[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Studies in the Theory of the Polarographic Diffusion Current. III. Diffusion Current Constants of Some Ions in Solutions Containing Gelatin. A Critique of the Strehlow–von Stackelberg Equation[1]

BY LOUIS MEITES AND THELMA MEITES

Using capillaries producing 7–16 mg. drops, precise measurements have been made of the variations with capillary characteristics of the diffusion current constants of four ions in various supporting electrolytes containing 0.009% gelatin. Although the data can be represented between $t = 1.5$ sec. and 4–6 sec. (depending on the nature of the reducible ion) by an equation of the form $I = k_1[1 + k_2(t^{1/6}/m^{1/3})]$, such an equation does not provide a better representation of the data than the best curve drawn through a plot of I *versus* t, and it fails at longer drop times. The assignment of empirical values for k_1 and k_2 is discussed.

The recent appearance of two independent derivations of a new theoretical equation for the polarographic diffusion current[2,3] has prompted its test with a wider variety of accurate data on the effects of m and t on the diffusion current than have previously been available. The present paper is a report of such a study with four ions in the presence of 0.009% gelatin: silver and cadmium in 0.1 F potassium nitrate, ferricyanide in 0.1 F potassium chloride, and iodate in 0.1 F potassium chloride–0.1 F hydrochloric acid.

Experimental

The apparatus was described in a preceding paper of this series.[4]

For this work we have modified the method of determining m according to Lingane and Kolthoff[5] by making the cup in which the drops are caught entirely removable from the cell, so that the globule of mercury is poured, rather than sucked, into a weighing bottle. Typical of the results secured with a stable capillary by this method are ten values for capillary I-81 measured on two different days: the extreme values were 2.5588 and 2.5604 mg./sec., and the probable error of a single value was 0.013%. Fifty determinations of t at this point gave a probable error of 0.10%: as all measurements of t were made in duplicate, the probable error of the mean would be 0.07%. The average deviation of a diffusion current measurement from the mean of two or more replicates was approximately 0.05%. Each galvanometer sensitivity used in the calculations was the mean of at least five measurements, and its probable error always fell between 0.02 and 0.04%.

The solutions used were prepared by weight dilution of more concentrated solutions. The stock silver nitrate solution, from the commercial salt, was standardized volumetrically against recrystallized potassium chloride, and gravimetrically by weighing silver chloride: the difference between the means of four determinations by each method was 0.01%. Potassium ferricyanide was thrice recrystallized from water, dried to constant weight at 140°, and was assumed to be pure: its solutions were always discarded before any precipitate of hydrous ferric oxide could be detected. Reagent grade potassium iodate was recrystallized five times from water and dried over anhydrous magnesium perchlorate. The cadmium solution was that used in the earlier work.[4]

An ordinary H-cell with a saturated calomel electrode and a 4% agar–saturated potassium chloride bridge was used except with silver, for which a Carritt-type cell,[6] with saturated calomel electrode, was employed. This cell has a long doubly-bent tube between its two compartments, so that any reaction (*e.g.*, precipitation of silver chloride) occurring at the solution–agar boundary is effectively isolated from the bulk of the solution. The level of the cell in the reference electrode side of the cell was always kept below that of the solution in the other compartment to eliminate errors due to leakage through the agar plug. In much of this work the hydrogen used to deaerate the solution was presaturated with water at the temperature of the thermostat (25.00 ± 0.05°) to prevent evaporation into or condensation from the gas stream.

Reaction of ferricyanide and silver with mercury was minimized by the use of an H-cell so designed that the mercury falling into the solution was caught in a small tube sealed to the bottom of the solution compartment, so that the reaction took place only at a relatively small area far removed from the capillary tip. Care was taken to avoid stirring these solutions once the capillary had been inserted, and to complete the measurements within the least possible time after mercury was allowed to come into contact with the solution. Under these conditions the diffusion current of silver was found to decrease between 0.2 and 0.4% during the entire time required for the nine to fifteen measurements made with each capillary, while the corresponding maximum error for ferricyanide was about half as great. Therefore, the uncertainty in the concentration caused by this error varies for each capillary between zero at the longest drop time to a maximum of 0.4% at the shortest, because of the direction in which t was varied during the measurements with each capillary.

