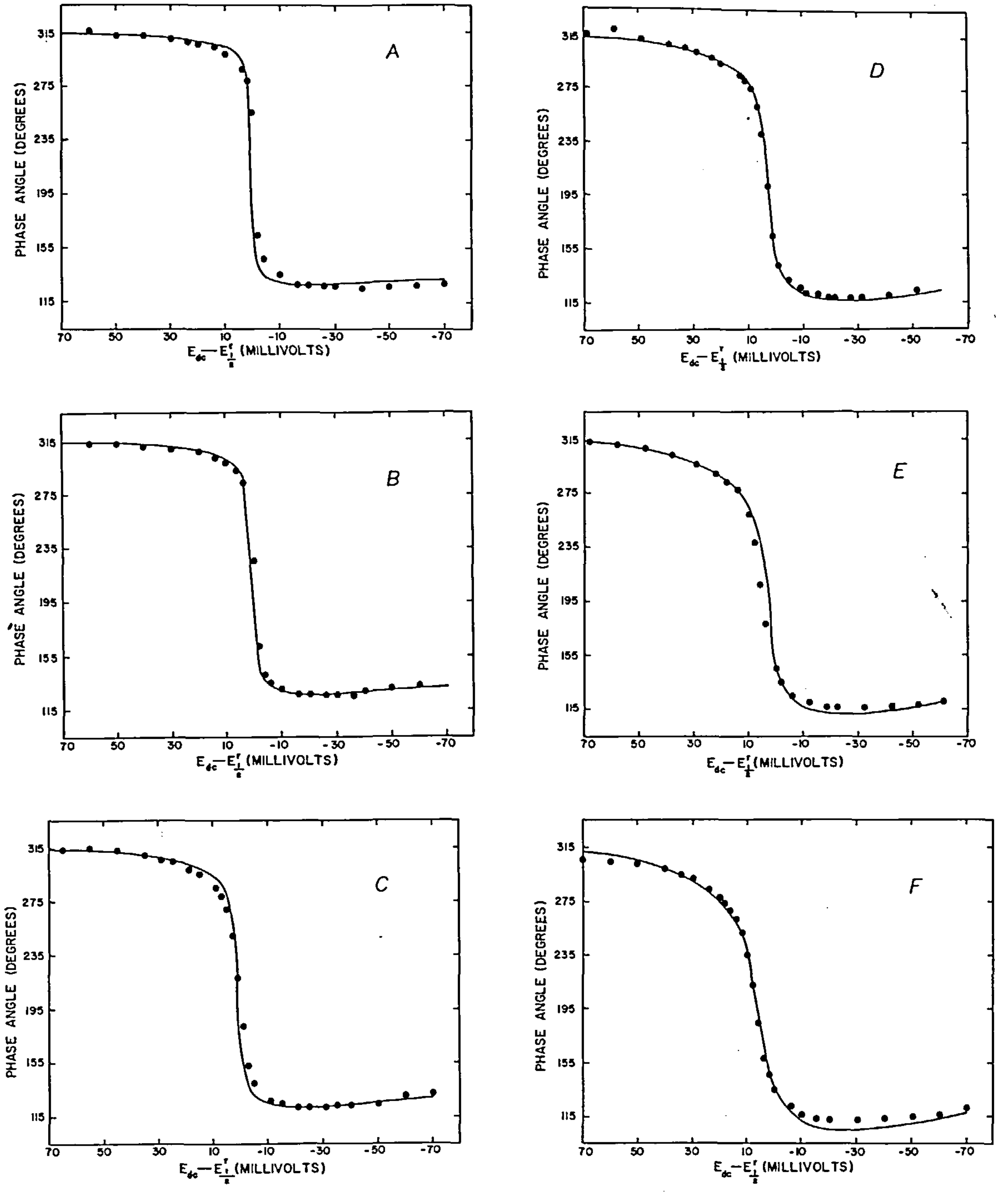


FIGURE 24. Second harmonic ac polarographic phase angle-direct potential results for Cd^{2+}/Cd(Hg) system. System: 3.19×10^{-3} *M* Cd^{2+} in 1.00 *M* Na_2SO_4. Applied: dc scan rate 50 mV/min, 10.0 mV peak-to-peak sine wave, frequencies listed below. Measured: second harmonic phase angle at end of mechanically controlled drop life. Readout aided by sample-and-hold circuitry. —— Theoretical second harmonic phase angle polarograms for same parameters as listed in Figure 24. o Experimental phase angles. A. Applied frequency = 18 Hz. B. Applied frequency = 25 Hz. C. Applied frequency = 68 Hz. C. Applied frequency = 190 Hz. D. Applied frequency = 395 Hz. E. Applied frequency = 1000 Hz. (Reprinted from reference 93 by courtesy of the American Chemical Society.)

exponentially and oxidation rates decrease exponentially as the potential becomes increasingly negative in accord with the equations:

$$k_{red} = k_s \exp[-(\alpha nF/RT)(E - E^0)] \qquad (34)$$

$$k_{ox} = k_s \exp[1 - \alpha)(nF/RT)(E - E^0)] \qquad (35)$$

where k_{red} and k_{ox} are the heterogeneous charge-transfer rate constants for reduction and oxidation, respectively. However, in the special situations just referred to, these relationships may be quite inapplicable. Not only may the dependence on potential deviate from the exponential form, but even the direction of variation of the rate constant with potential may be reversed. The ac polarographic investigation and characterization of systems exhibiting such "anomalies" has been a subject on which much attention has been showered in the past two years.

Within the class of systems under consideration, the thiocyanate-catalyzed reduction of In^{3+} at mercury has received particularly close attention. The dc polarogram of In^{3+} in concentrated aqueous thiocyanate solutions exhibits a pronounced minimum at potentials several hundred millivolts more negative than the half-wave potential. Qualitatively, this minimum is attributed to the gradual desorption of thiocyanate ions as the potential is made more negative. The first consequence is a decrease in the heterogeneous charge-transfer rate and an accompanying decrease of current as the adsorbed-thiocyanate-assisted pathway becomes less accessible and an alternative, less facile charge-transfer mechanism must take over. Eventually, the "normal" exponential increase of the rate of the alternative mechanism with increasingly negative potential leads to the rising branch of the minimum. The ac polarographic response in the potential region of the dc polarographic minimum has been scrutinized by deLevie and co-workers[74,141] and Timmer, Sluyters-Rehbach, and Sluyters.[77] Both groups reported the observation of a negative faradaic admittance in this potential region and a lack of evidence for specific adsorption of In^{3+}, although this cation is apparently adsorbed at more anodic potentials[77] corresponding to the "normal" wave. DeLevie and Husovsky showed that dc and ac polarograms yielded consistent rate data when comparison was possible. The data-analysis and presentation methods of the Utrecht and Georgetown groups differ markedly. The former group favors a formalism which invokes the concept of potential-dependent values of the standard rate constant, k_s, and α as a modification of the classical absolute rate theory formalism for heterogeneous charge transfer (Equations 34 and 35). In contrast, the Georgetown school utilize their recently developed formalism[74] which simply characterizes the charge-transfer rate in terms of a rate constant and its first derivative with respect to potential. This is a strictly operational formalism which is adequate for characterizing the linear response of the faradaic admittance to small amplitude perturbations. We favor the approach of deLevie and co-workers because of its generality and the fact that it does not attempt to retain a specific model for the charge transfer potential dependence which was not originally designed for the type of process under consideration. Also, while its proper application can lead to perfectly reasonable conclusions, the concept of a potential-dependent value of k_s suffers from a marked inconsistency arising from the fact that k_s is defined in most electrochemical literature as the heterogeneous charge-transfer rate constant *at the standard potential* (i. e., at a single characteristic potential) so that in the literature a potential-dependent value of k_s is inadmissible *by definition.* Of course, this difficulty is eliminated in the strict mathematical sense when one recognizes that the Utrecht group is really referring to a potential-dependent *apparent* value of k_s and they view the "true" k_s as potential-independent. Nevertheless, I fear that the concept in question is still an incipient pedagogical and philosophical nightmare. This problem has been acknowledged by the Utrecht group who have indicated an intention to publish further on this question.[142] In this writer's opinion, if one feels compelled to hold onto the classical Butler-Volmer rate equations in treating rate constants exhibiting nonexponential dependences on potential, then the modification of the classical formalism should be confined to allowing only for a potential-dependent α, which is adequate. However, at this point in time the "fresh" operational approach of deLevie et al. appears to be the more appealing of the alternatives. Perhaps this view is best supported by the success realized by deLevie and co-workers in applying their formalism to the thiocyanate-catalyzed reduction of In^{3+}. Their efforts led to a rather interesting and novel characterization of the charge-transfer mechanism underlying this electrode reaction at potentials corresponding to the descending branch of the dc polarographic minimum. Pospisil and de Levie[141] plotted rate constants obtained with different bulk concentrations of thiocyanate ion against various parameters which are related to the surface excess of absorbed thiocyanate ion (the surface excess can be varied for a given bulk concentration by varying the dc potential). An excellent correlation between the logarithm of the rate constant (log k) and the logarithm of the surface activity (log βa) was found as illustrated in Figure 25. A linear plot having a slope of 2 was found for all thiocyanate-ion concentrations. On this basis it was concluded that two thiocyanate ions are involved in the rate-determining step. By comparing the variations in reduction rate at constant surface activity with variations of bulk concentration of thiocyanate, the authors concluded that the bulk reacting species is In^{3+}, rather than $In(SCN)^{+2}$ or some complex richer in thiocyanate. The authors' arguments strongly support the mechanism

