TABLE VI

TEST OF EQUATION 4 FOR AQUEOUS AMMONIUM NITRATE SOLUTIONS

c^a	m^b	$\eta/\eta^{\circ c}$	α^d	$K_c{}^e$	$1 + m\frac{d \ln \gamma_\pm}{dm}$	$D_{\text{calcd}} \times 10^{5f}$	$D_{\text{obsd}} \times 10^5$
0.1	0.1007	0.998	0.981	2.9	0.879	1.750	1.769
.2	.2025	.994	.970	3.1	.856	1.733	1.749
.5	.5139	.985	.950	3.5	.810	1.700	1.724
1	1.055	.972	.923	3.5	.766	1.691	1.690
1.5	1.623	.960	.896	3.3	.720	1.674	1.661
2	2.224	.955	.870	3.1	.686	1.662	1.633
2.5	2.859	.958	.853	3.1	.662	1.642	1.605
3	3.533	.970	.841	3.1	.631	1.608	1.578
4	5.008	1.009	.824	3.2	.573	1.496	1.524
5	6.687	1.065	.807	3.3	.549	1.452	1.472
6	8.617	1.147	.803	3.5	.531	1.393	1.421
7	10.86	1.255	(.806)	(3.9)	.511	(1.312)	1.370
8	13.50	1.396	(.813)	(4.5)	.484	(1.202)	1.320

[a] c = moles/liter. [b] m = molality. [c] η/η° = relative viscosity. [d] α = degree of dissociation of ion-pairs (from conductivities). [e] K_c = molar scale dissociation constant of ion pairs. [f] D = diffusion coefficient.

The Diffusion of Ammonium Nitrate.—In equation 4 we now insert the values $n = 0$, $D^\circ = 1.928 \times 10^{-5}$, $D_{12} = 1.5 \times 10^{-5}$, $D_{H_2O}{}^* = 2.43 \times 10^{-5}$, and use the estimates of α obtained from the conductance data. The resulting calculated diffusion coefficients of ammonium nitrate agree with observation within 2% up to 6 M (8.6 molal) as shown in Fig. 2.

Considering the extremely high concentrations involved, this attempt at correlating the diffusion coefficients and conductances must be considered highly successful.

The lithium nitrate diffusion coefficients indicate only a small amount of ion-pair formation; this is consistent with the activity coefficient data and with some preliminary conductance measurements made in this Laboratory. In Fig. 2 the observed diffusion coefficients are compared with the predictions of theory for lithium and ammonium nitrates and chlorides. The ammonium sulfate data have not yet been analyzed in detail; until an adequate theory of the electrophoretic effect in unsymmetrical salts is available, it is of doubtful value to attempt this.

NEDLANDS, WESTERN AUSTRALIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

Polarographic Diffusion Coefficients

BY CHARLES L. RULFS

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A modified diaphragm-cell technique for the determination of the diffusion coefficients of polarographically-active substances in mM concentrations and in the presence of high concentrations of supporting electrolyte is described. The diffusion coefficients of cadmium, lead and thallous ions in three common supporting electrolytes have been determined within an estimated ±2%. The importance of the *actual vs.* the *infinite dilution* diffusion data in polarographic theory is discussed. A new technique for the evaluation of polarographic n values is described.

In connection with the exact relation between i_d and D it is generally recognized by polarographic workers that independent determinations of D are very essential. This paper describes the determination of the polarographic diffusion coefficients for cadmium, lead and thallous ions in three media. Unstirred diaphragm cells and a polarographic measuring technique have been employed as briefly described elsewhere.[1]

Experimental

All runs were conducted at 25.00 ± 0.05° in unstirred diaphragm cells which are bisected in a vertical plane into two 50-ml. compartments by 2-cm. diam. medium-porosity (10–15 μ nom. max. pore size) fritted glass discs. Each cell compartment has a small mercury-pool reservoir at the bottom with provision for external electrical contact. Each compartment is closed with a 2-hole rubber stopper carrying a nitrogen inlet tube and a bunsen valve. The valve may be opened to permit the insertion or withdrawal of a pipet or of a dropping mercury electrode tip. The cells are thermostated by immersion in an externally-controlled bath at 25 ± 0.05°.

