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The Faradaic Admittance of Electrochemical Processes. I. Apparatus Suitable for Phase Angle Measurement

BY HENRY H. BAUER AND PHILIP J. ELVING

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An improved apparatus for measuring the effects of a small superposed sinusoidal alternating potential on the behavior of electrochemical systems is described. From measurements of the series resistance, the capacity of the electrical double layer, and the gross alternating potential and current and phase angle, the characteristic properties of the faradaic process including the phase angle can be calculated readily. The theoretical basis for the experimental procedure is critically discussed; the procedure itself is given in detail.

The objective in alternating current polarography has been to measure accurately the faradaic alternating current. The greatest uncertainty connected with such measurements has been in correcting the observed values for the effects of series resistances and of the capacity of the electrical double layer.

The apparatus previously described[1] resulted in enormous improvement compared to earlier apparatus with respect to decreasing the series resistance; corrections, which had been of the order of 100 ohms with previously described apparatus, *e.g.*, ref. 2, were only of the order of 10 ohms as compared to measured values ranging from several hundred ohms at low frequencies down to 20 to 30 ohms at the highest frequencies used with fast systems, *e.g.*, Cd(II) and Tl(I). Corrections for the double layer capacity were made by assuming the validity of a theoretical expression[2] for the phase angle between the faradaic alternating current and the alternating potential.

Previous studies, however, give two different expressions[3] for the phase angle, one of which[4] results in angles of less than 45° and the other[2] in angles exceeding 45°. In such a situation it is manifestly impossible to correct satisfactorily for the double layer capacity by purely mathematical procedures; one needs to know which expression for the phase angle should be used. Consequently, it became imperative to develop a technique which would provide experimental data for some variable in addition to the values for the gross alternating current through the cell; the obvious variable to measure is the phase angle itself.

Experimental Design

The phase angle can be measured by an arrangement similar to that of Randles.[4] A seemingly ideal experimental arrangement is shown in Fig. 1. The direct potential is applied by means of potentiometer A and the direct current measured on galvanometer B. The actual d.c. potential of the dropping mercury electrode (d.m.e.) is measured by means of potentiometer C, using galvanometer D as a null instrument (possibly a vacuum-tube voltmeter (v.t.v.m.) could be used instead of the combination of C and D). The superposed alternating potential is drawn from the oscillator E through a continuously variable control; the alternating potential applied across the cell is monitored by the v.t.v.m. F. The alternating current is measured by the potential drop across the set of resistors G, using the amplifier–v.t.v.m. combination H. The phase angle is measured by impressing the alternating potential across the cell on the Y plates of a cathode ray oscilloscope (c.r.o.) and the alternating potential drop across the parallel combination of a variable resistance J and variable capacitance K on the X plates. When J and K are adjusted until the oscilloscope trace shows a linear relation, the phase angle of the current through the cell equals the phase angle of the current through the combination of J and K, which can be calculated readily.

The d.m.e. is maintained at ground potential for several reasons, *e.g.*, completely satisfactory screening of the electrode verges on the impossible, vacuum tube voltmeters of the sensitivity which F has must be grounded at one terminal, and many oscilloscopes work more satisfactorily with one terminal of at least one pair of plates connected to ground.

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(1) H. H. Bauer and P. J. Elving, *Anal. Chem.*, **30**, 334 (1958).

(2) B. Breyer, H. H. Bauer and S. Hacobian, *Australian J. Chem.*, **8**, 332 (1955).

(3) A. C. Aten, C. Büthker and G. J. Hoijtink, *Trans. Faraday Soc.*, **55**, 324 (1959).

(4) J. E. B. Randles, *Disc. Faraday Soc.*, **1**, 11 (1947).

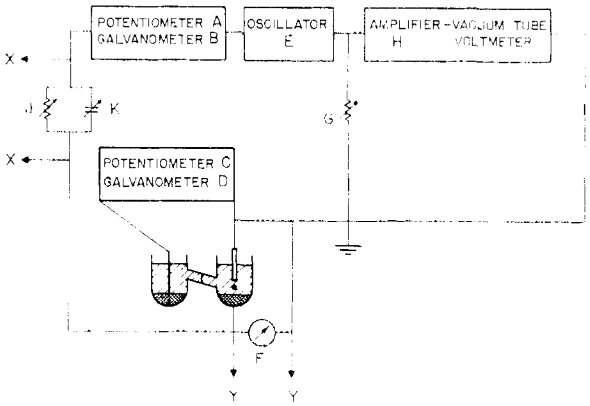

Fig. 1.—Comprehensive arrangement for measurement of parameters of the faradaic process at a dropping mercury electrode.