$$In^{3+} + 2SCN^-_{ads} \xrightarrow{slow} In(SCN)_2{}^+{}_{ads}$$

$$In(SCN)_2{}^+{}_{ads} + 3e^- \xrightarrow[fast]{} In^0 + 2SCN^-_{ads} \qquad (R11)$$

The absence of experimental evidence for significant adsorption of indium is not inconsistent with this mechanism because the electron-transfer step is considered to be much faster than the preceding adsorption step so that under conditions relevant to the data, the steady-state concentration of $In(SCN)_2{}^+{}_{ads}$ is very small.

DeKreuk, Sluyters-Rehback, and Sluyters[142] recently published a very thorough and enlightening analysis of the Eu^{3+}/Eu^{2+} reaction in 1 *M* KCl and 1 *M* KI electrolytes. In these media the europium system has been known for some time to exhibit certain anomalous features which have not been explained satisfactorily at a quantitative level. However, DeKreuk et al. succeeded in convincingly demonstrating that these systems are characterized by charge-transfer rates with nonexponential dependences on potential (i. e., "potential-dependent apparent k_s values"), whose origin was found in Frumkin-type double-layer effects. By introducing a modification of the Frumkin correction, the resulting "true" values of k_s and α were found to be potential-independent. The values of true rate parameters were $k_s = 1.4 \times 10^{-5}$ cm· s^{-1} and α= 0.59 in 1 *M* KCl and k_s =0.6 x 10^{-5} cm· s^{-1} and α = 0.52 in 1 *M* KI. The "normal" behavior of these constants obtained after removing the classical double-layer effects is rather interesting and in marked contrast to the In^{3+} system discussed above. Because iodide and chloride ions undergo strongly specific adsorption and their surface excesses are strongly potential-dependent in the region of the europium wave, it appears that the "true" reduction rate is not substantially influenced by the adsorbed halide ions. DeKreuk et al. inferred from this that the Eu^{3+}/Eu^{2+} couple undergoes charge transfer at a point outside the inner part of the double layer and that the reactants remain hydrated in the course of the reaction. Presumably an electron-tunneling mechanism is operative. This type of mechanism for electron transfer also was favored by Elliott to explain his observations on the effects of double-layer structure on the V^{3+}/V^{2+} system in perchlorate media.[143] This study involved variation of double-layer properties using organic surfactants of cationic, anionic, and neutral forms. The best qualitative explanation for the observations seemed to involve charge transfer via electron tunneling to a solvated ion located outside the inner Helmholtz plane.

Incidentally, DeKreuk et al. advanced the success they realized in the investigation of the europium system[142] as evidence of an advantage in data analysis of their formalism based on the concept of a potential-dependent value of k_s because it provided a framework for the convenient introduction of the Frumkin double-layer correction. However, the implication that other formalisms suffer a disadvantage in this regard is not true, except possibly at a subjective level. Pospisil and deLevie[141] had no difficulty in introducing one type of double-layer correction into their more general formalism and there seems to be no reason why the latter framework would not have led to the same conclusions reached by DeKreuk et al. had it been implemented with the appropriate double-layer correction. Once rate constants are obtained at various potentials with the operational formalism of deLevie et al., nothing dictates against comparing the results to any model which seeks to describe the potential dependence of the rate constant, including the simple Butler-Volmer model. The results of DeKreuk et al. certainly establish that the Utrecht group's approach is a mathematically self-consistent system. As stated earlier, this point is not questioned. The objections voiced above are confined to philosophical and pedagogical considerations.

Finally, another case of unusual potential was found by Sluyters-Rehbach, Breukel, and Sluyters[144] for the $Zn^{2+}/Zn(Hg)$ couple in 1*M* KBr, 1 *M* KI, 1 *M* $NaClO_4$, and 1 *M* KCl (barely detectable in the KCl case). The zinc system did not succumb to the type of quantitative explanation that worked so well in the case of the europium system. In the zinc case it was qualitatively evident that specific adsorption of anions accelerated the electrode reaction. However, further clarification of the zinc system is necessary. Perhaps examining the data in the format shown in Figure 25 would be fruitful.

Considering the number of systems exhibiting heterogeneous charge-transfer rates with "unusual" dependences on potential that have been uncovered in a relatively short period, one is led to ponder whether or not such behavior is really "unusual."

4. AC Polarography with Irreversible Systems

The somewhat belated recognition that irreversible processes do yield useful ac polarographic responses has received ample experimental support, particularly for the case where the origin of irreversibility is found in a very slow heterogeneous charge-transfer rate. Actually, the response of the indium system in thiocyanate media in the region of the dc polarographic

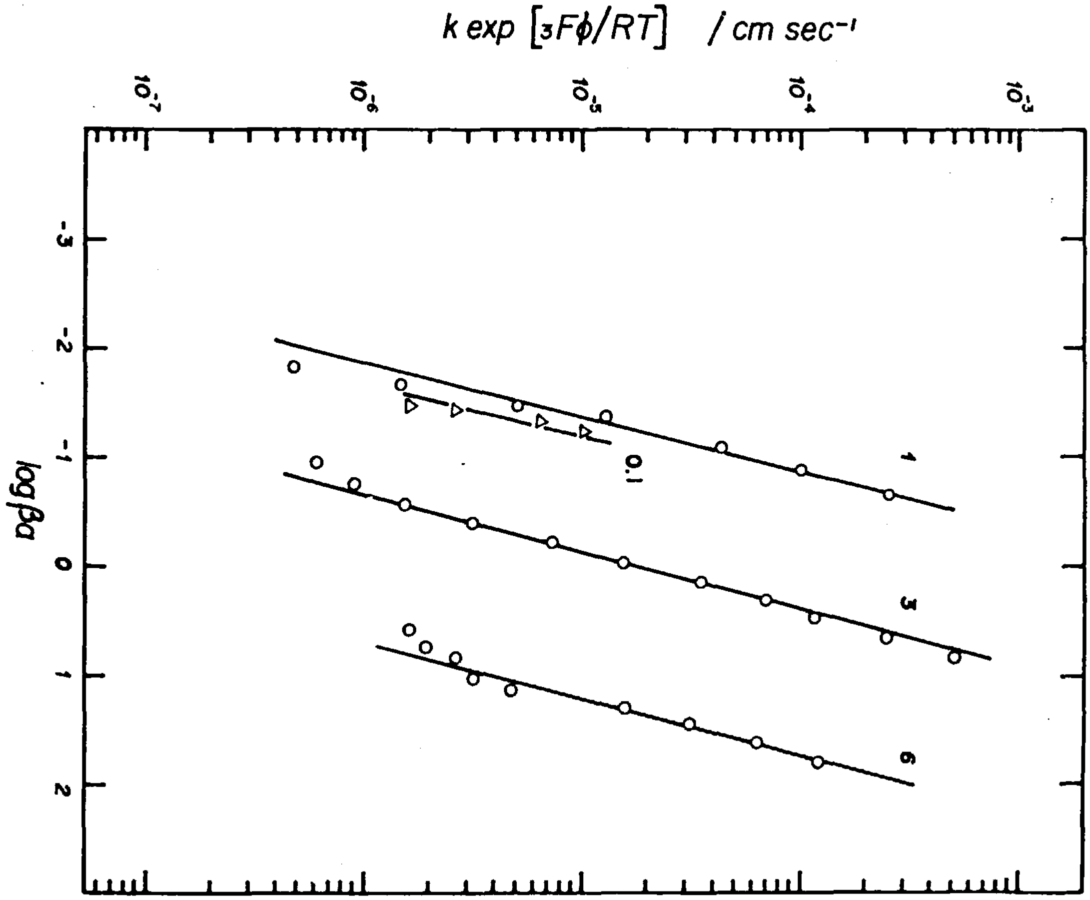


FIGURE 25. Rate constants for indium system in thiocyanate media versus the logarithm of the surface activity for different SCN concentrations. Rate constants corrected for double-layer potential assuming +3 charge on oxidized form. Concentrations (*M*) of NaSCN indicated on figure. Lines are drawn with slope 2. (Reprinted from reference 141 by courtesy of Elsevier Publishing Co.).

minimum, which was just discussed, falls into this category although it is a rather non-classical example. Similarly, the above-discussed europium systems and the zinc system in 1 *M* $NaClO_4$ are characterized by rate constants which lie very close to the irreversible domain and essentially irreversible behavior is obtained over at least a portion of the direct potential realm comprising the ac wave.

