[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Polarographic Currents from a Combination of Diffusion and Reaction

BY STANLEY LLOYD MILLER

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Solutions to the differential equations for the combination of diffusion and first-order reaction at a plane electrode are given, and applied with several approximations to the dropping mercury electrode. The agreement of the equations with the data of Kolthoff and Parry for the kinetic currents of ferric ion in the presence of hydrogen peroxide is good. The effective reaction layer thickness is discussed, and values of this thickness of 10^{-2} to 10^{-3} cm. are shown to be more significant in certain cases than the previously assumed value of 10^{-7} cm.

In a recent paper by Kolthoff and Parry[1] the investigation of the catalytic polarographic currents of ferric iron in the presence of hydrogen peroxide was described. In the interpretation of their data, they used the treatment of Brdicka and Wiesner[2] which involves the estimation of the effective thickness of the reaction layer. When the reaction layer was assumed to be 10^{-7} cm. thick, the rate constant for the reaction of ferrous ion with hydrogen peroxide was calculated to be 10^4 times larger than the known value. In this paper a different and more rigorous interpretation of this type of kinetic effect will be given, and the factors entering into the estimation of the reaction layer thickness will be discussed.

When ferric ion is present in a solution of hydrogen peroxide and a sufficiently positive potential (+0.20 volt *vs.* S.C.E.) is applied to the dropping electrode such that neither hydrogen peroxide nor oxygen is reduced at the electrode, the electrode reaction is

$$Fe^{+3} + e^- = Fe^{+2} \qquad (I)$$

and in the solution near the electrode the reaction is

$$2Fe^{+2} + H_2O_2 + 2H^+ = 2Fe^{+3} + 2H_2O \qquad (II)$$

The rate law for this reaction (neglecting side reactions and catalysis) has been shown by various investigators to be

$$d(Fe^{+3})/dt = k_r(Fe^{+2})(H_2O_2)$$

If the peroxide is in excess, the concentration of the peroxide will not change appreciably during the reaction. The peroxide concentration can then be absorbed into the rate constant such that $k = k_r$ (H_2O_2), and the reaction will appear to be a first-order reaction in ferrous.

In the general case, corresponding to eq. I, the electrode reaction is

$$A + e^- = B \qquad (III)$$

and in the solution near the electrode, corresponding to eq. II

$$B \xrightarrow{k} A \qquad (IV)$$

The change in concentration of species A with time due to diffusion at a plane electrode is given by Fick's second law of diffusion as $\partial A/\partial t = D_A \partial^2 A/\partial x^2$. This equation holds for every point in the solution. The change in concentration of A with time due to chemical reaction is $\partial A/\partial t = kB$. This also holds for every point in the solution. Therefore, for the combination of diffusion and reaction the change in concentration of A with time is

$$\frac{\partial A}{\partial t} = D_A \frac{\partial^2 A}{\partial x^2} + kB \qquad (1)$$

Similarly for B we have

$$\frac{\partial B}{\partial t} = D_B \frac{\partial^2 B}{\partial x^2} - kB$$

The change in concentration of B with time due to chemical reaction is negative because B is depleted by the chemical reaction.

At a plane electrode the following initial and boundary conditions will hold.

$$\begin{array}{lll} x \geqq 0 & t = 0 & A = A_0,\ B = 0 \\ x = 0 & t > 0 & A = 0 \end{array}$$

A and B are the concentrations in moles per liter, A_0 is the concentration in the body of the solution, and D is the diffusion coefficient in cm.^{2} sec.$^{-1}$.

Although in general D_A and D_B are not equal, in most cases the diffusion coefficients are approximately equal. To solve these differential equations would be quite difficult because of the boundary conditions unless the assumption that D_A and D_B are equal is made. Furthermore a steady state solution will give us the approximate influence of D_A and D_B on the current when they are not equal.

