(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.

Acknowledgment.—The authors wish to thank the U. S. Atomic Energy Commission which helped support the work described.

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

RECEIVED OCTOBER 16, 1959

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 $\cot \phi$ 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.

TABLE I

REPRODUCIBILITY OF THE DATA OVER A FREQUENCY RANGE

Freq. c.p.s.	Electrode A[a] cot ϕ	Electrode A[a] k,[c] cm. sec.$^{-1}$	Electrode B[b] cot ϕ	Electrode B[b] k,[c] cm. sec.$^{-1}$
45.5	1.11	0.35	1.12	0.33
90	1.04	1.4	1.085	0.66
176	1.08	0.98	1.06	1.3
271	1.045	2.2	1.01	9.7
358	0.997	37	1.015	7.5
441	1.05	2.5	1.01	12
620	0.988	2.5	0.877	1.2
880	.903	1.8	.863	1.3
1320	.808	1.1	.703	0.72
1800	.638	0.69	.613	.65
2280	.515	.58	.555	.63
2730	.436	.55	.398	.51
3140	.283	.46	.316	.48
3590	.210	.45	.206	.44
4450	.155	.47	.065	.42
5300	.050	.45	−0.150	.37

[a] $C_H = 0.74\ \mu$f.; $R_X = 46.2$ ohms. [b] $C_H = 1.02\ \mu$f.; $R_X = 37.3$ ohms. [c] Calculated from $\cot \phi = 1 \pm \frac{1}{k}\sqrt{\frac{\omega D}{2}}$, according to whether cot ϕ was found to be greater or less than 1.

ferences in C_H and R_X, is good, especially in the range above 1,800 c.p.s.

Frequency Dependence of the Phase Angle ϕ.—Neither equation 1 nor equation 2 satisfactorily describes the observed variation of cot ϕ with frequency; specifically:

(a) Cot ϕ is less than 1 in molar nitrate and chloride solutions but greater than 1 in molar sulfate solution.

(b) Cot ϕ is not in general a linear function of the square root of the angular frequency; often, the relation is approximately linear at frequencies up to a few hundred cycles and again at frequencies above a few thousand cycles but is curvilinear at intermediate frequencies (Fig. 1).

(c) The observed relation between cot ϕ and ω changes with total concentration of depolarizer (Fig. 2) and also with variation in the ratio of the bulk concentrations of oxidized and reduced species (Fig. 3).

Significance of the Calculated Rate Constant.—The observed variation of cot ϕ with ω indicates that values of k calculated from equations 1 or 2 cannot be good measures of the heterogeneous rate constant, since k thus calculated often changes with frequency, see Table I.

Even if only those results are used for which over limited frequency ranges, cot ϕ is a linear function of $\omega^{1/2}$, the calculated k cannot have a meaningful relation to the heterogeneous rate constant because of the observations:

(a) In solutions containing mixtures of sulfate and chloride, cot ϕ is a linear function of $\omega^{1/2}$ up to frequencies of one or two thousand cycles; however, equation 1 holds in sulfate solution and equation 2 in chloride solution; moreover, as sulfate is progressively replaced by chloride, the apparent k increases, becoming infinite in solutions, which are between 0.2 and 0.5 M chloride, and decreasing again to finite values at higher chloride concentrations (Fig. 4).

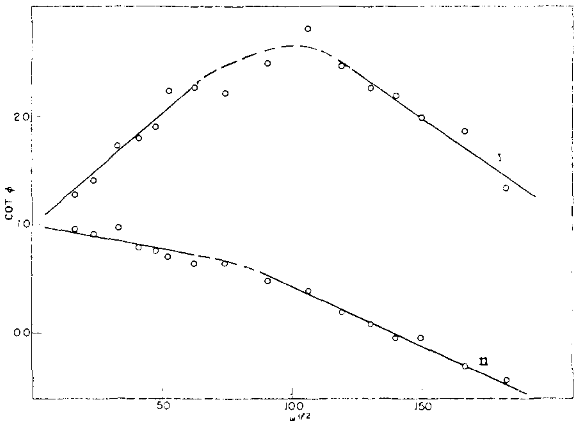

Fig. 1.—Non-linearity of cot ϕ vs. $\omega^{1/2}$ relation: I, 1 mM Cd(II) in 1 M Na_2SO_4 (acidified); II, 1 mM Cd(II) in 1 M KNO_3.