Particular attention has been devoted to the characteristics of the faradaic admittance attending the irreversible discharge of hydrogen ion on mercury, $H^+/H_2(Hg)$, a system whose popularity has long been second only to that of cadmium ion. Once again we find the Utrecht school leading the way. Dekker, Sluyters-Rehbach, and Sluyters[145],[146] have examined the hydrogen-evolution process in 1 *M* HCl, 7.5 *M* HCl, 5.2 *M* $HClO_4$, and 57% HI solutions, with particular attention accorded to the temperature dependence of the charge-transfer kinetic parameters and the double-layer characteristics. It should be noted that in these systems the reactant and supporting electrolyte are one and the same species. Consequently, these systems must be investigated using at least the Utrecht group's second-generation approach for the separation of faradaic and non-faradaic response, because there is no way of validly invoking the first-generation approach. Because the $H^+/H_2(Hg)$ reaction at mercury is totally irreversible and because of the high reactant concentrations, measurements were readily made under conditions where mass-transfer polarization effects are negligible, so that the complexities associated with coupled migration and diffusion did not demand consideration. For the evolution of hydrogen from 1 *M* HCl and 5.2 *M* $HClO_4$, the authors found activation enthalpies of about 20 kcal/mole and temperature-independent values of α near 0.52. The 7.5 *M* HCl and 57% HI systems differed markedly in that a temperature-dependent value of α was observed. A positive temperature coefficient, 1.56×10^{-3} deg. $^{-1}$, was found in 7.5 *M* HCl and a negative one, -1.4×10^{-3} deg. $^{-1}$, was found in 57% HI. The corresponding activation enthalpies were about 11 kcal/mole and 22 kcal/mole. The observation that the charge-transfer coefficient was temperature-dependent was attributed to variations in the double-layer structure with temperature, most likely arising from the temperature dependence of halide-ion specific adsorption. Thus, the authors imply that the specifically adsorbed halide ions assist in the hydrogen-evolution process. This conclusion had been reached on the basis of other types of data by other workers, but the data being considered provide a novel form of evidence for this effect.

A very important observation on the question of halide-ion catalysis of the hydrogen reaction was provided by deLevie and Pospisil.[147] Although they did not consider the foregoing data of the Utrecht group, they utilized earlier data on hydrogen evolution in the presence of various halide mixtures and showed that the relative rate enhancement attending the addition of halide correlated very nicely with the surface activity, a result similar to that found in the case of the thiocyanate-assisted reduction of In^{3+}. The relative rate enhancement at various potentials with the systems 0.1 *M* HCl + 1 *M* KCl, 0.1 *M* HCl + 1 *M* KBr, and 0.1 *M* HCl + 1 *M* KI were found to lie on a straight line of *unit* slope when plotted versus the logarithm of the surface activity of halide ion. This result supports a rate-determining step involving the formation of the species HX_{ads} (X = halide), followed by rapid charge transfer. From this result and the analogous result with the indium system in thiocyanate media, one must conclude that the rational parameter to consider when characterizing electrode reaction rates which are catalyzed by adsorbed species is the surface activity. The fly in the ointment is that the surface-activity data are often not available and some effort must be expended to obtain such data experimentally.

Finally, one should note the study of Yamaoka,[148] who used ac polarography to assess the relative charge-transfer rates of a series of six chromium complexes, all of which undergo totally irreversible electroreduction on mercury. Although the data did not justify a quantitative kinetic analysis, the author was at least able to observe and measure ac wave characteristics with the ions $Cr(H_2O)_6^{+3}$, $Cr(H_2O)_3NCS^{+2}$, $Cr(H_2O)_5N_3^{+2}$ *trans*-$Cr(H_2O)_4(N_3)_2^+$, *trans*-$Cr(H_2O)_4(NCS)_2^+$, and *cis*-$Cr(H_2O)_4(NCS)_2^+$, all of which once upon a time might have been considered as inaccessible to ac polarographic scrutiny because of the irreversibility problem.

C. Characterization of Adsorption Effects

It should be rather obvious from much of the foregoing discussion that separating the consideration of adsorption effects from heterogeneous charge transfer measurements is rather arbitrary because the two processes often interact intimately, as in many of the examples discussed in the previous section. However, the separation of topics is not altogether random, because in the present section we wish to consider investigations in which attention was focused on the adsorption step itself or where adsorption is a dominant factor in determining the ac response (e. g., as in the tensammetric waves). Our consideration of studies where the main role of adsorption is to assist or hinder charge-transfer kinetics may be considered terminated in the previous section.

1. AC Polarography with Adsorbed Macromolecules

One of the most promising of the recently expanding areas of investigation involves the ac polarographic characterization of solutions containing macromolecules. The most dominant observables in such cases are the so-called tensammetric waves which occur at very positive or negative potentials where the adsorbed macromolecule is desorbed from the electrode by virtue of increased affinity of the supporting electrolyte. Alternative mechanisms, such as a transformation in the state of the adsorbed film (change in molecular orientation or charge), might occasionally be operative, but the former adsorption-desorption mechanism is the most common. In the potential region where such double-layer transformations occur, a large differential double-layer capacity exists which is accompanied by a substantial non-faradaic ac wave. Typical fundamental and second harmonic tensammetric ac waves are illustrated in Figure 26. Bauer, Herman, and Elving recently presented a review of adsorption measurements at electrodes[24] which is recommended for those who wish to expand their knowledge in this area. Jehring[149] has published an excellent survey of recent developments in the utilization of tensammetric ac waves; he and his co-workers have contributed much to the expansion of these types of investigations[149-152] by examining the characteristics of tensammetric waves by fundamental and second harmonic ac polarography as well as by square-wave polarography. They have devoted careful attention to the current amplitude-time response at the dropping mercury electrode and stationary electrodes. A particularly novel and potentially useful application of the tensammetric wave pointed out by Jehring et al. is the characterization of approximate average molecular weights of polymers.[149,151,152] The basis for this application is illustrated in Figure 27, which shows the tensammetric response with a mixture of polyethylene glycols characterized by four different average molecular weights. A resolved peak is obtained for each of these average molecular weights, and it is also evident that peak width is a function of molecular weight. The rationale behind the resolution of the tensammetric waves corresponding to the different molecular weights is found in the fact that the molecules of higher molecular weight are the more strongly absorbed, all other factors being equal, so that the direct potential at which desorption ensues must be further removed from the point of zero charge than the more weakly adsorbed species of lower molecular weight. Thus, for a given polymer type (i. e., a given monomer unit and a given conformation) and electrolyte composition, *the position of the tensammetric peak is a measure* of molecular weight. Of course some care is required when trying to implement this concept, because other factors such as polymer concentration can influence the peak potential. However, with careful calibration using polymers of known physical characteristics, this idea might be put to practical use as an inexpensive and sensitive means of monitoring the degree of polymerization of a particular monomer, or the like. With regard to sensitivity, Jehring and Stolle[152] compared the sensitivities for tensammetric wave detection of fundamental harmonic measurements with a dropping mercury electrode, fundamental harmonic measurements at a stationary mercury drop, and second harmonic measurements with a stationary mercury drop. In the order just stated, the relative sensitivities of these techniques were found to be 1 : 25 : 250 for the determination of polyethylene glycol with an average molecular weight of 1000. The most sensitive measurement, that of the second harmonic, was able to detect polymer concentrations of 0.02 mg/liter.

