Cu_2O,[14] further relations can be obtained for them. Thus

$\Delta S^0_{298.16} = -22.28$ e.u., $\Delta F^0_{298.16} = -30{,}520$ cal. for CuO, and
$\Delta S^0_{298.16} = -18.00$ e.u., $\Delta F^0_{298.16} = -35{,}440$ cal. for Cu_2O

(c) **The Standard State Entropy of Cupric Ion.**—The heats of solution of cupric oxide in dilute acids were measured by Thomsen,[13] Berthelot[17] and Sabatier.[18] Their results are stated in Table III. If the salts are completely dissolved, and the solutions are dilute enough, the heat of solution, $\Delta H^0_{298.16}$ for the reaction $CuO + 2H^+ = Cu^{++} + H_2O$ should be independent of the particular acid used. This is true if we discount the value for (CuO, H_2SO_4 aq). We take the average value $\Delta H^0_{298.16} = -15.540$ cal. for this reaction. The free energy change for the same reaction may be obtained as

TABLE III

HEATS OF SOLUTION OF CUPRIC OXIDE IN DILUTE ACIDS

Solution	Heat of solution, cal. Thomsen[13]	Berthelot[17]	Sabatier[18]
(CuO, 2HCl aq)	−15,270	−15,000	−16,400
(CuO, 2HBr aq)	−15,270		−16,200
(CuO, 2HI aq)	−15,270		
(CuO, $2HNO_3$ aq)	−15,250	−15,000	−16,200
(CuO, $2HClO_3$ aq)	−15,910		
(CuO, $2(C_2H_5)HSO_4$ aq)	−15,200		
(CuO, H_2SO_4 aq)	−18,800	−18,400	−19,210

$$\begin{array}{ll}
Cu + 2H^+ = Cu^{++} + H_2(g) & \Delta F^0_{298.16} = 15{,}870 \text{ cal.}^{19} \\
CuO = Cu + {}^1/_2O_2(g) & \Delta F^0_{298.16} = 30{,}520 \text{ cal.} \\
\underline{H_2(g) + {}^1/_2O_2(g) = H_2O(l)} & \underline{\Delta F^0_{298.16} = 56{,}700 \text{ cal.}^{20}} \\
CuO + 2H^+ = H_2O(l) + Cu^{++} & \Delta F^0_{298.16} = -10{,}310 \text{ cal.}
\end{array}$$

So we have $\Delta S^0_{298.16} = -17.54$ e.u. for this reaction. Substituting entropies of CuO and H_2O,[21] we have

$$S^0_{Cu^{++}} = -24.1 \text{ e.u. at } 298.16\,^\circ\text{K.}$$

Latimer, Pitzer and Smith[22] have obtained −25.9 ± 3.0 e.u. and −26.6 ± 1 e.u., respectively, as values of the entropy of $Cu^{++}(aq)$ from data for the reactions $Cu(s) + 2H^+(aq) = Cu^{++}(aq) + H_2(g)$ and $Cu(s) + 2\,Ag^+(s) = Cu^{++}(aq) + 2Ag(s)$.

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[17] M. M. Berthelot, *Compt. rend.*, **86**, 528 (1878); *Ann. chim. phys.*, [5] **15**, 185 (1878); [7] **4**, 471 (1895).

[18] P. Sabatier, *Compt. rend.*, **125**, 301 (1897).

[19] From standard oxidation–reduction potential of Cu, Cu^{++}. The value is taken as −0.344 v. from W. M. Latimer and J. H. Hildebrand, "Reference Book of Inorganic Chemistry," The Macmillan Co., New York, N. Y., 1951.

[20] F. D. Rossini, *J. Research Natl. Bur. Standards*, **22**, 407 (1939).

[21] W. F. Giauque and J. W. Stout, THIS JOURNAL, **58**, 1144 (1936); L. Pauling, *ibid.*, **57**, 2680 (1935).

[22] W. M. Latimer, K. S. Pitzer and W. V. Smith, *ibid.*, **60**, 1829 (1938).