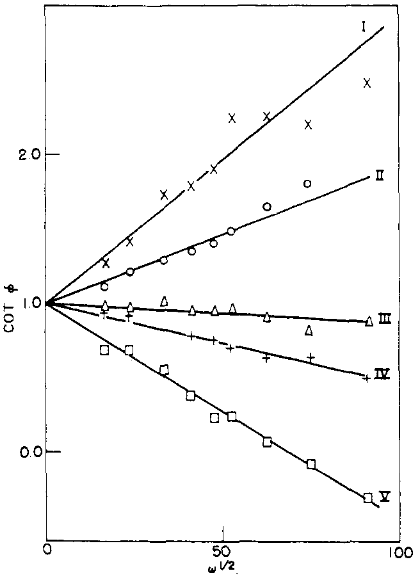

Fig. 2.—Change of apparent k with concentration of cadmium(II): I, II, theoretical lines for $\cot \phi = 1 + 1/k\sqrt{\omega D/2}$ with k = 0.1 and 0.21, respectively; III, IV, V, theoretical lines for $\cot \phi = 1 + 1/k\sqrt{\omega D/2}$ with k = 1.8, 0.47 and 0.17, respectively: ×, 1 mM Cd(II) in 1 M Na_2SO_4; ○, 0.2 mM Cd(II) in 1 M Na_2SO_4; △, 0.6 mM Cd(II) in 1 M KNO_3; +, 1.08 mM Cd(II) in 1 M KNO_3; □, 2.5 mM Cd(II) in 1 M KNO_3.

(b) In sulfate and in nitrate solutions, the apparent k varies with concentration of cadmium(II) (Fig. 2).

(c) With systems containing both cadmium amalgam and cadmium ion, the apparent k often passes through infinity, since at low frequencies cot ϕ exceeds 1 while at higher frequencies it is less than 1, see Fig. 3.

Comparison with Previously Described Technique.—In earlier work[7] where the phase angle was not measured, but where corrections were made for phase differences by assuming the validity of equation 2, a value of k = 0.165 cm. sec.$^{-1}$ was reported for the reduction of 5.55×10^{-4} M Cd(II) in 0.5 M HCl solution. In order to

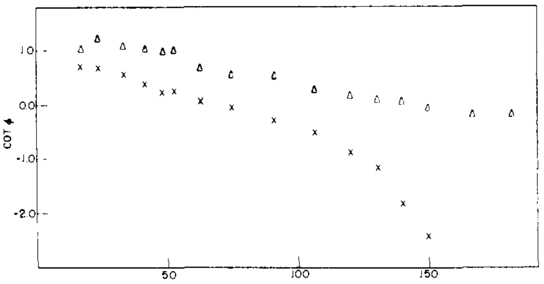

Fig. 3.—Effect of changes of ratio of bulk concentrations of oxidized and reduced forms: ×, 2.5 mM Cd(II) in 1 M KNO_3; Δ, 1 mM Cd(II) at 1.5 mM Cd(II) amalgam electrode in M KNO_3.

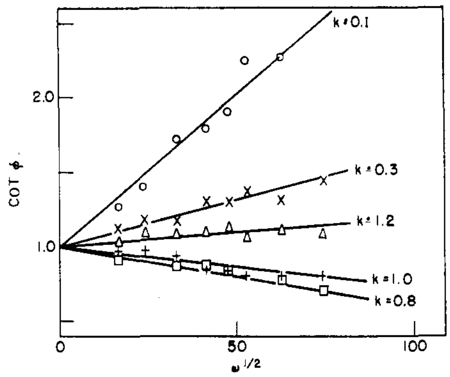

Fig. 4.—Base electrolyte effect on apparent k values at lower frequencies (up to 100 c.p.s.) for 1 mM Cd(II) at mercury electrode: O, 1 M $SO_4^=$; ×, 0.95 M $SO_4^=$ + 0.05 M Cl^-; Δ, 0.8 M $SO_4^=$ + 0.2 M Cl^-; +, 0.5 M $SO_4^=$ + 0.5 M Cl^-; □, 1 M Cl^-. The pH values of these solutions were all between 0 and 1.