The three-electrode system used in the cell is desirable because of the large resistances in the circuit, mainly J, which needs to be of the order of thousands of ohms.

The v.t.v.m. F should have a maximum sensitivity of at least 10 mv. r.m.s. full scale.

Oscillator E must be capable of working satisfactorily without one terminal being grounded.

The amplifier–v.t.v.m. combination H has been previously described.[1]

Quite thorough screening and common grounding of the apparatus is essential. The water used to jacket the thermostatted H-cell must be grounded.

Experimental Arrangement Used.—The experimental arrangement presently being used (Fig. 2) has proved to be stable and of satisfactory precision. Oscillator E (Heathkit audio generator Model AG-8) has a continuously variable output control plus a series of output voltage ranges (1, 10, 100 mv., 1, 10 v.). Hum or pickup, which is occasionally produced by this instrument, probably from the switch which sets the output voltage range, invariably can be removed by switching to a lower range; this is not always possible, however, in a particular series of experiments. This oscillator must be grounded at one end. Consequently, the arrangement of G and H of Fig. 1 cannot be used, since G also must be grounded at one end; the measured current, which has to be taken from the c.r.o., is thus less precise than is theoretically obtainable. The oscillator was calibrated against a Hewlett–Packard Model 200AB oscillator.

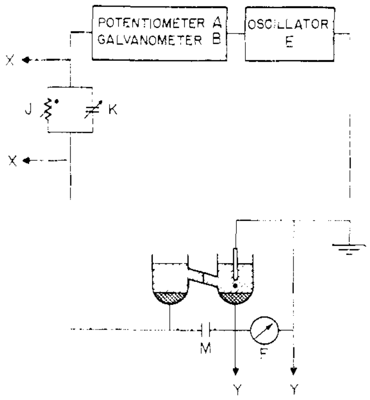

Fig. 2.—Arrangement used in present study for measurement of faradaic process parameters.

The alternating current is measured by observing the X-axis deflection on the c.r.o. (DuMont Model 401) with known resistance J and zero capacity K. This c.r.o. is sufficiently sensitive to permit such measurements to be made with an error of 2 to 5% under the present experimental conditions. The arrangement is such that a d.c. potential is fed to the X plates; the "X-D.C. Bal" and "X-position" controls on the c.r.o. must both be used to keep the trace on the screen. In many cases, the full sensitivity on the X-axis cannot be used since the adjustment available on the "X-D.C. Bal" control is then insufficient to keep the trace on the screen.

V.t.v.m. F is a Hewlett–Packard Model 400D, whose full sensitivity cannot always be used. Readings are taken at maximum age of the drop, when the alternating potential across the cell is at a minimum. As the drop falls, the meter F kicks more or less sharply; to avoid pinning, the 30 mv. r.m.s. full scale range must often be used when working with potentials of one or two mv. r.m.s. at the maximum age of the drop.

Potentiometer and galvanometer AB have been described.[5] M is a 500 μf. electrolytic capacitor. J is a Leeds & Northrup No. 4750 decade resistance box (0.01–11,111.1 ohms), provided with a case ground. K is a General Radio Type 219M decade capacitance box (0.001–1.11 μf.), which is lined with copper sheet to which one terminal is connected for a case ground; this terminal was removed from the case and led out as an insulated lead and the copper lining of the box was grounded.

All leads were made from multistrand conductor shielded wiring. The thermostatted H-type polarographic cell was enclosed in copper mesh, and the water in the constant-temperature bath (25 ± 0.5°) was grounded. All screens and instrument grounds were joined together by 14-gauge copper wire.

Theoretical Basis of the Experiment Procedure

The apparatus described in the present paper permits measurements to be made of the alternating current, of the phase angle of the alternating current and of the alternating potential across the cell; the latter can be represented as shown in Fig. 3.