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The Use and Limitations of Heterogeneous Rate Constants in Polarographic Kinetics

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The use of first-order heterogeneous rate constants is practicable only if the diffusion of the depolarizer from the bulk of the solution (kinetic waves) or of the electrode product from the drop surface (catalytic waves) is negligibly small. In such cases the expression for the conversion factor derived by previous authors is valid. The restriction does not preclude control of the kinetic current by the diffusion of a non-electrolyzable species. It is indicated to what degree the true conversion factor departs from the derived value when the restriction is not obeyed. The heterogeneous rate constant method is applied to a novel type of reaction. Also, the use of the factor $\sqrt{7/3}$ is discussed, and the behavior of the rising portion of kinetic waves derived.

It is the purpose of this article to investigate the conditions under which first-order kinetic phenomena at the dropping mercury electrode (d.m.e.) may be interpreted by the use of heterogeneous or surface rate constants.[1,2] These constants, denoted $(k)_h$, have the units cm. sec.$^{-1}$, and are often incorporated into equations as μk[3–5] or δk,[1,6] where k is the conventional first-order rate constant and μ or δ a factor of unit cm. Equations for reaction-affected currents are much simpler if expressed in terms of $(k)_h$ than k; consequently heterogeneous constants have been used almost exclusively in the past. The value of μ can be determined rigorously by equating the two current expressions based on the two rate constants and solving for μ directly. This has been done in several instances, and μ found to be given by a relatively simple expression; but the conditions that must be generally satisfied if the expression is to hold, and hence the restrictions that must be placed on the use of $(k)_h$ as a substitute for k, have not been adequately stated. Although the conclusions arrived at here are valid only for first-order rate constants, in practice the reactions usually involve two reactants, one of which is maintained at a constant concentration.

The Kinetic Current.—In a recent article,[7] Delahay has discussed the system

$$A \underset{k_b}{\overset{k_f}{\rightleftarrows}} B \qquad (1)$$

in which B is a species that depolarizes the d.m.e. and A is a species that does not. It was shown that if k_f is so small that the surface concentration of A is the same as the bulk concentration, the current

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[1] Paul Delahay, THIS JOURNAL, **73**, 4944 (1951).

[2] Paul Delahay, *ibid.*, **74**, 3506 (1952).

[3] K. Wiesner, *Z. Elektrochem.*, **49**, 164 (1943).

[4] K. Wiesner, *Coll. Czech. Chem. Comm.*, **12**, 64 (1947).

[5] R. Brdička and K. Wiesner, *ibid.*, **12**, 39, 138 (1947).

[6] Paul Delahay and Jacob E. Strassner, THIS JOURNAL, **73**, 5269 (1951).

[7] Paul Delahay, *ibid.*, **74**, 3506 (1952).

equations corresponding to the use of both types of constants are identical provided

$$(k_f)_h = \sqrt{k_f D_B/K} = k_f\sqrt{D_B/k_b} \qquad (2)$$

where $K = k_b/k_f$, and D_B is the diffusion coefficient in cm.^{2} sec.$^{-1}$. Thus

$$\mu = \sqrt{D_B/k_b} \qquad (3)$$

as found earlier by Koutecký and Brdička.[8] Delahay concluded that the relation (2) holds only under the above mentioned condition of constant C_A, *i.e.*, when k_f is so small that no diffusion gradient is set up, and the current is entirely reaction controlled. It can, however, be shown that the same proportionality holds no matter how large k_f, and how much the surface concentration is reduced below the bulk concentration, *i.e.*, even if the current is partly controlled by the diffusion of A. The only restriction is that it not be contributed to by the diffusion of B from the bulk of the solution.

A rigorous derivation of the combined diffusion and kinetic current has been given by Koutecký and Brdička.[8] They find that, providing only that the current contribution of the diffusion of B be relatively negligible, the current is expressed by the equation

$$i = nFsC_A{}^*\sqrt{Dk_f/K}\,\exp\,(k_f t/K)[1 - \text{erf}\,\sqrt{k_f t/K}]$$

where i is the instantaneous current at time t, s the electrode area, and $C_A{}^*$ the bulk concentration of A. Converted to the d.m.e. in the usual manner, this would give

$$i = 1255\,nm^{2/3}t^{2/3}C_A{}^*\sqrt{Dk_f/K}\,\exp\,(k_f t/K)[1 - \text{erf}\,\sqrt{k_f t/K}]$$

where i is in μamp. and $C_A{}^*$ in mmole/l. Comparing this equation with that of Delahay[1] obtained under the same restriction, but by the use of a heterogeneous rate constant, it is found again that $(k_f)_h = \sqrt{k_f D/K}$.