Fifty ml. of nitrogen-saturated and temperature-equilibrated supporting electrolyte solution are pipetted through the bunsen valve into compartment II of a clean cell *simultaneously* with the filling of compartment I with a 2 mM solution of the ion under study in the identical supporting electrolyte. The cell is "pretreated" by standing filled for 2 to 3 hours, after which a glass probe is inserted and the *free* liquid is aspirated out of each compartment (making no attempt, however, to *dry* the frit). The compartments are carefully refilled and the time of filling is noted. The hydrostatic head of liquid in the two compartments must now be checked for equality; the surface of liquid in the bath is a convenient reference point for levelling. Minor adjustment may be made by the addition of more mercury in one of the pools. Each cell is immersed in the bath below the internal level of liquid, of course, but its exact depth is most conveniently fixed at whatever point will afford an equal distance from the mercury reservoir to the tip of the inserted dropping electrode for all cells. After 20 to 24 hours, the dropping electrode is inserted in the II compartment and a polarographic measurement is made of the concentration of diffused metal ion. The polarographic readings may well be repeated at 6- or 8-hour intervals up to about 72 hours.

For a diaphragm cell with compartments of equal volume, McBain and Liu[2] derive the relation

$$KDt = \log C_0 - \log (C_0 - 2C_t) \qquad (1)$$

where C_0 is the initial concentration of transportable material in compartment I, C_t is its concentration in compartment II after an elapsed time, t (and $C_t = 0$ when $t = 0$), D is the diffusion coefficient, and K is a cell constant. Potassium chloride solutions afford the best-characterized reference material for the calibration of such a cell. For the present purposes, a value of $1.87_0 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ will be used for 0.1 M KCl into water at 25° until C_t is *ca.* 0.006 M. A 25-ml. aliquot was withdrawn from the II

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(1) D. F. Boltz (ed.), "Selected Topics in Modern Instrumental Analysis," Prentice-Hall, Inc., New York, N. Y., 1952, pp. 57–58.

(2) J. W. McBain and T. H. Liu, THIS JOURNAL, **53**, 59 (1931).

compartment after 20 to 30 hours and titrated with 0.02 *N* silver nitrate solution. Expressing *t* in seconds, cell constants of 2.0 to 3.9 × 10^{-2} were found for five such cells. Replicate calibrations on any given cell checked within ± 0.6%. It should be noted that such cells will always show a gradual increase (about 2% per year) in cell constant when heavily used, and may infrequently evidence sudden larger increases for no accountable reason (*e.g.*, one of the five cells in the present study jumped from 3.0 to 3.5).

The polarographic measurements were made on a Fisher Elecdropode whose galvanometer scale and shunts were calibrated. It is convenient to reduce all measurements to an equivalent number of *galvanometer deflection units* on some one shunt position. Since equation 1 is independent of the particular concentration units employed, it may be revamped to the form

$$KDt = \log G_0 - \log (G_0 - 2G_t) \qquad (2)$$

where G_0 is the galvanometer deflection for the 2 m*M* solution in I, and G_t is the deflection observed in *II* after *t* sec. All metal-ion solutions were precisely calibrated at 2.0, 1.0, 0.5, 0.25, 0.125 and 0.0625 m*M* concentrations in the appropriate electrolyte (including gelatin or traces of acid, where used) to correct for any non-linearity in the i_d (or, *G*) *vs.* *C* relationship. It should be emphasized, therefore, that the polarograph is employed only as a suitable technique for the desired concentration measurements. Using careful standard-series calibrations, temperature control with 0.05°, and mercury heads of 60 to 70 cm. which could be controlled within at least 2 mm., it is reasonable to expect that the concentration measurements (beyond the first 20–30 hours) during a run should be reliable within 0.5% to 1.0%.

To minimize any danger of bulk flow through the diaphragm, the supporting electrolyte concentrations in I and II must be *identical*. The metal-ion solution is made up from a portion of the same electrolyte solution that is used in I. If the test involves gelatin (or traces of acid, as with lead), this must be present in identical amount in both I and II. The density gradient between I and II does not exceed 0.5 mg./ml. under these conditions.