Gelatin solutions were prepared as previously described.[4] In all of these measurements the gelatin concentration was $(9.0 \pm 0.3) \times 10^{-3}$%.

Potassium nitrate and potassium chloride were recrystallized once from water and dried at 120°. Other materials were ordinary reagent grade and were not further purified.

Data and Discussion

These new data, as plotted in Figs. 1–4, confirm our earlier suggestion[4] that the addition of gelatin is invariably accompanied by a pronounced minimum in the diffusion current constant–drop time curve. (This type of plot was first suggested by Buckley and Taylor[7] and was later adopted by Loveridge.[8]) This minimum occurs at 1.3 sec. with ferricyanide, 1.5 sec. with iodate and 1.6 sec. with silver and cadmium, the differences probably not being significant. The data of Lingane and Loveridge[9] for lead and of Loveridge[8] for tetramminozinc ions in the presence of 0.01% gelatin give curves whose minima also fall at 1.6 sec. The depth of this minimum relative to highest segment of the curve at longer drop times varies between 3.6% for iodate and 5.3% for silver: Loveridge found 5.8% for tetramminozinc ion and 4.0% for lead.

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[1] Tables I-IV, summarizing data on I as a function of t or of $t^{1/6}/m^{1/3}$, are available as Document 2929 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $0.50 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $0.90 for photocopies (6 × 8 inches) readable without optical aid.

[2] J. J. Lingane and B. A. Loveridge, THIS JOURNAL, **72**, 438 (1950).

[3] H. Strehlow and M. v. Stackelberg, *Z. Elektrochem.*, **54**, 51 (1950).

[4] L. Meites and T. Meites, THIS JOURNAL, **72**, 3686 (1950).

[5] J. J. Lingane and I. M. Kolthoff, *ibid.*, **61**, 825 (1939).

[6] D. C. Carritt, Ph.D. Thesis, Harvard University, 1947.

[7] F. Buckley and J. K. Taylor, *J. Research Natl. Bur. Standards*, **34**, 97 (1945).

[8] B. A. Loveridge, Ph.D. Thesis, Harvard University, 1947.

[9] J. J. Lingane and B. A. Loveridge, THIS JOURNAL, **66**, 1425 (1944).

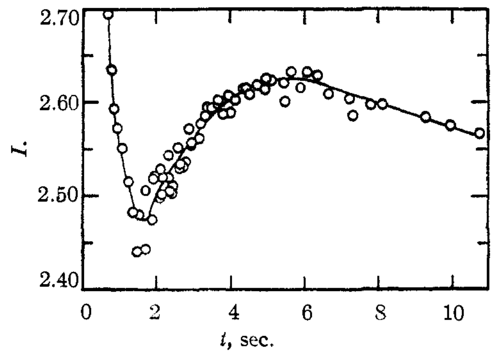

Fig. 1.—Variation with t of the diffusion current constant of silver in 0.1 F potassium nitrate and 0.009% gelatin.

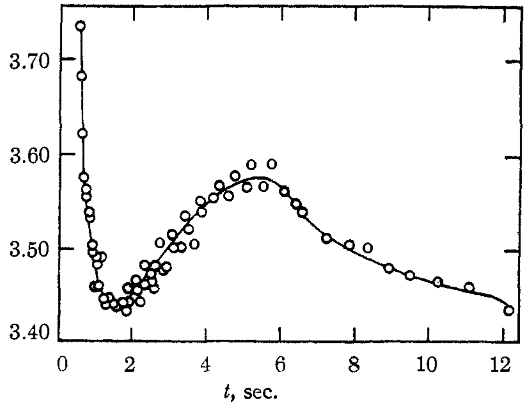

Fig. 2.—Variation with t of the diffusion current constant of cadmium in 0.1 F potassium nitrate and 0.009% gelatin.