Actually, the greatest activity involving the ac polarographic characterization of macromolecules appears to be taking place in the biopolymer area. Palecek and co-workers[118,153,154] and Berg et al.[120] have examined the ac polarographic response of aqueous solutions containing deoxyribonucleic acid (DNA) using a mercury

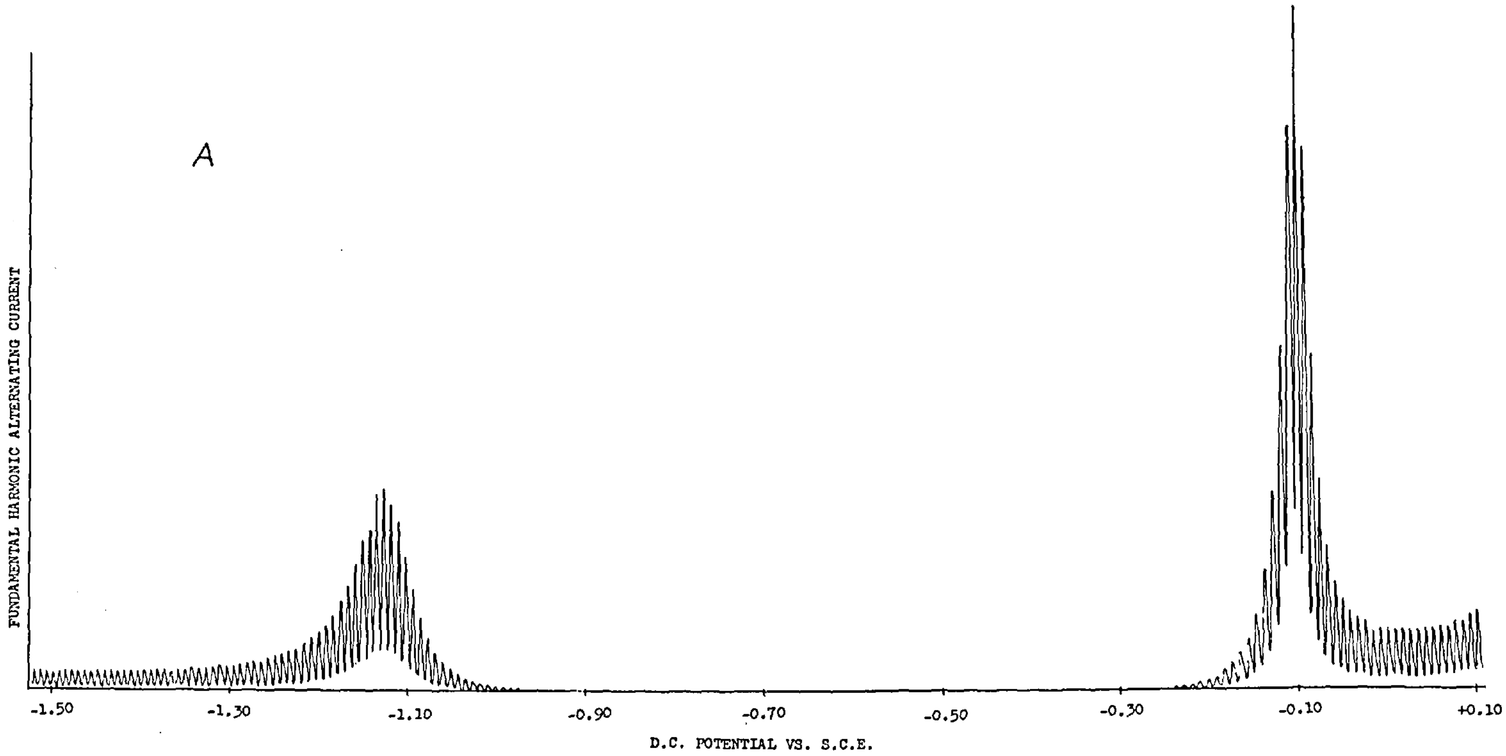


FIGURE 26. Fundamental and second harmonic ac polarograms showing tensammetric waves of cyclohexanol. System: 0.050 *M* cyclohexanol in 0.50 M KNO_3, 25°C. Applied: dc scan rate 100 mV/min, sine wave of 20 mV peak-to-peak amplitude and 38.6 Hz frequency. Measured: A - 38.6-Hz ac component. B - 77.2-Hz ac component.

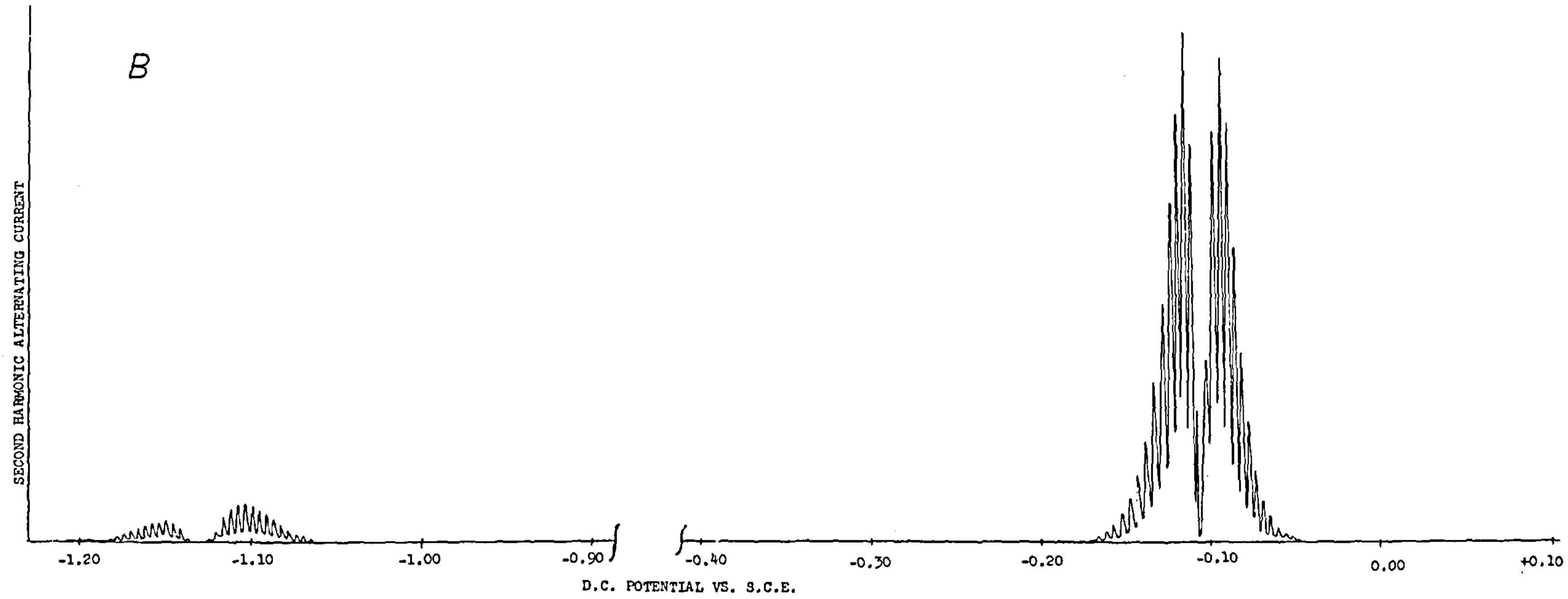


FIGURE 26 (see preceding page for caption).

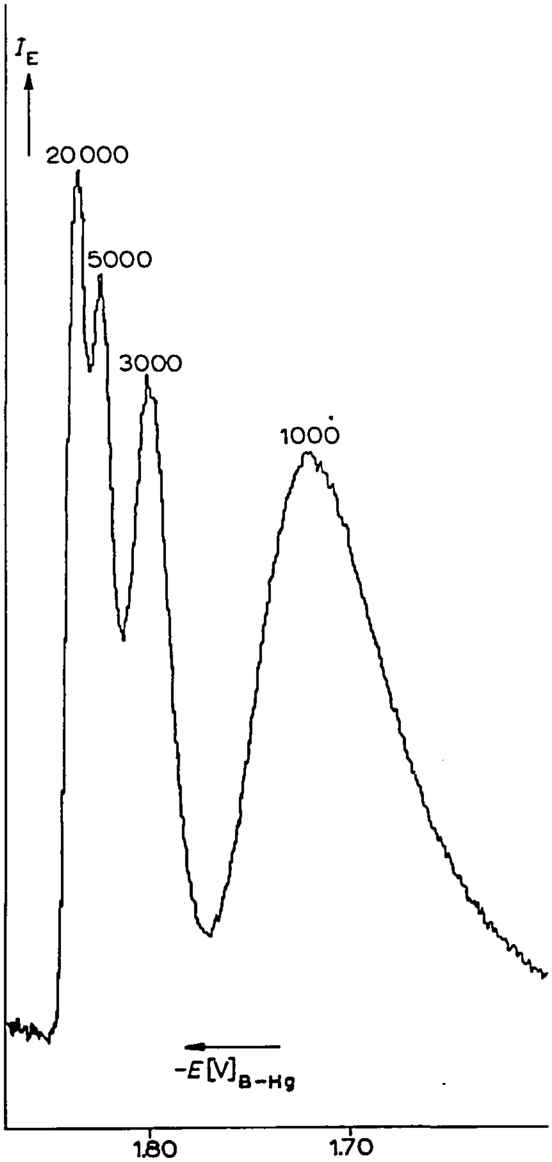


FIGURE 27. Square-wave polarogram showing tensammetric waves from a mixture of polyethylene glycols of different average molecular weight in 1 *M* LiCl. Solution contains four polyethylene glycol samples whose average molecular weights are 1000, 3000, 5000, and 10,000. The concentrations of each sample are 20.0, 7.5, 3.0, and 15.0 (in mg · ℓ^{-1}), respectively. (Reprinted from reference 149 by courtesy of Elsevier Publishing Co.)