investigate the efficacy of the earlier method, the same system was restudied by the present technique. Unfortunately, the lower precision of current measurement available with the present apparatus, as opposed to the amplifier–v.t.v.m. arrangement used earlier, prevented meaningful measurements being carried out at frequencies above *ca.* 5300 c.p.s., whereas the earlier data had been obtained up to 14,000 c.p.s.

Previously, the value of the diffusion coefficient was taken as 0.7×10^{-5} cm.^{2} sec.$^{-1}$, instead of using a geometric mean of the values for oxidized and reduced species which would be 1.11×10^{-5} cm.^{2} sec.$^{-1}$. With the latter value, the earlier reported k would be 0.21 cm. sec.$^{-1}$.

It was found in the present study that the cot ϕ *vs.* $\omega^{1/2}$ relation is non-linear for this system (Table I) and calculated k values decrease with increasing frequency. It is possible that at frequencies close to 14,000 c.p.s., the apparent k would be comparable to or less than 0.21 cm. sec.$^{-1}$ Clearly, the previous method which involved curve-fitting could give only an average k value over the frequency range used.

In the previous work, special capillaries were used with drop times of 10 to 12 sec., including a quiescent period of 4 to 5 sec. If any surface contamination were occurring, it would have been greater than in the present work where t was between 3 and 4.5 sec., which would be in accord with the present finding of somewhat higher k values.

Correlation of the Present Results with Other Work.—At first sight the present results appear to be in contradiction to previous work in which values for the heterogeneous rate constant were reported on the basis of studies where equation 1 had been applied. A detailed comparison, however, shows that there is no essential contradiction:

(a) Many investigations[2,3] have been reported, where equation 1 apparently was found to be valid. However, the reported frequency range was more restricted than in the present work; it did not exceed 400 c.p.s. It is interesting that in all of the experiments in the present study extending over a wide frequency range, the variation of cot ϕ with ω can be represented diagrammatically as in Fig. 5. The results cited[2,3] refer to experiments where line A (Fig. 5) extends up to frequencies of a few hundred cycles; this was also found in the present studies on sulfate and nitrate solutions, when both cadmium amalgam and cadmium ion were present in the bulk phases.

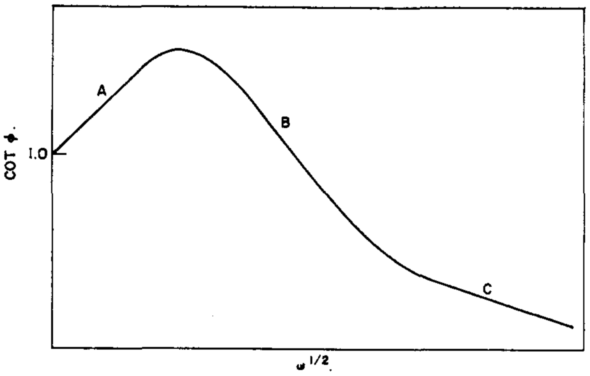

Fig. 5.—Schematic representation of type of results obtained: line segments A and C seem to pass through the origin of cot ϕ = 1. Sometimes only one or two of these three segments are seen in the frequency range studied.

(b) Instances[3,9–11] have been observed both where equation 2 rather than equation 1 appeared to hold and where cot ϕ exceeded 1 in one range of frequencies but was less than 1 in another frequency range. These observations were regarded as anomalous and were, at times, attributed to adsorption of the electroactive species. It is not considered likely, however, that such adsorption could occur in the case of the Cd(II)–Cd(Hg) system.

(c) Experiments[12,13] with cadmium in sulfate solution have been reported where equation 1 was apparently valid; this also has been observed in the present work for frequencies up to one or two thousand cycles. Nevertheless, the apparent k has been found in the present study to change with changing cadmium concentration. Within the

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(9) H. A. Laitinen and J. E. B. Randles, *Trans. Faraday Soc.*, **51**, 54 (1955).