In calibrations using 0.1 *M* KCl *vs.* water, however, a more significant gradient of about eight times this magnitude does exist; and a question of its effect, especially with the innovation of vertical diaphragms, may well be raised. Aside from the general reasonableness of the results obtained with the technique, there are several specific evidences that the question is not a serious one. A run employing 10 m*M* cadmium ion gave a $\bar{D}$ value agreeing to better than 1% with the average $\bar{D}$ from two runs on 2 m*M* solutions. Potassium chloride calibration runs as short as 14 hours agree, within the experimental error of the titrations, with calibrations as long as 46 hours duration; the average density gradients for such cases would be appreciably different.

As pointed out by Strnad,[3] low concentrations of lead ion in the KNO_3 media will give usable polarographic waves only upon the addition of a trace of acid. For this reason, about 0.02 *N* nitric acid was employed in *both* compartments *and* in the polarographic calibrations for the lead runs in this electrolyte. Single points where diffusion had proceeded in the absence of the acid and the solution was acidified with a drop of concd. acid just prior to reading, fell on the same line as data from cells in which the acid was present throughout the run.

Results

The diffusion of 2 m*M* solutions of cadmium, lead and thallous ions in 1 *M* and 0.1 *M* KNO_3 and in 0.1 *M* KCl was studied. Duplicate runs were conducted for each ion in each medium, and from 3 to 5 different cells were employed in each run. Plotting the data as $(\log G_0/G_0 - 2G_t) \times 10^2$ on the horizontal axis *vs.* $K \times t_{\text{sec.}} \times 10^{-2}$ on the vertical axis, yields a line whose reciprocal slope × 10^4 is $\bar{D}$ for the ion in cm.^{2} sec.$^{-1}$ at 25°. In general, the data were taken after 20 hr. and up to about 75 hr. At the conclusion of a run, the solutions in the II compartments of the cells were of the order of 0.1 m*M* in metal ion. Hence the graphically-calculated $\bar{D}$ values, which are based upon plotting the data as a single *best* straight line, apply to a mean concentration gradient of 1.95 *vs.* 0.05 m*M*. Within the present limitations of the technique, this point is not a significant one in the case of either cadmium or lead ion as can be seen from an inspection of Figs. 1 and 2. In the case of these ions the experimental points for very short times (low concentrations) show a perfectly random scattering about the *best* lines drawn on the basis of the more-accurate, later points. Their $\bar{D}$ values can as well be termed $\bar{D}^0$ values for the particular media. Thallous ion, however, seems to have a very pronounced concentration-dependence of $\bar{D}$. Here, the points prior to, say, 36 hr. will define a $\bar{D}$ some 10 to 15% higher than $\bar{D}$'s based on subsequent points. As a practical means of demarcation, the mean $\bar{D}$ for the run must be distinguished from a $\bar{D}^0$ for thallous ion which, arbitrarily, will be taken as that which is defined by points prior to 36 hr. This will give only an approximation to the truth, of course, but the limited precision of the very early readings would scarcely justify a more elegant treatment.

Representative data for four of the nine systems studied have been selected for presentation in the two figures. The experimental points illustrate the degree of precision obtainable using five different cells and two separate runs per ion. The situation regarding the marked concentration-dependence of thallous ion and the manner in which the data for this ion were treated will also be clear. The data not shown in the figures did not deviate in any significant fashion from these specimens. The final $\bar{D}^0$ values for the three ions in three media are compared with the D^0 values calculated from electrical conductivity in Table I. The mean $\bar{D}$ values of thallous ion, which were not included, are 1.57, 1.52 and 1.48 × 10^{-5} cm.^{2} sec.$^{-1}$ for 1 *M* and 0.1 *M* KNO_3 and 0.1 *M* KCl, respectively. Single point data were also obtained for the three ions in 0.1 *M* KNO_3 with 0.01% of gelatin present giving $\bar{D}$'s of 1.24, 0.74 and 0.65 for thallium, lead and cadmium, respectively. It will be evident from the figures that single points (after only 40 hours) could be in error as much as 10%.