electrode. The ac polarographic behaviors of several homopolynucleotides have been examined by Palecek.[119] These workers found that native DNA (double helix) yields a single ac polarographic wave of tensammetric character at -1.2 V vs. S. C. E. in various media, whereas denatured DNA (random coil) gives two waves, one of tensammetric character at the same potential as with native DNA and a "new" wave at -1.4 V vs. S. C. E. There has been some disagreement regarding the origin of the second wave of denatured DNA, but the latest results which establish the existence of a dc response at the potential of the second ac wave[153,154] strongly support the view that this wave contains a faradaic component in nearly neutral solutions. This difference between the behaviors of native and denatured DNA is attributed to the difference in accessibility of reducible components of DNA, such as deoxyadenylic and deoxycytidylic acid. In the double helix these groups are inaccessible to heterogeneous charge transfer, so that only a tensammetric wave is possible, while in the "open" random coil of denatured DNA some of the reducible groups are able to "contact" the electrode and undergo reduction. This difference in ac polarographic response provides a very sensitive means of characterizing preparations of DNA with regard to the relative amounts of native and denatured forms. In Palecek's related studies of homopolynucleotides, it was found that those comprised of reducible bases (i. e., polycytidylic acid and polyadenylic acid) produce a faradaic response and exhibit dc polarographic activity, whereas those containing nonreducible groups (e. g., polyuridylic acid) yield only tensammetric waves. The ac polarograms of various homopolynucleotides appear to be quite characteristic of the monomer unit from which the polymer is constructed, as shown in Figure 28.

Relevant to the foregoing studies of polynucleotides is the work of Vetterl[155] who has examined the ac polarographic behaviors of nucleoside monomers which are found in nucleic acids, such as cytidine, deoxycytidine, adenosine, deoxyadenosine, guanosine, deoxyguanosine, uridine, and thymidine. The ac polarograms of these species are remarkably complex and often characteristic of the molecular species.

A number of interesting studies have been reported for a variety of other types of biopolymers. Stoner and Srinivasan[156] have examined the surface activity of the blood proteins, fibrinogen, thrombin, and Hageman factor on mercury and solid electrodes using a square wave capacitance-measurement technique. Hageman factor was found not to be adsorbed onto mercury or platinum under the conditions employed, while fibrinogen and thrombin were strongly adsorbed. Goldstein and Konigsbuch[157]

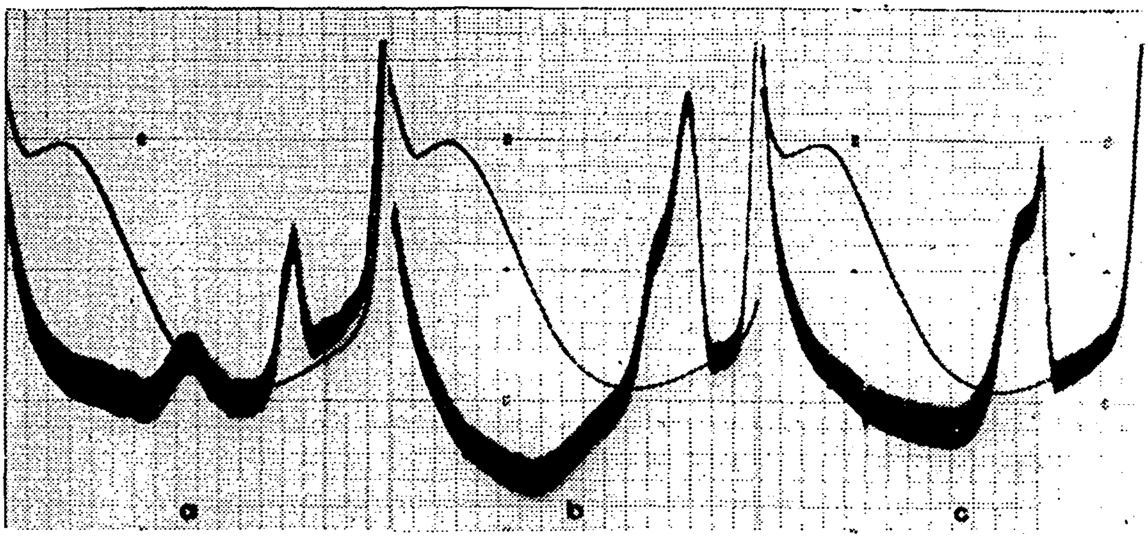


FIGURE 28. Ac polarograms of synthetic 5 x 10^{-4} M polynucleotides in 0.5 M ammonium formate with 0.1 M sodium phosphate: (a) - polycytidylic acid; (b) - polyadenylic acid; (c) - polyuridylic acid. —— curve of background electroyte. All curves start at 0.0 V vs. S.C.E.; 100 mV/scale unit; sensitivity 2.5 μA/scale unit. (Reprinted from reference 119 by courtesy of Elsevier Publishing Co.)

have applied ac polarography to the investigation of proteohormones, particularly preparations containing FSH (follicle-stimulating hormone) and LH (lutenizing hormone) in media containing Co^{2+} and Co^{3+} ions, so that the well-known Brdicka catalytic dc polarographic wave is generated by -S-H- and –S-S- groups within proteins. It was found to be possible to differentiate preparations which were either rich in FSH or LH. Cyanocobalamin (vitamin B_{12}) has been found to give tensammetric ac polarographic waves by Imhoff and Collat.[158] These workers found that cyanocobalamin appears to induce a double-layer relaxation which is not solely diffusion-controlled, but seems to involve some metastable adsorbed state prior to establishing the equilibrium state. The ac polarography of adenosine triphosphate (ATP) showed that surface activity of this molecule depends on its state of complex formation in solution.[159] Sohr and co-workers indicate that ATP reacts with transition-metal ions to form dimeric complexes, and that the formation of these is accompanied by an increase in surface activity.

These ac polarographic studies of macromolecules should be considered to be at the pioneering stage, even though it is possible to find some very scattered reports of this type dating back many years. Although the information already obtained has been shown to be usefully applicable to various forms of polymer research, the work is still primarily at the qualitative and phenomenological stage. More detailed data-collection efforts are possible and quantitative physicochemical characterization of many of the adsorption processes is not out of the question. It is very encouraging that this upsurge of activity in ac measurements with macromolecules is coincident with significant theoretical progress regarding adsorption effects in ac polarography (section IIA). If these two areas of progress can be combined, some rather significant developments might be forthcoming. In the meantime, it should be evident that workers are finding without much difficulty a variety of macromolecular species which exhibit potentially useful and informative ac polarographic responses. One word of warning is appropriate before terminating the discussion of the present subject. The reader who is interested in potential applications of tensammetric waves should first become familiar with the available information in the literature regarding medium effects before proceeding with experimentation, for tensammetric waves behave rather differently from faradaic waves in many respects. For example, we have mentioned that wave position depends on concentration. Electrolyte type and concentration also significantly influence the wave position, and other phenomena which are abnormal in the faradaic sense can occur. A recent paper by Bauer, Campbell, and Shallal[160] presents some recent data which effectively illustrates these remarks.