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(11) H. A. Laitinen and H. C. Gaur, *ibid.*, **104**, 730 (1957).

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(13) H. Gerischer, *Z. Elektrochem.*, **57**, 604 (1953).

TABLE II

VALUES REPORTED FOR THE HETEROGENEOUS RATE CONSTANT FOR THE REDUCTION OF Cd(II)[a]

Result no.	Support. electrol. (M)	Cadmium concn., mM		Temp., °C.	k, cm. sec.$^{-1}$	Technique	Ref.
		(in Hg)	(in soln.)				
1	Na_2SO_4, 0.5	400	0.2–4.0	NR[a]	0.042	Hanging drop; a.c. bridge	13
2	Na_2SO_4, 0.5	NR	NR	20	.026	Hanging drop; voltage-step	15
3	NR	NR	NR	0	.0038	Hanging drop after 2 hr.; a.c. bridge	12
4	NR	NR	NR	0	.037	Hanging drop after 20 minutes; a.c. bridge	12
5	NR	NR	NR	0	∼ .2	Dropping electrode; a.c. bridge	12
6	Na_2SO_4, 0.5	0	0.5	25	.25[b]	Dropping electrode; a.c. polarography	[e]
7	K_2SO_4, 0.5	NR	NR	22	∼ .08	Radiofrequency	16
8	Na_2SO_4, 1	400	0.1-1	25	.045	Hanging drop; current-step	14
9	Na_2SO_4, 1	0	0.2	25	∼ .3[b]	Dropping electrode; a.c. polarography	[e]
10	Na_2SO_4, 1	0	1.0	25	∼ .1[b]	Dropping electrode; a.c. polarography	[e]
11	KNO_3, 1; pH 2	NR	NR	22	6.3	Radiofrequency	16
12	KNO_3, 1	∼1	∼1	20	∼0.6[c]	Dropping electrode; modified bridge	3
13	KNO_3, 1	1.22	0	25	∼1.0[d]	Dropping electrode; a.c. polarography	[e]
		1.5	1		∼1.0[d]		
		0	1.08		∼0.4[d]		
14	KCl, 1; pH 2	NR	NR	22	2.9	Radiofrequency	16
15	KCl, 0.5	0	0.5	25	∼1.5	Dropping electrode; a.c. polarography	[e]
16	HCl, 0.5	0	0.56	25	0.17	Dropping electrode; a.c. polarography	7
17	HCl, 0.5	0	1.08	25	∼ .5	Dropping electrode; a.c. polarography	[e]
18	HCl, 1	0	1	25	∼ .6		

[a] Data not reported for items marked NR. [b] Calculated from data of frequencies up to 1000 c.p.s.; at higher frequencies, the results deviate from theory. [c] In another paper,[2] the authors mention a tendency to deviate from theory at higher frequencies. [d] In result 12, $\cot \phi = 1 + \frac{1}{k}\sqrt{\frac{\omega D}{2}}$ (frequencies up to a few hundred cycles); in result 13, $\cot \phi = \frac{1}{k}\sqrt{\frac{\omega D}{2}}$ (frequencies above a few hundred or a thousand cycles). [e] Results obtained in present study. [f] The experimental technique did not involve measurement of the phase angle.

latter limitation, the present results are in accord with those of Delahay[12] who reported a value of k ∼0.2 cm. sec.$^{-1}$. The present k values (data up to 1000 c.p.s.) are ∼0.1 cm. sec.$^{-1}$ for 1 mM Cd(II) in 1 M Na_2SO_4 (acidified) and ∼0.3 cm. sec.$^{-1}$ for 0.2 mM Cd(II).

Changes in the apparent k with changing concentration have been observed in the Ti(IV)–Ti(III) system.[12]

(d) The non-linearity of the relation between cot ϕ and $\omega^{1/2}$ has been observed previously by Randles[2] in the case of cadmium and thallium.