TABLE I

DIFFUSION COEFFICIENTS IN CM.^{2} SEC.$^{-1}$ × 10^5 AT 25°

Medium	Tl^+	Pb^{++}	Cd^{++}
H_2O, calcd. D^0	2.00	0.98	0.72
1 *M* KNO_3	1.79	.67	.66
0.1 *M* KNO_3	1.67	.75	.76
0.1 *M* KCl	1.67	.75	.70
D^0 0.1 *M* KCl *vs.* D^0	−16.5%	−23%	−2.8%

Discussion

Evidently, it is not safe to generalize regarding the effect of ionic strength on the $\bar{D}^0$ values Thus, the lead and cadmium values are repressed for 1 *M* *vs.* 0.1 *M* KNO_3, but the thallous ion is faster in the stronger electrolyte. The fact that univalent and bivalent ions are being compared may be significant in this connection.

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(3) F. Strnad, *Collection Czechoslov. Chem. Communs.*, **11**, 391 (1939).

It is entirely reasonable, in view of the known ability of nitrate and chloride ions to form weak complexes,[4-6] that $\bar{D}^0$ for cadmium ion in 0.1 *M* KNO_3 should exceed the calculated $\bar{D}^0$ value; but it is rather surprising, on the other hand, that the remaining $\bar{D}^0$ values of cadmium and lead in both nitrate and chloride media are *below* the calculated $\bar{D}^0$. Based on this consideration *alone* (*i.e.*, complexation) it is also unexpected that the $\bar{D}^0$ of lead or of cadmium should be lower in 1 *M* than in 0.1 *M* KNO_3.

Apparently, gelatin does have a depressant effect, varying from moderate to large, on polarographic diffusion coefficients. But the observed effect of gelatin in actual polarography could well be a *net* effect comprised from a number of factors including real changes in D^0, adsorption effects, changes in the dropping characteristics, interference in the diffusion layer, etc.

The last line of Table I compares "actual" with the "infinite-dilution" diffusion coefficients. The modest difference for cadmium and the approximately 20% differences for lead and thallium are a striking contrast, but a very real necessity for the agreement of polarographic theory with observation. Lingane and Loveridge[7] and others[8,9] derived an improved form of the Ilkovic equation which takes account of the curvature of the electrode surface.

$$i_{\mathrm{d}} = 607nD^{1/2}Cm^{2/3}t^{1/6}\left(1 + \frac{39D^{1/2}t^{1/6}}{m^{1/3}}\right) \qquad (3)$$

In the case of 0.1 *M* KCl electrolyte, substitution of the experimentally-determined $\bar{D}^0$ values in eq. 3 leads to calculated current values within 1% (on an average for the three ions studied) of the observed currents with a given d.m.e. The discrepany averages 10% too low when the comparable calculation is based on the classical Ilkovic expression.

A recent paper by von Stackelberg, *et al.*,[10] describes the determination of polarographic diffusion coefficients by (a) calculation through the Strehlow–Stackelberg equation,[8] and (b) the Cottrell technique.[11] Comparable measurements for cadmium, lead and thallous ions are only in poor to semiquantitative agreement with the results of the present study.

A simplified version of the present technique has a practical utility in the ascertainment of *n* values in studies involving uncharacterized polarographic processes. It is applicable only for diffusion-controlled processes involving substances which are stable in solutions of the desired supporting electrolyte for at least one day. But even relatively-

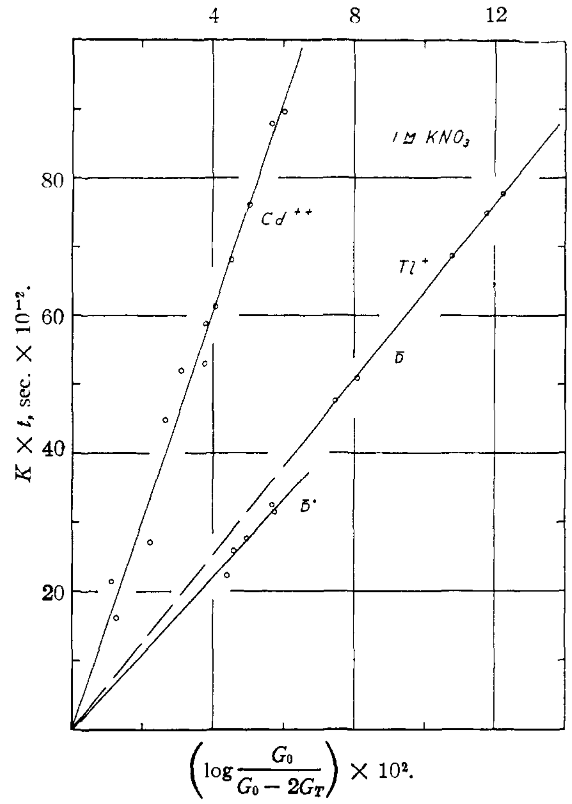

Fig. 1.—Diffusion data in 1 *M* KNO_3.