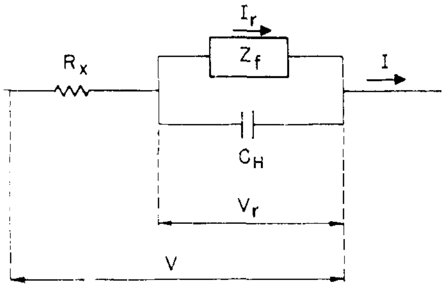

Fig. 3.—Schematic representation of the alternating current parameters for a faradaic process at an electrode.

C_H represents the capacity of the double layer, R_X the series resistance, composed of solution resistance, resistance of the d.m.e. and possible contact resistance, and Z_f the faradaic impedance. It is noteworthy that this representation, which determines the way in which corrections are made for C_H and R_X, contains the assumption that Z_f is an element entirely in parallel with C_H and entirely in series with R_X; this assumption has been made so often that it is easy to dismiss it lightly as axiomatic.

V is the alternating potential across the cell (measured by F of Fig. 2, since the sensitivity of the c.r.o. is not sufficiently great for V to be measured by the Y-axis deflection, as in principle it could be); V_r the alternating potential across the double layer (and hence, if Fig. 3 represents the physical reality, across Z_f); I the total alternating current flowing through the cell; I_r the faradaic alternating current.

To obtain I_r and ϕ, the phase angle between I_r and V_r, from the measured values of I, ϕ' (the

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(5) H. H. Bauer and P. J. Elving, *Anal. Chem.*, **30**, 341 (1958).

phase angle between I and V) and V, calculations are made using the vector diagram shown in Fig. 4 (after Randles[4]).

V and I are drawn at an angle of ϕ'. IR_X, parallel to I, is subtracted from V to give V_r. $V_r\omega C_H$, normal to V_r, is subtracted from I to give I_r. A projection from V_r (at point of intersection with IR_X) normal to the extension of I_r gives the values of I_rR_s and $I_r/\omega C_s$, where R_s and C_s are the resistance and capacitance, respectively, which, in series, are equivalent to Z_f. The significance of R_s and C_s remains an open question at this point.

Manipulation of the symbols of Fig. 4 according to simple trigonometric formulas results in the expressions

$$\frac{I_r}{V_r} = \left[\frac{\left(\frac{I^2}{V}\right) + \omega^2 C_H{}^2\left(1 + \frac{I^2}{V^2}R_X{}^2 - 2\frac{I}{V}R_X\cos\phi'\right) - 2\frac{I}{V}\omega C_H\sin\phi'}{1 + \frac{I^2}{V^2}R_X{}^2 - 2\frac{I}{V}R_X\cos\phi'}\right]^{1/2} \quad (1)$$

$$\cot\phi = \frac{\frac{I}{V}\left(\cos\phi' - \frac{I}{V}R_X\right)}{\frac{I}{V}\sin\phi' - \omega C_H\left(1 + \frac{I^2}{V^2}R_X{}^2 - 2\frac{I}{V}R_X\cos\phi'\right)} \quad (2)$$

$$R_r = \frac{\frac{I}{V}\left(\cos\phi' - \frac{I}{V}R_X\right)}{\frac{I^2}{V^2} + \omega^2 C_H{}^2 \times \left(1 + \frac{I^2}{V^2}R_X{}^2 - 2\frac{I}{V}R_X\cos\phi'\right) - 2\frac{I}{V}\omega C_H\sin\phi'} \quad (3)$$

$$\frac{1}{\omega C_S} = \frac{\frac{I}{V}\sin\phi' - \omega C_H\left(1\ \alpha\ \frac{I^2}{V^2}R_X{}^2 = 2\frac{I}{V}R_X\cos\phi'\right)}{\frac{I^2}{V^2} + \omega^2 C_H{}^2\left(1 + \frac{I^2}{V^2}R_X{}^2 - 2\frac{I}{V}R_X\cos\phi'\right) - 2\frac{I}{V}\omega C_H\sin\phi'} \quad (4)$$

In order to use equations 1 to 4, it is necessary to know C_H and R_X in addition to the directly measured variables I, V, ϕ' and ω.