The expression (3) for μ is closely related to the average distance travelled by an ion in the time $1/k_b$, which is the average lifetime of the ion B.[8] Thus μ can be thought of as defining a reaction volume in which reaction (1) takes place and which covers all territory satisfying the following requirement, *viz.*, that an ion B produced at any point within it has a good chance of reaching the surface before disappearing by the backward reaction. Indeed, Wiesner[9] very early conjectured an expression for μ not unlike equation (3) on the basis of this reaction volume concept.[10]

In the light of this concept the logic of equation (3) will persist only if the mean lifetime $1/k_b$ is very much smaller than the drop time. But this is precisely what is ensured by the restriction that the diffusion current of B be negligible; for it requires that both K and k_f be large, and hence that k_b, which equals Kk_f, be larger still. Thus we come again to the conclusion that the validity of equation (3), and the applicability of the heterogeneous rate constant method for first-order kinetic currents, are subject to the restriction that the diffusion of B from the bulk of the solution be negligible compared with its formation by reaction (1). It should be observed, though, that the above statements concerning μ assume dimensionless diffusing bodies, and no longer hold when k_b is so large that $\sqrt{D/k_b}$ approaches ionic dimensions. Instead of obeying equation (3), μ may be expected to approach a limiting value related to the diameter of the ion B. This will not occur until $k_b >$ about 10^9 sec.$^{-1}$.

A small fixed value of μ will also be found if the reaction to which $(k_f)_h$ corresponds is an electron transfer at the electrode surface, as in the study of electrode processes. In that case μ corresponds to the distance an electron can traverse in its passage between ion and electrode. This distance is independent of k_b or the diffusion coefficient; the restrictions regarding the use of equation (3) therefore cannot apply, and the value of μ will remain the same whether diffusion or electron transfer is the rate determining process. Unlike the reactions that give rise to kinetic currents, these electrode reactions are true surface reactions, and the surface rate constants have a real physical significance. They must, however, be converted to volume constants if they are to be interpreted quantitatively by absolute rate theory, and to this end μ is assigned a value of the order of ångström units.[12]

The Catalytic Current.—The same principles apply to first-order catalytic currents, which arise from processes of the type

$$A \xrightarrow[\text{process}]{\text{electrode}} B \xrightarrow{k_b} A \qquad (4)$$

These currents can also be expressed in terms of an heterogeneous rate constant,[11] but since it is the electrode product which here reacts, the restriction is that the rate of diffusion of electrode product B away from the electrode surface must be negligible compared to its disappearance by reaction (4). On comparison with the rigorous expression obtained for this condition by the use of the normal rate constant,[11,13] the conversion factor is again found to be $\sqrt{D_B/k_b}$, where k_b is now the rate of depolarizer formation and $1/k_b$ the average lifetime of an ion of electrode product.

The analogy with the kinetic case is clear. Provided that $k_b > 100$ sec.$^{-1}$, the current for both cases can be expressed as

$$\bar{\imath} = nFC^0\bar{s}k_b\sqrt{D/k_b}\,\text{[13,14]} \qquad (5)$$

where C^0 is the surface concentration and the bulk concentration of B in the catalytic and kinetic cases, respectively. In equation (5) the current is the kinetic current, which under the given condition virtually equals the total current. When the diffusion current of B is considerable, equation (5) fails to give correct values for the catalytic current.

The value of μ necessary to make the equation fit under these conditions can be obtained by comparing the right-hand side of equation (5) with the rigorous relationship between the catalytic current (with the diffusion current subtracted out) and k_b

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(8) J. Koutecký and R. Brdička, *Coll. Czech. Chem. Comm.*, **12**, 337 (1947).

(9) K. Wiesner, *Chem. Listy*, **41**, 6 (1947).