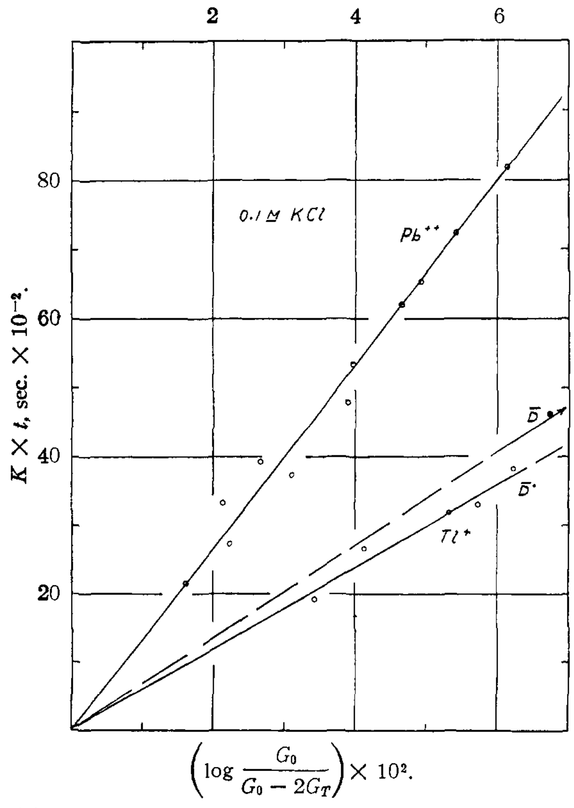

Fig. 2.—Diffusion data in 0.1 *M* KCl. The scale has been chosen to emphasize the $\bar{D}^0$ points for thallium, hence the principal points defining the upper, *mean* $\bar{D}$, line lie outside these coördinates.

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(4) H. M. Hershenson, M. E. Smith and D. N. Hume, THIS JOURNAL, **75**, 507 (1953).

(5) E. L. King. *ibid.*, **71**, 319 (1949).

(6) P. M. Strocchi and D. N. Hume, *ibid.*, **76**, in press (1954).

(7) J. J. Lingane and B. A. Loveridge, *ibid.*, **72**, 438 (1950).

(8) H. Strehlow and N. von Stackelberg, *Z. Elektrochem.*, **54**, 51 (1950), but with 17, in place of 39, in the second term in parentheses. A later form retains the 17 but replaces 607 with 619, giving results only about 3% less than 3. But *D* values calculated *from* polarography by the latest form would be *ca.* 6% below the requirement for 3.

(9) T. Kambara and I. Tachi, Proc. Intern. Polarographic Congress, Part I, Prague, Feb. 1951, p. 126.

(10) M. von Stackelberg, M. Pilgrim and V. Tome, *Z. Elektrochem.*, **57**, 342 (1953).

(11) F. G. Cottrell, *Z. physik. Chem.*, **42**, 385 (1902), and see ref. 1, p. 24.

short, single-point runs yield more realistic $\bar{D}$ values than those estimated by analogy or approximated through a modified Stokes–Einstein relation. A single previously-calibrated cell serves the purpose, but its constant should be redetermined at reasonable intervals. This cell need not include any provision for the mercury pool and contacts. Data from several polarograms at concentrations near 0.05 to 0.20 mM should be available, as well as that for the higher concentration to be used in compartment I. The cell is filled with equal volumes of nitrogen-saturated electrolyte in compartment II and of electrolyte plus 2 to 5 mM substance in I. Time and date of filling are noted, the cell is stoppered to prevent evaporation, and supported level and in as vibration-free a manner as possible in the laboratory thermostat-bath. After 24 (minimum) to 48 (preferable) hours, a portion of the solution in II is transferred to a polarograph cell, deaerated, and measured polarographically.