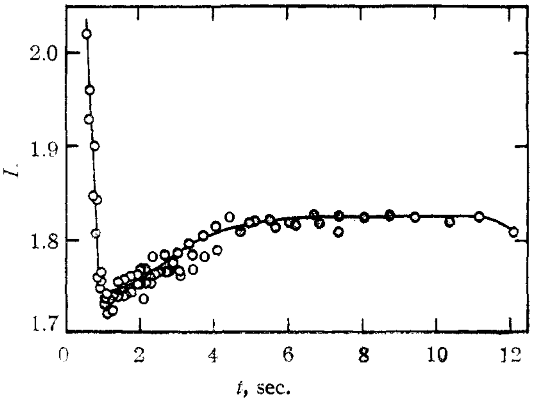

Fig. 3.—Variation with t of the diffusion current constant of ferricyanide in 0.1 F potassium chloride and 0.009% gelatin.

At longer drop times the curve passes through a maximum and then decreases. In every case, *in the presence of 0.009% gelatin*, I is independent of t to ±0.5% or better at drop times between 4 and 7.5 sec. This is to be compared with the suggestion made by Kolthoff and Lingane[10] that, *in general*, I was independent of t to ±3% or better at drop times between 3 and 6 sec.

This behavior violates equation (1), according to which I should increase continuously with increasing t for any one capillary.

$$I = 607\ nD^{1/2}[1 + 17D^{1/2}(t^{1/6}/m^{1/3})]^2 \qquad (1)$$

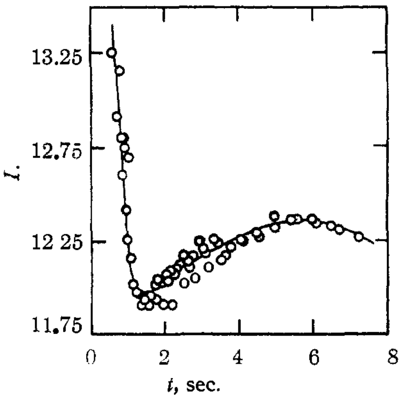

Fig. 4.—Variation with t of the diffusion current constant of iodate in 0.1 F potassium chloride–0.1 F hydrochloric acid and 0.009% gelatin.

(The derivation given by Lingane and Loveridge[2] results in an identical equation except for the coefficient of the second term, which they give as 39. In view of the importance of the introduction of the factor $\sqrt{7/3}$ in the assignment of this value, it is of interest to note that the alternative values of 17 and 39 differ by a factor of almost exactly 7/3.) Lingane and Loveridge[2] show one point (t = 8.9 sec.) on their curve for lead which falls well below the extension of the line representing equation (1), and the data of Loveridge[8] contain a similar point for tetramminozinc. Thus they actually found an equation of this form to hold only up to drop times of about 6 sec., which is very nearly the position of the maximum in the I *versus* t curves. As Strehlow and von Stackelberg secured no points at drop times greater than 6.9 sec., they were unable to find any evidence of this error.

Our curves (Figs. 5–8) unanimously demonstrate the failure of equation (1) at high drop times. The values for silver begin to fall below the straight line at t = 4.0 sec., with iodate they fall off above 5.0 sec.; and with cadmium and ferricyanide[11] the equation is no longer applicable above 5.5 and 6.0 sec., respectively. The corresponding values of $t^{1/6}/m^{1/3}$ lie between 1.0 for silver and 1.3 for ferricyanide. It is noteworthy that such features as the minimum and the region of near-constancy occur at values of t which appear to be independent of the reducible ion and the supporting electrolyte, but that no single feature of the I *versus* $t^{1/6}/m^{1/3}$ curve can be defined without reference to these factors.

Not only does equation (1) fail to reproduce the data at high drop times, but it also fails at low drop times. The cause of this failure, described as the "rinse effect" by Strehlow and von Stackelberg, has been recognized for many years. As a result, equation (1) predicts values which are too low as $t^{1/6}/m^{1/3}$ decreases below 0.65 for silver and cadmium, 0.6 for iodate, and 0.55 for ferricyanide: these limits are presumably to be interpreted as indicating

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[10] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 62.

[11] The values for ferricyanide with capillary J, for which mt is 26.5 mg., are impossible to reconcile with equation (1), and hence they have been omitted in the subsequent calculations. Further data with capillaries delivering large drops are needed before the discrepancy can conclusively be assigned to the theory or to experimental errors. Such data are being gathered in this Laboratory and will be presented elsewhere.