(e) Apparent k values calculated from equation 1 differed by a factor of 10^3 from k values calculated from d.c. polarization curves.[11]

(f) A possible objection to the validity of the present experimental results is that the measurements might not have been made at the correct polarizing potential. However, experiments performed 15 and 40 mv. on both sides of the potential E_S where the faradaic admittance is a maximum gave results differing only in degree, and not in kind, from those obtained at E_S (Fig. 6).

(g) Preliminary values[16] of k and α obtained by a new technique, in which the faradaic rectification is measured by a radio-frequency method, show that the behavior of cadmium in sulfate solution (k ∼0.08) is quite different from its behavior in nitrate (k ∼6.3) and chloride (k ∼2.9) solutions.

(h) Reported k values for cadmium (Table II) show no agreement. Results 1 to 4 and 8 are open to question because of the use of a hanging drop.[12] Results 6, 9, 10, 13, 15, 17 and 18 are a few of the values found in the present study and are quoted here to show that results in the present work are not in disagreement with other work listed; it has been emphasized throughout, however, that these values are not necessarily meaningful measures of the heterogeneous rate constant. Result 16 was previously obtained by the present authors using a different experimental arrangement. Result 12 was obtained using experiments over a narrow frequency range and assuming the validity of equation 1. The frequency range used to obtain result 5 was not reported.

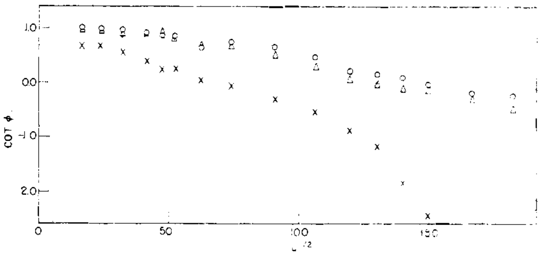

Fig. 6.—Effect of polarizing potential on cot ϕ *vs.* $\omega^{1/2}$ relation; 2.5 mM Cd(II) in 1 M KNO_3: ×, measurements at E_S; O, at 40 mv. less negative than E_S: △, at 40 mv. more negative than E_S.

Thus, there is no real agreement between the rate constant values given in the literature.

Summary.—It is evident that equations 1 and 2 are often applicable to results obtained in a particular system (fixed concentration of depolarizer and a specified background medium) over a limited frequency range. However, the equations are not of general applicability, and attempts to calculate heterogeneous rate constant values from them produce misleading results, *e.g.*, the apparent k

(14) T. Berzins and P. Delahay, THIS JOURNAL, **77**, 6448 (1955).

(15) W. Vielstich and P. Delahay, *ibid.*, **79**, 1874 (1957).

(16) G. C. Barker, *Anal. Chim. Acta*, **18**, 118 (1958).

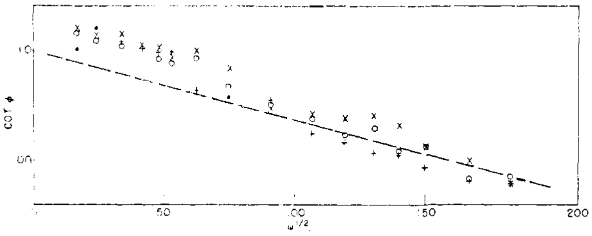

Fig. 7.—Cot ϕ *vs.* $\omega^{1/2}$ for equilibrium and near-equilibrium systems: ×, 1.5 m*M* Cd(II) in 1 *M* KNO_3 at 0.64 m*M* cadmium amalgam electrode; O, 0.64 m*M* cadmium amalgam electrode; +, 1.0 m*M* Cd(II) in 1 *M* KNO_3 at 1.5 m*M* cadmium amalgam electrode; ———, theoretical line for $k = 0.4$ cm. sec.$^{-1}$ if $\cot \phi = 1 - 1/k\sqrt{\omega D/2}$. Below 1000 c.p.s., the points are all considered to be quite significantly away from the theoretical line.

values change with frequency and with depolarizer concentration, and can be made infinite by using background electrolytes containing mixtures of sulfate and chloride or of sulfate and nitrate.