It is difficult to evaluate the absolute *accuracy* of the results here reported in any completely objective manner. Both the polarographic measurements (statistically, at least, with reference to a number of points in the latter two-thirds of the runs) and the replicate runs on the cell constants are *precise* within about ±0.6%. The facts that data from at least 3 and up to 5 different cells are included in any given run, and that the final $\bar{D}$'s of duplicate runs using fresh solutions and new calibrations, checked within ±1.2% in the worst case and ±0.9% on an average, are reassuring. But all such criteria are more related to *precision* than to *accuracy*. As an estimate, however, it would appear that the technique as described yields $\bar{D}$ values with a precision of about ±1.0% and which should be accurate within about ±2%. The literature on diaphragm-cell measurements of conventional diffusion coefficients indicates that the technique may be improved to about ±0.5%.

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Ann Arbor, Michigan

[Contribution from the Institute of Inorganic, Analytical and Physical Chemistry, Faculty of Pharmacy, University of Zagreb, Croatia, Yugoslavia]

Polarographic Characteristics of +5 Vanadium in Phosphate, Borate and Carbonate Buffers

By I. Filipović, Z. Hahl, Z. Gašparac and V. Klemenčić

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The polarographic behavior of +5 vanadium has been studied in phosphate, borate and carbonate buffers in the range from pH 2 to 12.5. The dependence of half-wave potential and height of polarographic waves on pH have been determined. In phosphate buffer at $p\text{H} < 2$, the two waves produced correspond to the reversible electrode reduction of +5 to +4 vanadium and to the irreversible electrode reduction of +4 vanadium to the +2 state, respectively. From pH 2 to 9 four waves are developed: the first two correspond to the adsorption–reduction of hydrogen polyvanadate ions; the third wave to the irreversible electrode reduction of +5 to - 4 vanadium; and the fourth to a reduction of +4 to +2 vanadium. With increasing pH the adsorption current falls and at pH 9 the adsorption wave disappears. From pH 9 to 12.5, in all three buffers, only two waves remain; the first, which corresponds to the reduction of +5 to +4 vanadium, decreases and the second, which partly corresponds to a reduction of +5 to +4 vanadium, increases with increasing pH. Above pH 12.5 a single wave is left, corresponding to a reduction of +5 to +2 vanadium. These results are attributable to the existence of five different kinds of +5 vanadium ions in equilibrium in the interval of pH examined. Two well developed waves arise about 0.5 v. apart in borate solution.

Solutions of vanadium have been frequently investigated by the polarographic method.[1] The reduction of +5 vanadium on the dropping mercury electrode in acid solutions (0.05 M sulfuric acid) produces two polarographic waves, one starting from zero, the other from −0.98 applied e.m.f. *vs.* S.C.E. In ammoniacal solutions containing 1 M ammonium chloride and less than 6 M ammonia, two very close waves arise in the interval −1 to −1.3 v. *vs.* S.C.E. With an increase of ammonia concentration the first wave shifts toward more negative, and the second toward more positive potentials, so that only one wave remains at concentrations above 6 M ammonia. In strongly basic solutions (0.1 M lithium hydroxide) a single wave develops, starting at about −1.7 v. *vs.* S.C.E. Hence it is evident that the polarographic behavior of +5 vanadium depends on pH. To elucidate the chemical mechanism of the electrode process, a systematic polarographic investigation of +5 vanadium in buffer solutions has been carried out.

Experimental

Apparatus.—The current–voltage curves were recorded according to the usual technique with a Heyrovský photographically recording polarograph, Model V-301, manufactured by Československa Zbrojovka, Brno. The voltage on the bridge was controlled by a normal Weston standard cell from the Cambridge Instrument Co. With a head of 60 cm. of mercury, the capillary (thermometer capillary, Schott & Gen.) had a rate of flow, m, of 1.825 mg. sec.$^{-1}$ at short-circuited electrode and S.C.E. A modified polarographic cell from the Cambride Instrument Co. was used, which permitted the passage of an inert gas over the solution during measurement. The anode was either a saturated calomel, or a saturated mercurous sulfate electrode, type Cambridge Instrument Co. Before every measurement, oxygen was removed from the solution by bubbling through hydrogen obtained electrolytically and purified by means of alkaline pyrogallol solution. The polarographic cell was kept in a thermostat at 25.0°. Correction was made

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(1) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. II. Interscience Publishers, Inc., New York, N. Y., pp. 447–452.