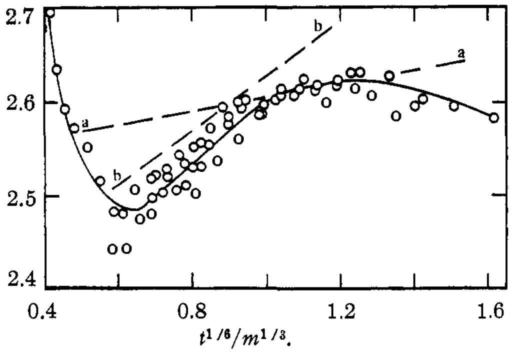

Fig. 5.—Variation with $t^{1/6}/m^{1/3}$ of the diffusion current constant of silver in 0.1 *F* potassium nitrate and 0.009% gelatin. The line aa represents equation (1), and the line bb represents equation (6).

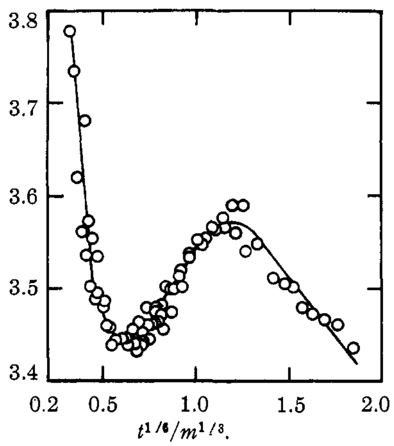

Fig. 6.—Variation with $t^{1/6}/m^{1/3}$ of the diffusion current constant of cadmium in 0.1 *F* potassium nitrate and 0.009% gelatin.

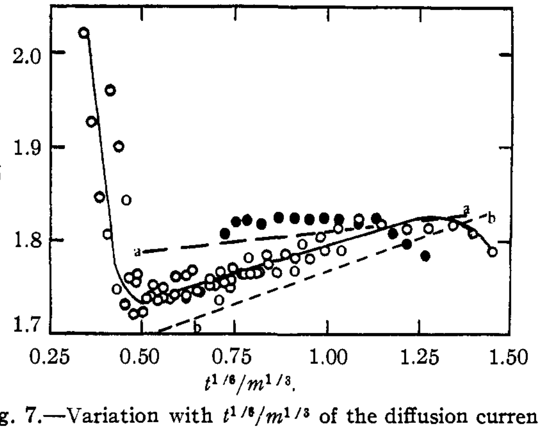

Fig. 7.—Variation with $t^{1/6}/m^{1/3}$ of the diffusion current constant of ferricyanide in 0.1 *F* potassium chloride. Solid circles represent values secured with capillary J. The line aa represents equation (1), and the line bb represents equation (6).

the points at which strict diffusion control is replaced by streaming past the electrode surface to an extent which increases with decreasing drop times. When these values are compared with the drop times at the minima of the *I versus t* curves, the agreement is, on the whole, good except with silver ion, for which equation (1) would indicate that diffusion control does not apply below $t = 1.9$ sec.

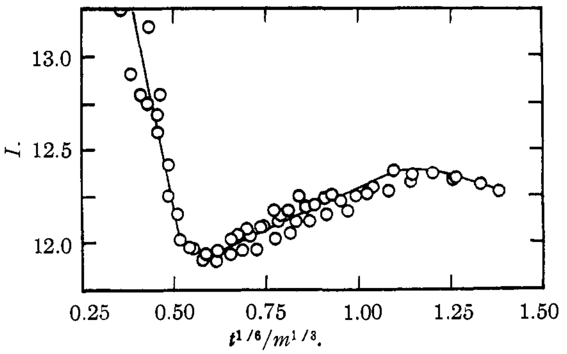

Fig. 8.—Variation with $t^{1/6}/m^{1/3}$ of the diffusion current constant of iodate in 0.1 *F* potassium chloride–0.1 *F* hydrochloric acid and 0.009% gelatin.