(10) For a further discussion of the concept, see D. M. Kern, Ph.D. Dissertation, University of California, 1949, and ref. 11.

(11) S. Miller, THIS JOURNAL, **74**, 4130 (1952).

(12) J. B. B. Randles, *Trans. Faraday Soc.*, **48**, 832 (1952).

(13) P. Delahay, *ibid.*, **74**, 3500 (1952).

(14) P. Delahay, *ibid.*, **74**, 3497 (1952).

and the drop time t_1 plotted by Delahay.[13] In Table I the necessary correction factor c in the expression

$$\mu = c\sqrt{D/k_b}$$

is indicated for various values of k_b, assuming a drop time of 3 seconds. The relative importance of the diffusion portion of the current is given by the ratio $\bar{i}_d/\bar{i}_t$, $\bar{i}_t$ being the total current. In accord with the above discussion, c is seen to approach unity as i_d/i_t approaches zero. Thus equation (5) can be used to express the kinetic component of the current only if the diffusion component is negligible.

TABLE I

k_b, sec.$^{-1}$	c	$\bar{i}_d/\bar{i}_t$
0.01	0.08	0.98
0.1	.23	.86
1.0	.57	.45
10	.84	.15
100	1.0	.04

The values of c may be in error by as much as 10% because of errors involved in reading off points from Delahay's semi-logarithmic plot. The table shows that the effective reaction layer becomes increasingly narrower as the diffusion current becomes increasingly important. At large k_b values the $\sqrt{D/k_b}$ expression is correct.

The Factor $\sqrt{7/3}$ in Reaction-affected Currents.—In making the calculations for the table, a factor of $\sqrt{7/3}$ was inserted in equation (5) in order to make it coincide with the limiting expression given by Delahay, and thus provide values of c which would approach 1 as k_b became large. It has been the custom to insert this factor whenever converting from a fixed to a growing electrode surface by analogy with the pure diffusion case, where the correction is demanded by theory. Normally, this factor reflects the fact that as the electrode surface uniformly expands, the diffusion layer is continually being spread more thinly to cover the new surface: the resulting contraction, superimposed upon the usual widening of the layer with time, steepens the diffusion gradient and brings more depolarizer to the surface. Thus there is a current density greater than that expected from the simple Fick's law equation, in addition to there being an ever increasing area. This increased current density requires the additional factor $\sqrt{7/3}$.

For currents governed by equation (5), however, the gradient at the surface is not one which is built up slowly during the life of the drop and extends far into the solution. Rather, it reaches a steady state configuration almost instantly within the narrow confines of the reaction volume. As the surface expands, the reaction volume recovers its width very rapidly: it is always essentially at equilibrium with the growing drop. Hence the current density is not affected by the growth of the surface, and the increase in current is the result of the increase in area only.

Accordingly the factor $\sqrt{7/3}$ should be omitted from current equations for processes that do not involve time-dependent diffusion gradients. This applies to the limiting equations for catalytic and kinetic currents. As the current includes a larger and larger diffusion component, the factor will approach $\sqrt{7/3}$, but the exact manner in which it does so can be discovered only by solving the basic differential equations at a growing rather than a fixed area electrode. The uncertainty in this factor is transmitted to the value of the rate constants in all the current–rate constant relationships that have so far been derived; only in the limiting cases described by equation (5) can a correction be confidently made.

An Application.—The main advantage of the use of heterogeneous surface constants in obtaining expressions for reaction-affected currents is that they often afford a simple non-mathematical short-cut to a relation between rate constant and current. It is important, however, that the restriction discussed above be considered.

An illustration of the simple solution of a kinetic problem by the proper use of the heterogeneous rate constant is the following. Let us consider the case

$$\text{A} \underset{\text{process}}{\overset{\text{reversible electrode}}{\rightleftharpoons}} \text{B} \xrightarrow{k_b} \text{non-depolarizing species}$$

at the d.m.e. This mechanism has been suggested by L. I. Smith, *et al.*,[15] for the polarographic oxidation of hydroxychromans and hydroxycoumarans. According to Vavřín[16] the oxidation of *l*-ascorbic acid occurs by a similar reaction path. Both authors recognized that the rate of the follow-up reaction would influence the observed $E_{1/2}$, but they did not give an exact relationship in terms of the true homogeneous rate constant k_b.