Implications of the Results

There would appear to be three ways of rationalizing the present findings:

(a) The experimental arrangement does not adequately simulate the equilibrium conditions, for which the theoretical treatments have been made.

(b) Oversimplifications have been made in the theoretical treatments.

(c) Invalid postulates have been used in setting up the theoretical treatments.

The first point can to a certain extent be rebutted. It is generally agreed that for rate constants appreciably greater than 2×10^{-2} cm. sec.$^{-1}$, the interfacial concentrations of the electroactive species are the same as they are under true equilibrium conditions. Moreover, the results obtained do not follow the equations no matter what polarizing potential is used (Fig. 6). Above all, systems containing equal and nearly equal concentrations of the oxidized and reduced forms in the bulk phases still do not satisfy the equations (Fig. 7).

On the second point, the present authors have been unable to find oversimplifications or incorrect mathematical procedures, which would explain the present situation.

It is strongly indicated, therefore, that the postulates used in setting up the theories are somehow at fault. It is interesting to recall that the phase angle ϕ between the alternating current and the alternating potential is related to the phase angle ϕ between the periodic concentration changes and the alternating potential by the relation[2]

$$\phi = \theta + \pi/4 \tag{3}$$

Thus, the difference between equations 1 and 2, whether cot ϕ is greater or less than 1, is the difference between saying that the concentration changes lag behind or lead the alternating potential.

The results can then be restated by saying that whether and by how much the concentration changes produced by the alternating potential lag or lead the potential depends on the frequency, on the bulk concentrations of the two forms of the depolarizer and on the nature of the supporting electrolyte.

It is evident that more explicit consideration should be given in the theories to the rectifying properties of electrodes. Mathematical treatments[16,17] of the redoxokinetic effect (or faradaic rectification) show that even for an equilibrium system, where $C_0 = C_R$, $D_0 = D_R = D$, and a very small alternating potential V is applied, the electrode behaves as a non-linear element if $\alpha \neq 0.5$; part of the energy supplied by the alternating potential appears as a direct potential, ψ, across the interface, given by

$$\psi = -\left(\alpha - \frac{1}{2}\right)\frac{nFV^2}{2RT}\frac{1}{k}\sqrt{\frac{\omega D}{2}}\,\frac{1 + \frac{1}{k}\sqrt{\frac{\omega D}{2}}}{2 + \frac{2}{k}\sqrt{\frac{\omega D}{2}} + \frac{\omega D}{2k^2}} \tag{4}$$

Perhaps the question, whether the concentration changes lag or lead the potential, depends on the nature of the rectifying action of the particular system, more explicitly on whether α is greater or less than 0.5. Further experimental and theoretical investigation is necessary before this suggestion can be elaborated.

Experimental

Cadmium and background electrolyte solutions were prepared from analytical reagent grade chemicals. Cadmium amalgam was prepared by shaking fresh shavings of cadmium metal with mercury in a nitrogen atmosphere.

The concentration of the cadmium amalgams was measured polarographically, using the simple Ilkovic equation and a value[18] for the diffusion coefficient of cadmium in the amalgam of 1.61×10^{-5} cm.^{2} sec.$^{-1}$. The amalgam concentration was measured just prior to each experiment, since the amalgams became more dilute over a period of time due to aerial oxidation.

Short capillaries of relatively wide bore were used; at a mercury column height of the order of 30 cm., the capillary characteristics were *t* between 3 and 4.5 sec. and *m* between 2 and 3 mg./sec. The capillaries were replaced whenever a new sample of amalgam was used.

The resistance of solution, capillary, pool and contacts together was of the order of 35 ohms in most experiments but occasionally as high as 70 ohms (presumably due to relatively narrow-bore capillary tubing).

The apparatus has been described.[1] An alternating potential of an amplitude of 1 mv. r.m.s. across the cell was used.

Acknowledgment.—The authors wish to thank the Atomic Energy Commission, which helped support the work described.

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[17] K. S. G. Doss and H. P. Agarwal, *Proc. Indian Acad. Sci.*, **34A**, 263 (1951); **35A**, 45 (1952).

[18] W. C. Cooper and N. H. Furman, THIS JOURNAL, **74**, 6183 (1952).