2. *Adsorption Kinetics*

Experimental efforts to elucidate kinetics of adsorption processes appear to have diminished in number recently relative to the significant activity which was led by Lorenz and co-workers (see Reference 8 for bibliography) in the early and middle sixties. In recent years Armstrong and co-workers have been most active in this area both from a theoretical (see section IIA-21) and from an experimental viewpoint. An important set of results was recently presented by Armstong, Race, and Thirsk,[25] who studied the double layer relaxation of aqueous solutions of cyclohexanol and butyric acid at frequencies up to 150 KHz using impedance measurements. They found no evidence for deviations from pure diffusion control in either case and could conclude only that the relaxation time for the heterogeneous adsorption step must be less than 10^{-6} s. A lower limit of 10^{-10}s., which corresponds to the rotational relaxation time, was assigned. The significant point is that these conclusions are at variance with earlier work of Lorenz. Armstrong et al. attribute the disparity to inadequate correction for the ohmic resistance in the earlier studies. Armstrong, Porter, and Thirsk[29] did succeed in detecting a non-diffusional relaxation in a very thorough study on the adsorption of sulfide ion onto mercury. The relaxation had the attributes of one associated with a chemical reaction coupled to the adsorption step, but data analysis using the theory for a homogeneous coupled chemical reaction did not lead to reasonable results. The authors concluded that the relaxation was attributable to a heterogeneous dissociation of *adsorbed* HS^- ion.

3. *Using Adsorption as an Aid to Mechanistic Elucidation*

Electrochemists who are not primarily interested in the adsorption step per se often view the detection of adsorption effects as a near-disaster because these may complicate or even preclude the quantitative characterization of phenomena of interest. However, if one possesses sufficient electrochemical intuition and a little luck, one often can put adsorption to work in a constructive manner even when it is not the process of concern. A recent example which illustrates this point particularly effectively and involves heavy utilization of ac polarographic data was presented by Britz and Bauer[161] who examined the reduction of m-nitrophenol at mercury in alkaline aqueous media. The overall reduction process (the long-time result) leads to the formation of the corresponding hydroxylamine, but the pathway to this final result is not completely known. Previous workers established that the initial charge transfer step is a one-electron reduction to the m-nitrophenol anion radical, which undergoes subsequent chemical decomposition and further reduction, ultimately taking on three additional electrons. Evidence that the anion radical underwent disproportionation also had been forwarded. Britz and Bauer obtained faradaic admittance and phase angle data over a wide frequency range, beginning at 5 Hz. A low-frequency "anomaly" in the phase-angle data was attributed to disproportionation with the aid of some reasonably convincing arguments. A high frequency "anomaly" suggested that m-nitrophenol was adsorbed at the potentials of the reduction wave, an interpretation which was confirmed by independent means (e. g., electrocapillary measurements). Finally, evidence for further reduction of the initial products was obtained from low-frequency admittance data. Thus, consistent with earlier reports based on other techniques, the authors were faced with a mechanism which involved contributions to the ac response arising from a second-order follow-up chemical reaction, adsorption, and multi-electron transfer, along with the ever-present diffusion process. Even with the present fairly well-developed state of ac polarographic theory, such a complex mechanism would be viewed by most as rather intractable to quantitative kinetic analysis. However, Britz and Bauer were able to progress beyond this point simply by adding varying amounts of an electrochemically inert surfactant, t-butanol, and observing its effects. As increasing amounts of t-butanol were added, the first observation was an enhancement of the faradaic admittance and a suppression of the low-frequency anomaly in the phase-angle data. The very reasonable interpretation advanced was that the surfactant was hindering the disproportionation step. This leads to the conclusion that the chemical step must occur on or very near the electrode surface—i.e., it is likely that the disproportionation is heterogeneous. Upon adding still larger amounts of t-butanol, the authors found that the admittance passed through a maximum at about 2% t-butanol; further additions of surfactant substantially suppressed the ac wave height. This reversal was attributed to the suppression of the heterogeneous charge transfer rate by the surfactant. The surfactant-induced suppression of the disproportionation and heterogeneous charge transfer steps work in opposition as far as ac wave height is concerned, which is the reason for the maximum in the effect of t-butanol. At sufficiently high surfactant concentrations it was found that the phase angle behavior followed expectations for a simple quasi-reversible system—i.e., the surfactant had also displaced adsorbed m-nitrophenol, so that adsorption of the latter was no longer a problem. Consequently, it was possible to calculate values of k_s for the initial charge-transfer step at these high surfactant concentrations. By evaluating k_s at various surfactant concentrations and invoking what amounted to a semi-empirical extrapolation to zero surfactant concentration, the value of k_s in the absence of surfactant was estimated to be about $2\ \mathrm{cm} \cdot \mathrm{s}^{-1}$. Thus, addition of the surfactant not only enables the authors to draw further qualitative conclusions regarding the nature of the disproportionation step, but it also simplified the effective mechanism sufficiently that quantitative kinetic data could be obtained for the initial charge transfer step.

D. Acquisition of Data Relevant to Homogeneous Chemical Reactions

1. Thermodynamic Parameters

One of the oldest applications of conventional dc polarography involved its application to the acquisition of thermodynamic parameters for chemical processes, such as the stoichiometry and equilibrium constant of a redox reaction (from values of n and E^0) and the equilibrium constant of a chemical reaction coupled to the charge-transfer step (from formal cell potentials). The equilibrium constant data are obtainable because with a diffusion-controlled ("reversible") electrode process the dc polarographic half-wave potential, $E^r_{1/2}$, is a good measure of the formal electrode potential for the half-cell reaction giving rise to the polarographic wave. If an electrode process is also diffusion-controlled under ac polarographic conditions, then the fundamental harmonic ac polarographic peak potential, E^r_p, is equal to the reversible dc half-wave potential and can be employed in the same manner. On this basis ac polarography has occasionally been implemented to obtain chemical equilibrium constants and the like. Because the position of a maximum can be estimated more accurately than that of an inflection point, the reversible ac polarographic peak potential should be a more accurate assessment of the formal potential. Nevertheless, until very recently the dc polarographic method has been the favored approach. Some of the reasons for this may be rather mundane; for example, perhaps people find it difficult to "break the habit" of using dc polarography or possibly the lesser availability of ac polarographic instrumentation is a factor. On the other hand, undoubtedly some workers have avoided using ac polarography for the purpose under consideration because the conditions required for strictly diffusion-controlled behavior are more stringent than for dc polarography. Whatever the reasons have been in the past for favoring dc polarography, the recent literature suggests that they are becoming less compelling. In the last two years an unusual output of chemical equilibrium-constant data has resulted from ac polarographic measurements and considerable attention has been devoted to this application of ac polarography. Bond and co-workers have set the pace with nine publications on this topic[162-170] which evaluate the use of conventional and rapid ac polarography for complex metal ion formation-constant measurements and apply these techniques to a number of systems involving metal halide complexes. The authors employed the DeFord-Hume equations for calculating the formation constants. The data obtained are summarized in Table 8. Bond et al. quite effectively implemented the previously-discussed advantages of rapid ac polarography for work in fluoride media in the process of determining the metal-fluoride stability constants.[163-167,169,170] The speed of rapid ac polarography not only circumvented difficulties with fluoride corrosion of glass capillaries, but in one novel application this property permitted the determination of stability constants of sparingly soluble complexes.[170] In the latter case the authors were able to effect the essential measurements in supersaturated solutions before the onset of the slow precipitation process, by virtue of the short measurement time required in rapid ac polarography. In almost all instances where

TABLE 8

Metal Ion Stability-Constant Data Obtained by AC Polarography

System	Stability Constants^a	Ref.
1. Cd^{2+} in fluoride media, ionic strength held at 1.0 M by $NaClO_4$, 30° C	$\beta_1 = 5.8$ (CdF^+) $\beta_2 = 4$ (CdF_2)	163
2. Bi^{3+} in acidic fluoride media, ionic strength held at 2.0 M by $NaClO_4$, 30°C	$\beta_1' = 26$ (BiF^{2+}) $\beta_2' = 2$ (BiF_2^+) $\beta_3' = 500$ (BiF_3)	164
3. Cu^{2+} in fluoride media, ionic strength held at 1.0 *M* by $NaClO_4$, 30°C	$\beta_1 = 4.1$ (CuF^+)	165
4. Zn^{2+} in fluoride media, ionic strength held at 1.0 *M* by $NaClO_4$, 25°C	$\beta_1 = 10$ (ZnF^+)	162,166
5. Sn^{2+} in acidic fluoride media, ionic strength held at 1.0 *M* by $NaClO_4$, 25°C	$\beta_1 = 1.2 x 10^4$ (SnF^+) $\beta_2 = 4.8 x 10^6$ (SnF_2) $\beta_3 = 2.9 x 10^9$ (SnF_3^-)	167
6. Bi^{3+} in acidic chloride media containing 1 *M* $HClO_4$, ionic strength held at 2.0 by $NaClO_4$, 30°C	$\beta_1 = 1.46 x 10^2$ ($BiCl^{2+}$) $\beta_2 = 6.0 x 10^3$ ($BiCl_2^+$) $\beta_3 = 4.0 x 10^5$ ($BiCl_3$) $\beta_4 = 7.9 x 10^6$ ($BiCl_4^-$)	168
7. Sb^{+3} in acidic chloride media, ionic strength held at 5.0 *M* by $HClO_4$, 30°C	$\beta_1 = 2.0 x 10^2$ ($SbCl^{2+}$) $\beta_2 = 1.5 x 10^4$ ($SbCl_2^+$) $\beta_3 = 1.0 x 10^6$ ($SbCl_3$) $\beta_4 = 1.2 x 10^7$ ($SbCl_4^-$)	168
8. Sb^{3+} in acidic fluoride media, ionic strength held at 2.0 *M* by $NaClO_4$, 30°C	$\beta_1' = 10^3$ (SbF^{2+}) $\beta_2' = 5 x 10^5$ (SbF_2^+) $\beta_3' = 2 x 10^8$ (SbF_3) $\beta_4 = 9 x 10^{10}$ (SbF_4^-)	169
9. Pb^{2+} in fluoride media, ionic strength held at 1.0 *M* by $NaClO_4$, 25°C	$\beta_1 = 25$ (PbF_2 $\beta_2 = 3.5 x 10^2$ (PbF_2)	170
10. Pb^{2+} in mixed fluoride-chloride media, ionic strength held at 1.0 *M* by $NaClO_4$, 25°C	$\gamma_{11} = 525$ ($PbClF$)	170