In this instance, the limiting diffusion current will not be affected by the follow-up reaction. In the rising portion of the wave, the current can be described as

$$\bar{i} = nF\bar{s}(\mu k_b)C_B^0 + K_B C_B^0 \qquad (6)$$

and

$$i = K_A(C_A^* - C_A^0) = i_d - K_A C_A^0 \qquad (7)$$

where K_A and K_B are the Ilkovic constants for A and B, C_A^0 the surface concentration of A, and C_B^0 the surface concentration of B. By analogy with the catalytic current case (μk_b) can be simply related to k_b if the second term of (6), the diffusion term, is negligible, *i.e.*, if k_b is sufficiently large, in which case $\mu = \sqrt{D_B/k_b}$. Applying this restriction, and combining this expression and equations (6) and (7) with the Nernst equation, we find

$$E = E_0 - \frac{RT}{nF}\left[\ln\frac{\bar{i}_d - \bar{i}}{\bar{i}} + \ln\frac{nF\bar{s}\sqrt{k_b D_B}}{K_A}\right] \qquad (8)$$

or

$$E_{1/2} = E_0 - \frac{RT}{nF}\ln\frac{nF\bar{s}\sqrt{k_b D_B}}{K_A}$$

Replacement of $\bar{s}$ by $3/5 \times 8.5 \times 10^{-3}\ m^{2/3}t_1^{2/3}$ cm.^{2} and the Ilkovic constant by $605\ nm^{2/3}t_1^{1/6}D_A^{1/2}$ yields at 25° the equation

$$E_{1/2} = E_0 - \frac{0.059}{n}\log 0.81\sqrt{D_B/D_A} - \frac{0.059}{2n}\log k_b t_1 \qquad (9)$$

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(15) L. I. Smith, I. M. Kolthoff, Stanley Wawzoneck and R. M. Ruoff, THIS JOURNAL, **63**, 1018 (1941). The relevant material can be found also in Kolthoff and Lingane, "Polarography," 2nd edition, Vol. 1, John Wiley and Sons, Inc., New York, N. Y., p. 264–266.

(16) Z. Vavřín, *Coll. Czech. Chem. Comm.*, **14**, 367 (1949).

where t_1 is the drop time. If it is supposed that diffusion of B may be considered negligible if the second term of the right side of equation (6) is less than 5% of the first, equation (9) will hold for $k_b >$ about 100 sec.$^{-1}$ for normal t_1 values. Though $E_{1/2}$ is a function of k_b, the shape of the wave remains unaltered, as seen from equation (8). The expressions obtained by Smith and Vavřín have a similar form, though they do not contain k_b and t_1. Since E_0 is not known for the reactions studied and k_b cannot be varied in a controlled manner, there are as yet no data available to test equation (9). However, it is planned to investigate the dependence of $E_{1/2}$ on t_1, which has not yet been studied for this type of reaction.

It should be pointed out that the analogy between this and the kinetic case is not complete, because there the surface concentration of reactant remains constant, whereas here it may diminish under the influence of a high reaction rate. It is possible that under such circumstances, the restriction on diffusion is somewhat relaxed. In a study of the second-order kinetic case,[17] in which the surface concentration of reactant is variable, it was found that equations of type (6) held quite well over a wide range of reaction–diffusion ratios.

The $E_{1/2}$ of Catalytic Waves.—It is interesting to compare this relationship of $E_{1/2}$ and k_b with that obtaining in the ordinary catalytic wave. It is found by the argument given below that in the latter case $E_{1/2}$ and k_b are independent.