R_X can be obtained by measuring I, V and ϕ' at a potential where no faradaic process occurs, for the same solution as the one on which measurements of the faradaic impedance were made. Under these conditions, the cell is representable as a series combination of R_X and C_H' (different from the value of C_H in Figs. 3 and 4, since the polarizing potential is different). For such a series network, these equations hold

$$\cot\phi'' = \omega C_H' R_X \quad (5)$$

$$V/I = [R_X{}^2 + 1/(\omega C_H')^2]^{1/2} \quad (6)$$

Equations 5 and 6, which contain the two unknowns C_H' and R_X, can be solved simultaneously to give the value of R_X.

C_H is obtained by making measurements, at the same polarizing potential as that used to measure the faradaic impedance, in a solution containing only the background electrolyte. Equations 5 and 6 are used in conjunction with these data to give the value of C_H needed in equations 1 and 4 (if the electrode area differs from that previously used, C_H must be corrected for this change assuming direct proportionality). The value of R_X thus obtained for the background solution is not used, since the contact and solution resistances may be different from those in the solution which also contains the electroactive species.

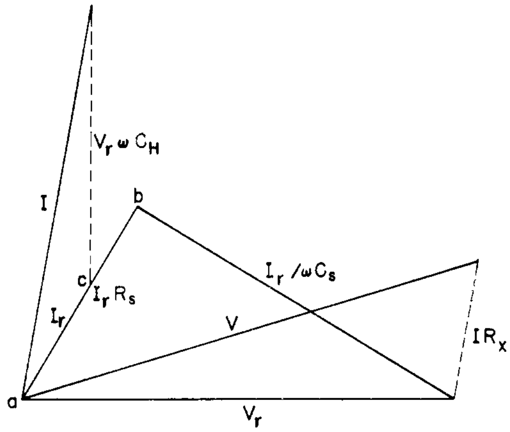

Fig. 4.—Vector relationship for the alternating current parameters for a faradaic process (after Randles[4]): I_r = *ac*; I_rR_s = *ab*.

Experimental Procedure

(1) **Selection of Polarizing Potential.**—The polarizing potential at which the measurements are to be made is determined as follows:

For testing the theoretical equations concerning the faradaic admittance discussed[1,2,4] previously, one proceeds on the basis that these equations should be most nearly valid at the potential at which Z_f is a minimum. At a fixed output from oscillator E (Fig. 2), the polarizing potential is varied until the observation of a minimum on meter F indicates that the faradaic admittance of the solution is at a maximum. It is best to use a low frequency, *e.g.*, 50 c.p.s., for this purpose, so that the impedance of the cell is determined almost entirely by R_X and Z_f, and not by C_H; at high frequencies, C_H acts as a very low impedance shunt to Z_f.

The polarizing potential to be used must be located in this way for each value of the resistance J which will be used in the measurements; since J is large, the polarizing potential at the dropping electrode is appreciably different from that shown on the potentiometer A due to the IR drop across J. The capacitance K should be, for the sake of simplicity, at zero during this operation.

(2) **C.r.o. Sensitivity.**—The sensitivity of the oscilloscope is set by means of the built-in square wave calibrating signal at 100 mv. peak to peak, equivalent to 35.4 m.v. r.m.s. for a sinusoidal signal.

(3) **Measurement Procedure.**—Measurements are made over as wide a frequency range as possible. At each frequency the following measurements are made at the polarizing potentials determined as described at the maximum age of the drop:

(a) The applied alternating potential is adjusted to the desired value as read on meter F. The alternating potential should not exceed 7 mv. (for a one-electron process), 5 mv. (2-electron process) or 3 mv. (3-electron process).[1]

(a) The c.r.o X-axis deflection is noted for a particular value of J at zero K.

(c) J and K are adjusted to give a straight line on c.r.o. screen.

(d) The drop-time is measured.

(4) **Calculations.**—I is calculated from the X-axis deflection (the IR drop across J) using the appropriate value of the resistance of J and the X-axis sensitivity.

ϕ' is calculated from the equation for the parallel combination of resistance J and capacitance K through the equation

$$\tan \phi' = \omega KJ$$

(5) **Determination of R_X.**—The series of operations 2 to 4 is carried out at a polarizing potential where no faradaic process occurs.