$^a\beta_n$ = equilibrium constant for reaction of the type

$$M^{j+} + nX^- \rightleftharpoons MX_n^{(j-n)}$$

where M^{+j} = metal ion, X^- = halide ion. specific complex formed given in parenthesis beside equilibrium constants.

β_n' = equilibrium constant for reaction of the type

$$M^{j+} + nHX \rightleftharpoons MX_n^{(j-n)} + nH^+$$

other notation same as with βn's

γ_{11} = equilibrium constant for mixed complex formation of the type

$$M^{j+} + X^- + Y^- \rightleftharpoons MXY^{(j-2)}$$

comparison was possible, good agreement was obtained between the data depicted in Table 8 and results of other workers using different procedures. Throughout these papers one finds careful attention paid to the question of whether or not the ac polarographic response is reversible. This ideal response was not obtained in all cases. In some systems the problem of quasi-reversible behavior was alleviated by adding small amounts of reagent which accelerated the heterogeneous charge-transfer step, driving the response into the reversible realm without disturbing appreciably the chemical equilibrium under scrutiny.[164,169] In some cases the quasi-reversible behavior could not be removed by such chemical trickery, yet the shift in the ac polarographic peak potential with added ligand was found to be a valid observable for calculating the equilibrium constant.[165,166] It was found that even though the observed ac peak potential E_p was not equal to $E^r_{1/2}$, the relevant quantity, which is the shift ΔE_p of the peak potential caused by the added ligand, was equal to the corresponding shift $\Delta E^r_{1/2}$ of the reversible dc polarographic half-wave potential, so that a valid measure of the formal potential shift was obtained. As a result, even decidedly quasi-reversible systems such as $Zn^{2+}/Zn(Hg)$ in fluoride media yielded reasonable stability constants using the ac peak potential as the observable.

This essentially empirical finding that valid stability constants might be obtained from measurements of ac peak potentials, even when the reversibility criteria do not hold, has been a prediction implicit in ac polarographic theory for many years. If slow charge transfer is the kinetic perturbation responsible for deviations from reversible behavior, one finds for most conditions that the ac polarographic peak potential is a rather sluggish function of the charge-transfer rate *as long as k_s is sufficiently large that the dc wave is at least nearly reversible.* Consequently, the variations in the relative influence of charge-transfer kinetics which necessarily accompany variation in ligand concentration can have a relatively small effect on the peak potential and this observable will remain primarily responsive to the thermodynamics of the complexation reaction. In fact, in the common case where $\alpha \cong 0.5$ one finds that $E_p = E^r_{1/2}$ despite significant effects of charge-transfer kinetics, provided that the dc process is not well into the quasi-reversible realm. In the latter event neither the observed dc half-wave potential $E_{1/2}$ nor the ac peak potential can be equated to $E^r_{1/2}$.

Of course in situations where a kinetic perturbation of any type causes E_p to deviate from the thermodynamically significant $E^r_{1/2}$, one can always "correct" for the kinetic perturbations on this observable if one has knowledge of the relevant rate constants and an appropriate theoretical expression for the ac wave. In other words, a complete kinetic characterization of a system will always permit the evaluation of $E^r_{1/2}$. Although this is often easier said than done, there are some recent examples where such operations have been accomplished. This was achieved for the cyclooctatetraene system in dimethylformamide containing tetrabutylammonium perchlorate whose kinetic study was discussed earlier (section IVB-1). In this case the first wave is characterized by values of E_p and $E_{1/2}$ that are more *negative* than $E^r_{1/2}$ due to slow charge transfer, while with the second wave these observables are more *positive* than $E^r_{1/2}$ because of the follow-up protonation process. Both effects combine so that the observed separations of the dc half-wave potentials $(E_{1/2,1} - E_{1/2,2})$ and ac peak potentials $(E_{p,1} - E_{p,2})$ for the two waves are much smaller than the thermodynamically-significant separation which is required to calculate the equilibrium constant for the disproportionation step:

$$\mathrm{COT}^{-} \rightleftharpoons \mathrm{COT} + \mathrm{COT}^{-2} \qquad \text{(R13)}$$

However, with the aid of the rate parameters associated with the kinetic perturbations (Table 4), it was possible to correct the observed potential separations and obtain the reversible values. The results are given in Table 9, which provides the observed parameters, the kinetic correction which had to be invoked, and the calculated thermodynamic potential separations for both ac and dc measurements. It is interesting to note that the ac kinetic correction is smaller than for dc polarography, mainly because a much smaller ac correction is needed to account for the effect of the follow-up chemical reaction, and this is the predominant correction in this case. DeLevie and Pospisil[171] also considered the problem of evaluating $E^r_{1/2}$ in situations where deviations from reversibility originate in slow charge transfer. They recommend a procedure which amounts to obtaining the dimensionless kinetic parameters $\lambda/\sqrt{2\omega}$ from the well-known phase-angle cotangent relationship for quasi-reversible processes,[7]

$$\cot \Phi = 1 + (2\omega)^{\frac{1}{2}}/\lambda \qquad (36)$$

where

$$\lambda = \frac{k_s f}{D^{\frac{1}{2}}} (e^{-\alpha j} + e^{\beta j}) \qquad (37)$$

$$j = \frac{nF}{RT} (E_{dc} - E^r_{\frac{1}{2}}) \qquad (38)$$

$$D = D_O^{\beta} D_R^{\alpha} \qquad (39)$$

$$\beta = 1 - \alpha \qquad (40)$$

$$f = f_O^{\beta} f_R^{\alpha} \qquad (41)$$

The f_is are activity coefficients and other notation is the same as employed earlier. The quantity $\lambda/\sqrt{2\omega}$ obtained from Equation 36 is employed to obtain the Koutecky F (χ) function using the fact

$$\chi = \frac{\lambda}{\sqrt{2\omega}} \left(\frac{24}{7}\,\omega t\right)^{\frac{1}{2}} \qquad (42)$$

together with tables of F (χ). Having obtained F(χ) at various potentials along the wave it is then possible to reconstruct the reversible dc polarogram from the observed dc polarographic currents using the relationship

$$i_{rev.} = \frac{i_{meas.}}{F(\chi)} \qquad (43)$$

This technique was applied by deLevie and Pospisil to obtain the reversible half-wave potential for the $Zn^{2+}/Zn(Hg)$ system in 1 *M* $NaClO_4$. Of course, given the quantity $\lambda/\sqrt{2\omega}$, one could almost as readily reconstruct the reversible ac polarogram from the observed quasi-reversible response.

Finally, the work of Kodama, Noda, and Murata[172] should be noted. These investigators evaluated the stability constant of the Tl(I)-diethylene-triaminepentaacetate complex with the ligand in both the basic form and the monoprotonated one. Both ac and dc polarography were employed and excellent agreement between the two methods was realized.

While the reports cited in this section seem to be a reminder that even though ac polarography and related techniques are basically relaxation methods, a term which one normally associates with kinetic applications, there are sound basis and precedent for applying this methodology to thermodynamic measurements. If one recalls some earlier remarks regarding the behavior of the minimum in second harmonic ac polarography (current magnitude polarograms), one tends to conclude that the full power of the ac approach for the purpose under consideration is yet to be implemented.