The equations for the rising part of the curve are

$$\partial C_A/\partial t = D_A(\partial^2 C_A/\partial x^2) + k_b C_B$$
$$\partial C_B/\partial t = D_B(\partial^2 C_B/\partial x^2) - k_b C_B$$

with the boundary conditions $C_A = a$ and $C_B = 0$ for $t = 0$; and for $x = 0$, $\partial C_A/\partial x = -(D_B/D_A)\cdot\partial C_B/\partial x$ and $C_A/C_B = [nF/RT] \exp (E_0 - E)$. If D_A and D_B are assumed equal, application of the Laplace transformation in the usual manner yields the result

$$(\partial C_A/\partial x)_{x=0} = (1 + q)^{-1}[a\sqrt{k_b/D}(e^{-k_b t}/\sqrt{\pi k_b t} + \operatorname{erf} \sqrt{k_b t})]$$

where $q = [nF/RT] \exp (E_0 - E)$. The term inside the square brackets is the expression for $(\partial C_A/\partial x)_{x=0}$ under limiting current conditions. It follows that $E_{1/2} = E_0$ and that the current dependence on E is exactly what it would be if the limiting current were a normal diffusion current.

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(17) To be published in THIS JOURNAL.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Solubility Product of Ferrous Hydroxide and the Ionization of the Aquo-Ferrous Ion

BY D. L. LEUSSING AND I. M. KOLTHOFF

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The solubility products $S_{1\text{Fe(OH)}_2} = a_{\text{FeOH}^+} \times a_{\text{OH}^-}$ and $S_{2\text{Fe(OH)}_2} = a_{\text{Fe}^{++}} \times a^2_{\text{OH}^-}$ have been determined in air-free suspensions of ferrous hydroxide at 25°. Average values of S_1 of 4×10^{-10} and of S_2 of $8 \pm 3 \times 10^{-16}$ were found. The ferrous ion forms an unstable complex with ammonia. The ionization constant of the aquo-ferrous ion $a_{\text{FeOH}^+}a_{\text{H}^+}/a_{\text{Fe}^{++}}$ was calculated to be equal to 5×10^{-9}. A brief discussion is given of the relation between our results and those in the literature.

In an investigation of the complexes formed between ferrous iron and thioglycolate it was necessary to know the value of the solubility product of ferrous hydroxide. Many and varying values of the solubility product have been reported in the literature. A summary of these values is given in Table I.

All these values have been calculated on the basis of the dissociation of an aqueous solution of ferrous hydroxide into ferrous and hydroxyl ions.

TABLE I

DATA ON THE SOLUBILITY OF FERROUS HYDROXIDE REPORTED IN THE LITERATURE

A. Solubility of ferrous hydroxide in water

Solubility (*M*)	Reference	
6.7×10^{-5}	Whitman, *et al.*	1
1.35	Lamb	2
7.5	Bineau	3
0.73	Murata	4

B. Solubility product of ferrous hydroxide in water

$S\text{Fe(OH)}_2 =$ $[\text{Fe}^{++}][\text{OH}^-]^2$	Method	Reference	
3.2×10^{-14}	Solubility	Whitman, *et al.*	1
9.9×10^{-15}	Conductivity	Lamb	2
8.7×10^{-14}	Solubility	Krassa	5
2.9×10^{-15}	Conductivity	Murata	4
1.56×10^{-15}	Solubility	Murata	4
2.13×10^{-15}	Colorimetric *p*H	Murata	4
4.5×10^{-21}	Potentiometric	Britton	6
4.8×10^{-16}	titration	Elder	7
3.9×10^{-15}	*p*H	Shipley & McHaffie	8
7×10^{-13}	Polarographic	Shrager	9
1.7×10^{-15}	E.m.f.	Randall	10
2.4×10^{-14}	Potentiometric titration	Arden	11

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(1) W. G. Whitman, R. P. Russell and G. H. P. Davis, THIS JOURNAL, **47**, 70 (1925).

(2) A. B. Lamb, *ibid.*, **32**, 1214 (1910).

(3) M. A. Bineau, *Compt. rend.*, **41**, 509 (1879).

(4) K. Murata, *J. Chem. Ind.Japan*, **35**, 523 (1932).

(5) P. Krassa, *Z. Elektrochem.*, **15**, 490 (1909).

(6) H. T. S. Britton, *J. Chem. Soc.*, **127**, 2110 (1925).

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(10) M. Randall and M. Frandsen, THIS JOURNAL, **54**, 40 (1932).

(11) T. V. Arden, *J. Chem. Soc.*, 882 (1950).