Within these limits, however, an equation of the form of equation (1) appears to represent the data satisfactorily. For each ion there are from 31 to 42 points in this interval, and from these points we have calculated the least-squares best values for the numerical coefficients in the equation

$$I = k_1[1 + k_2(t^{1/6}/m^{1/3})] \qquad (2)$$

The equations thus secured are

$$\text{Ag}^+\text{: } I = 2.271[1 + 0.146_6(t^{1/6}/m^{1/3})] \qquad (3a)$$

$$\text{Cd}^{++}\text{: } I = 3.234[1 + 0.094_4(t^{1/6}/m^{1/3})] \qquad (3b)$$

$$\text{Fe(CN)}_6^{-3}\text{: } I = 1.670[1 + 0.074_5(t^{1/6}/m^{1/3})] \qquad (3c)$$

$$\text{IO}_3^-\text{: } I = 11.472[1 + 0.069_2(t^{1/6}/m^{1/3})] \qquad (3d)$$

According to equation (1), the coefficients in equation (2) are given by the expressions

$$k_1 = 607nD^{1/2} \qquad (4a)$$

$$k_2 = AD^{1/2} \qquad (4b)$$

where *A* is a numerical constant, whose value is 17 according to Strehlow and von Stackelberg, or 39 according to Lingane and Loveridge. Following Strehlow and von Stackelberg, we have calculated values of $D^{1/2}$ for these ions from equations (3) and (4a), and then used these values to calculate *A* from equation (4b). The results are

Ag^+:	$D^{1/2} = 3.74 \times 10^{-3}$ cm./sec.$^{1/2}$;	$A = 39.2$
Cd^{++}:	2.66	35.4
Fe(CN)_6^{-3}:	2.75	27.1
IO_3^-:	3.15	22.0

By fitting a straight line visually to his data, Loveridge[8] secured equations which, rewritten in the form of equations (3), are

$$\text{Pb}^{++}\text{: } I = 3.628[1 + 0.082_7(t^{1/6}/m^{1/3})]^{12} \qquad (5a)$$

$$\text{Zn(NH}_3)_4^{++}\text{: } I = 3.729[1 + 0.103_0(t^{1/6}/m^{1/3})] \qquad (5b)$$

These equations give $A = 33.5$ for the tetramminozinc ion, and 31.7 for lead. In mean, therefore, *A* is 31.5 ± 4.6 from all the data, or 33.4 ± 3.2 if the iodate value is excluded. Therefore the constant given by Lingane and Loveridge appears to be much

(12) According to Strehlow and von Stackelberg, these data lead to the equation $I = 3.718[1 + 0.0535\ (t^{1/6}/m^{1/3})]$. We have been unable to secure so low a slope even by including points for which *t* is as low as 1.18 sec. Taking $t = 1.4$ sec. as the lower limit, which corresponds to the value $t^{1/6}/m^{1/3} = 0.6$ given by Lingane and Loveridge[8] as the apparent limit of validity of equation (1), and omitting the point for which $t = 8.9$ sec., our least-squares calculations give $I = 3.596\ [1 + 0.094_0\ (t^{1/6}/m^{1/3})]$, in good agreement with Loveridge. We shall use the latter equation in the following calculations.

more nearly correct than that of Strehlow and von Stackelberg.

These figures depend on the correctness of the coefficient 607 in equation (4a). Values of the diffusion coefficients of 5 mM ferricyanide in 0.1 F potassium chloride and of 5 mM silver in 0.1 F potassium nitrate, calculated from the work of Laitinen and Kolthoff,[13] lead, however, to the values 575 and 544, respectively. Therefore, the best available empirical modification of equation (1) is

$$I = 560nD^{1/2}[1 + 29D^{1/2}(t^{1/6}/m^{1/3})] \qquad (6)$$

The values predicted by this equation fall on the lines bb in Figs. 5 and 7, while the lines aa represent equation (1). The latter are plainly unsatisfactory: concerning the former, it is of interest to note that equation (6) reproduces the data to within about 0.5% if the values of D^0 calculated from equivalent conductance data[13] are used instead of the experimental values of Laitinen and Kolthoff. Whether this is due to experimental errors in the latter or to changes in D caused by the addition of gelatin is impossible to decide at this time.

Although the considerations outlined do not constitute a proof of the correctness of the factor 560 in equation (6), it does seem apparent that the value 607 is subject to considerable doubt pending further study.