2. *Kinetic Parameters*

The measurement of rates of homogeneous chemical reactions coupled to the charge-transfer step by ac polarography and related techniques remains a rather dormant area, despite the fact that the theory is well-developed, even to the point of implementing double-layer corrections.[69,70] The problem appears to be primarily one of motivation on the part of workers in the field, as no significant fundamental barriers

TABLE 9

Half-Wave and Peak Potential Separations for Cyclooctatetraene

Temperature °C	Observed dc half-wave potential separation mV	Δ_{dc} mV	$E^r_{\frac{1}{2},1}-E^r_{\frac{1}{2},2}$ mV	Observed ac peak potential separation mV	Δ_{ac} mV	$E^r_{p,1} - E^r_{p,2}$)
25	219	60	279	240	32	270
35	219	90	309	260	52	312

Δ_{dc} = calculated "kinetic correction" required to convert the observed separation of dc polarographic half-wave potentials for first and second reduction steps to the corresponding "reversible" half-wave potential separation, $E^r_{\frac{1}{2},1} - E^r_{\frac{1}{2},2}$

Δ_{ac} = calculated "kinetic correction" to convert the observed ac polarographic peak potential separation for first and second reduction steps into the corresponding "reversible" peak potential separation, $E^r_{p,1} - E^r_{p,2}$.

to progress are identifiable. After all, a very distant cousin of ac polarography, high-level faradaic rectification, has been applied with good success to a wide variety of protolytic reactions which represent one of the most difficult categories because of the double-layer problem (see Reference 70 and references contained therein). Furthermore, the few recently published chemical rate determinations using ac polarography seemed to have been effected without undue difficulty. One of these studies involved a complexation reaction between Cd^{2+} and ethylenediaminetetraacetic acid which precedes the charge-transfer step.[173] A rate constant of 2.3×10^9 l · mole^{-1} s^{-1} was obtained for the process

$$Cd^{2+} + HY^{3-} \rightarrow CdY^{2-} + H^+ \qquad (R14)$$

which was in good agreement with values obtained by alternative methods. A second study yielded the protonation rate of the cyclooctatetraene dianion in dimethylformamide[106] which had no precedent for comparison, but good self-consistency was realized between fundamental and second harmonic assessments of this number. The rate constants at different temperatures are given in Table 4.

Whether or not activity in this area will reach a level which is more consistent with the potential gains to be realized is difficult to predict. However, regardless of what is witnessed in the next few years, the application of ac polarography to the characterization of homogeneous chemical rate processes represents a field in which the promise is great and the tools for exploitation are available.

E. Miscellaneous Applications

1. Systems Exhibiting Dc Polarographic Maxima

Although generally ignored since it was noted some time ago, there seems to be a renewed interest in exploiting the fact that ac polarograms are often perturbed very little by the processes that give rise to a dc polarographic maximum. Ac polarographic theory provides a sound rationale for this observation as well as some useful guidelines regarding the conditions under which the ac wave will or will not be influenced by the convective mass transport attending the maximum. A dc polarographic maximum manifests a spontaneous, abnormal stirring (streaming) of the mercury drop and the adjacent solution whose origin is qualitatively well-understood.[47] The result is an enhancement of the flux of electroactive material at the electrode surface, so that the dc polarographic current exceeds the diffusion-controlled level. Normally, a potential is eventually reached where the abnormal stirring ceases and the current drops to the diffusion-controlled level so that a maximum is observed. However, the relaxation time associated with the stirring phenomenon is too large to directly alter the ac components of the flux which exist in ac polarography. The only mechanism whereby the stirring can normally influence the ac response is by altering the *magnitudes* (not the fluxes) of the dc surface concentration components of the electroactive species (see section IIC). In cases where electrochemical and chemical equilibrium conditions prevail on the dc time scale, these concentration magnitudes are affected relatively little by the enhanced mass transfer associated with the maximum and, consequently, one witnesses little or no effect on the ac wave. One concludes that the process associated with a dc polarographic maximum of either the first or the second kind[47] will influence an ac polarographic response significantly only when the dc process is not solely mass-transfer controlled (reversible) under the prevailing conditions. Fujiwara et al.[174] provided some rather novel data to support the foregoing concept. They utilized the fact that a polarographic response depends on magnetic field strength only when the streaming associated with a polarographic maximum influences the current. Magnetic field effects on the ac wave were observed only when a dc maximum and nonreversible behavior were simultaneously operative. Hawkridge and Bauer[175] demonstrated the fidelity of the above conclusions quite effectively with the $Cu^{2+}/Cu(Hg)$ system in 0.9 *M* $LiNO_3$. Bond and Waugh[168] utilized this property of the ac wave in obtaining the stability constants for the chloride complexes of Bi^{3+} and Sb^{3+} (see Table 8). These data were inaccessible by dc polarography because pronounced maxima distorted the polarogram and precluded direct measurements of the half-wave potentials.

2. Systems Yielding Multiple Ac Polarographic Waves

Bond and Canterford have presented some new data concerning the question of the independence of ac polarographic responses arising from two or more components in the same solution.[176,177] Their primary concern was with analytical applications with multicomponent systems, but the implications of their findings and remarks apply to ac polarographic measurements in any context, which is why the subject is being considered separately from the discussion of analytical applications. The message of these papers should be heeded whenever one encounters a multicomponent system, regardless of whether the additional redox couples are initially present in the solution or are generated by chemical or electrochemical steps in the vicinity of the electrode (e. g., the cyclooctatriene system in mechanism R11). The problem arises because in the early days of ac polarographic investigation it was alleged that if the ac waves arising from two or more components are resolved, the responses would be independent–e. g., the characteristics of a more cathodic wave would be independent of the presence and amount of the species yielding a more anodic wave. This viewpoint was accepted in many circles as a general property of ac polarography. The most frequently encountered manifestation of this outlook is the statement that in aqueous media it is unnecessary to remove dissolved oxygen from the solution prior to running an ac polarogram because the irreversible ac wave of oxygen contributes relatively little to the polarogram and thus does not interfere. Obviously, assumptions such as these cannot be generally valid because although the alternating current associated with a particular wave may not overlap subsequent waves, the chemistry and electrochemistry of the former remains operative–i. e., the dc process associated with the first wave continues throughout the remainder of the potential region being scanned. Consequently, whenever the products or intermediates associated with the first wave encountered in a polarographic scan can influence subsequent electrode processes, an interference will exist regardless of whether or not the associated ac polarographic currents are resolved. Papers which provide experimental evidence in support of the latter point first appeared some time ago, but they are few in number and are widely scattered through the literature. Perhaps because of this some workers continue to invoke the naive assumption that resolved currents mean non-interfering electrode processes. Hopefully, the new attack on this question by Bond and Canterford will adequately highlight the pitfalls in this assumption and will induce workers to carefully "check it out" before assuming that multiple waves are mutually independent. Bond and Canterford[176] find that the electroreduction of oxygen has detectable influences on the ac polarograms of Cd^{2+}, In^{3+}, Pb^{2+}, and Tl^{+} in neutral media, presumably because of the influence of OH^- ion, which is formed in the oxygen reduction. In highly acidic media this interference was suppressed. A rather intriguing interference of the $Sn^{2+}/Sn(Hg)$ wave was found to be associated with the simultaneous occurrence of the Fe^{3+}/Fe^{2+} electrode process.

V. SUMMARY

To the reader who is only casually familiar with electrochemical measurements based on periodic perturbations, perhaps one of the most surprising aspects of this review is its illustration of the level and scope of influence of the methodology considered. Hopefully, it has been made evident that the literature gives witness to notable growth in the three areas of importance to any experimental method:theory, instrumentation, and application. One finds successful application to chemical systems whose types encompass the entire range of solution chemistry, from the molecule of life (DNA) to the simplest elemental ions. Having never bothered to actually keep a quantitative record of the output, even this writer was rather surprised upon first realizing that a yield in the neighborhood of 100 publications per year has characterized this field in the last 3½ years. Even in the present era of the "information explosion" this must be considered a nontrivial level of activity. Because many scientists, even among electrochemists, view ac polarography and related techniques as a special peripheral area, it was considered worthwhile to attempt to convey in this review the point that such an outlook is inconsistent with the level and scope of activity one finds in the literature. Consequently, a subject-oriented review was attempted, rather than one oriented toward specific outstanding papers. The latter would have been the easier choice as a shorter, more conveniently organized review could have been generated. Hopefully, the disadvantages with the approach adopted are offset by the fact that this review makes the reader aware of the role being played by the ac polarographic method in widely diversified areas of scientific endeavor. Even more important, it is hoped that an appreciation for the future potentialities of the method and its possible evolutionary pathways has been generated.

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