(6) **Determination of C_H.**—The series of operations 2 to 4 is carried out at the potential of the d.m.e. used under (1) above but using a solution containing no electroactive substance.

(7) **Determination of m.**—The rate of flow of mercury (in mg./sec.) is determined.

(8) **Faradaic Process Parameters.**—The characteristic properties of the faradaic process, *i.e.*, I_r/V_r, ϕ, R_s and C_s, are calculated by means of equations 1 to 4.

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ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

The Faradaic Admittance of Electrochemical Processes. II. Experimental Test of the Theoretical Equations

BY HENRY H. BAUER, DAVID L. SMITH AND PHILIP J. ELVING

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This study is an evaluation of the two equations obtained to describe the behavior of a simple oxidation-reduction reaction under the influence of a small superposed alternating potential. The cadmium system, which is the most thoroughly studied system, was investigated under a variety of conditions. While either equation may be applicable to results for a particular system involving fixed concentration of depolarizer and background medium over a narrow frequency range, neither equation is of general applicability, *e.g.*, neither describes satisfactorily the observed variation of the phase angle and hence of the heterogeneous rate constant with frequency and depolarizer concentration. The difficulties would seem to be associated with the use of invalid postulates in setting up the theories which led to the equations. It is suggested that a more rigorous mathematical treatment of the problem would involve consideration of the rectifying properties of the system.

It has been mentioned[1] that the equation for the phase angle, ϕ, between the faradaic alternating current and the alternating potential in a simple oxidation-reduction reaction has been given in two forms

$$\cot \phi = 1 + \frac{1}{k}\sqrt{\frac{\omega D}{2}} \qquad (1)$$

$$\cot \phi = 1 - \frac{1}{k}\sqrt{\frac{\omega D}{2}} \qquad (2)$$

where ω is the angular frequency, k the heterogeneous rate constant and D the geometric mean of the diffusion coefficients of the oxidized and reduced species.

The difference between the two equations is that equation 1 predicts a phase angle which is less than 45° (cotangent greater than 1), whereas equation 2 predicts one greater than 45° (cotangent less than 1). Both equations predict a linear relation between cot ϕ and $\omega^{1/2}$, independent of the depolarizer concentration.

Reported experimental results have on occasion appeared to support equation 1[2-4] and at other times equation 2.[5-7] The experimental conditions in these conflicting studies were not, however, identical. In some cases, measurements were made under equilibrium or near-equilibrium conditions, involving approximately equal amounts[8] of the oxidized and reduced species, no externally applied direct potential and no measurable direct current flow. In other experiments, polarographic conditions were used in which no true equilibrium state existed, equality of concentrations of the electroactive species being obtained in the interfacial layer by application of the requisite polarizing potential and a net direct current flowed.

The purpose of the present study was primarily to determine the phase angle under a variety of conditions, in order to ascertain the physical significance of equations 1 and 2.

Results and Discussion

Reproducibility of Data.—The present data were obtained by duplicate experiments, using different capillaries which produced drops of different surface area, in order to test the over-all reproducibility of the present work (Table I). The agreement of the data, in spite of appreciable dif-

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[1] H. H. Bauer and P. J. Elving, THIS JOURNAL, **82**, 2091 (1960).

[2] J. E. B. Randles, *Dis. Faraday Soc.*, 1, 11 (1947).

[3] J. E. B. Randles and K. W. Somerton, *Trans. Faraday Soc.*, **48**, 937, 951 (1952).

[4] K. Rosenthal and B. Ershler, *Zhur. Kiz. Khim.*, **22**, 1344 (1948).

[5] G. S. Buchanan and R. L. Werner, *Australian J. Chem.*, **7**, 239 (1954).

[6] B. Breyer, H. H. Bauer and S. Hacobian, *ibid.*, **8**, 322 (1955).

[7] H. H. Bauer and P. J. Elving, *Anal. Chem.*, **30**, 334 (1958).

[8] "Equal amounts" have been construed in different ways by various authors, *e.g.*, as meaning (a) equal solution concentrations, (b) equal thermodynamic activities and (c) equal fluxes (mass transfers) at the electrode.