It may be remarked that the values of I calculated from the Ilkovič equation, 2.533 for silver and 1.761 for ferricyanide, are found on Figs. 1 and 3 at drop times of 2.5 sec., but, again, not at equal values of $t^{1/6}/m^{1/3}$.

Acknowledgment.—The work described in this paper was supported by Contract Number AT (30-1)-842 between the U. S. Atomic Energy Commission and Yale University.

NEW HAVEN, CONN. RECEIVED JULY 28, 1950

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[13] H. A. Laitinen and I. M. Kolthoff, THIS JOURNAL, **61**, 3344 (1939).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY]

The Conductance of Methanol, Acetone, Ethyl Acetate and Acetic Anhydride Complexes of Aluminum Bromide in Nitrobenzene at 25°[1]

BY ROSS E. VAN DYKE

The conductance of aluminum bromide in nitrobenzene on addition of methanol, acetone, ethyl acetate and acetic anhydride has been determined. The curves for methanol and acetone are remarkably similar, while that for ethyl acetate was found to be similar to those obtained for dimethyl ether as complexing agent.[2a] The curves obtained with acetic anhydride are markedly different from any of the other curves obtained. The electrical conductivity of some of these complexes is considered in the light of their reported catalytic activity in alkylation reactions.[3]

I. Introduction

The conductance of aluminum bromide and of gallium chloride and gallium bromide on addition of dimethyl ether, trimethylamine and ammonia in nitrobenzene solution have been reported recently[2a,b] These studies have yielded new and interesting information concerning the nature and stability of these complexes in solution. Ipatieff and Schmerling[3] report that the monomolecular addition compounds of aluminum chloride with ethers, ketones or alcohol are active catalysts for the alkylation of isobutane in the presence of hydrogen chloride in nitromethane solution. On the other hand, they report that if the aluminum chloride is coördinated to two moles of alcohol or if the salt is dissolved in ether, acetone, etc., the resultant solution does not catalyze the alkylation reaction. If aluminum chloride is dissolved in nitromethane the monomolecular addition complex of nitromethane and aluminum chloride is also catalytically active.

The studies to be reported in this paper have been carried out in nitrobenzene as solvent. Nitrobenzene also forms a brilliant yellow monomolecular addition compound with the aluminum halides. Nitrobenzene is readily purified for conductance studies and has a dielectric constant almost equal to that for nitromethane. It appears reasonable, therefore, to discuss the results of these studies in nitrobenzene in relation to the observations on catalytic activity of some of these complexes in nitromethane.

The conductances of aluminum bromide on addition of varying amounts of methanol, acetone, ethyl acetate, acetyl bromide and acetic anhydride in nitrobenzene at 25° have been determined and are reported here.

II. Experimental

A. **Apparatus and Procedure.**—Conductance measurements were carried out as described previously.[2] Sealed ampules of aluminum bromide were placed in the cells which had been baked out.[2a] The cell was evacuated and filled with dry nitrogen just before breaking the ampule. Upon introduction of solvent and the liquid complexing agents a dry nitrogen atmosphere was maintained over the solution.

Liquid complexing agents were introduced by means of a micro weight pipet which was equipped with ground glass inlet and outlet.

All additions of complexing agents were determined by weight difference on the analytical balance. This method was found to be quite reproducible and sufficiently precise for the concentration range under consideration.

B. **Materials.**—Nitrobenzene[4] was purified and handled as described in earlier papers.[2a,b] The purified product had a specific conductance of 1 × 10^{-10} mho. Anhydrous aluminum bromide was prepared, purified and filled into ampules as previously described.[2a] Methanol was purified by preliminary drying of Baker C.P. product over barium

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[1] The contents of this paper have been presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the Chicago Meeting, September, 1950.

[2] (a) Van Dyke and Kraus, THIS JOURNAL, **71**, 2694 (1949); (b) Van Dyke, *ibid.*, **72**, 2823 (1950).

[3] Ipatieff and Schmerling, "Advances in Catalysis," Vol. I, p. 51.

[4] Kindly furnished by Calco Chemicals Division, American Cyanamid Company.