These equations can be solved, then, by means of the Laplace Transformation[3] and also by the usual methods of differential equations.[4,5] The solution for A is

$$A = A_0 \left[1 - \frac{e^{-\sqrt{\frac{k}{D}}\,x}}{2} \left\{ 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}} - \sqrt{kt} \right) \right\} - \frac{e^{\sqrt{\frac{k}{D}}\,x}}{2} \left\{ 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}} + \sqrt{kt} \right) \right\} \right] \qquad (2)$$

and for B is

$$B = A_0 - A \qquad (3)$$

where

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-y^2}\,dy$$

When $k = 0$, which corresponds to pure diffusion, we have from eq. 2, $A = A_0 \operatorname{erf}(x/2\sqrt{Dt})$ which is the same result as has been previously found for

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[1] I. M. Kolthoff and E. P. Parry, THIS JOURNAL, **73**, 3718 (1951).

[2] R. Brdicka and K. Wiesner, *Collection Czech. Chem. Commun.*, **12**, 39 (1947).

(3) D. M. Kern, Ph.D. Dissertation, Univ. of California, 1949. The solution of this particular problem is given as far as eq. 8.

(4) I. M. Kolthoff and S. E. Khalafalla (personal communication) have solved these equations and obtained the same results for equations 2 and 6, but they used a different method for approximating the current.

(5) H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids," Oxford Univ. Press, 1947, pp. **111** and **270**, give solutions to equations similar to the above.

pure diffusion.[6] When $t \rightarrow \infty$, we obtain from eq. 2

$$A = A_0(1 - e^{-\sqrt{k/D}\,x}) \tag{4}$$

and from eq. 3

$$B = A_0 e^{-\sqrt{k/D}\,x} \tag{5}$$

This means that a steady state is set up.

The gradient of A at $x = 0$ is given by

$$(\partial A/\partial x)_{x=0} = A_0\sqrt{k/D}\,(e^{-kt}/\sqrt{\pi kt} + \operatorname{erf}(\sqrt{kt})) \tag{6}$$

When $k = 0$ we have from eq. 6

$$(\partial A/\partial x)_{x=0} = A_0/\sqrt{D\pi t} \tag{7}$$

which is the same as for pure diffusion.[6] As t becomes large, eq. 6 tends rapidly to $A_0\sqrt{k/D}$.

The current at the rapidly obtained steady state is given by

$$i = nFsD(\partial A/\partial x)_{x=0} = nFs\sqrt{Dk}A_0 \tag{8}$$

where s is the area of the plane electrode, F is the faraday, n is the number of electrons in the reduction of A. This current is the total current and not just the kinetic current.

Since a steady state is quickly set up by the combination of diffusion and reaction, the concentration of A and B do not change with time, so at large t $\partial A/\partial t = 0$, and $\partial B/\partial t = 0$. In other words, it has been shown that the solution of the partial differential equations gives a steady state at large t; since the steady state should be independent of the initial conditions provided the steady state boundary conditions are the same, we will assume that sufficient time has elapsed to reach a steady state and solve the resulting equations under these conditions.

The partial differential equations, 1, thus become a pair of ordinary differential equations.

$$\begin{aligned} D_A\,d^2A/dx^2 + kB &= 0 \\ D_B\,d^2B/dx^2 - kB &= 0 \end{aligned} \tag{9}$$

with the boundary conditions

$$\begin{array}{ll} x = 0 & A = 0 \\ x \gg 0 & A = A_0,\ B = 0 \end{array}$$

The solution of these equations is

$$A = A_0(1 - e^{-\sqrt{k/D_B}\,x}) \tag{10}$$

$$B = A_0(D_A/D_B)e^{-\sqrt{k/D_B}\,x} \tag{11}$$

Evaluating the gradient of A at $x = 0$, we have $(dA/dx)_{x=0} = \sqrt{k/D_B}A_0$ and the current is given by

$$i = nFs(D_A/D_B)\sqrt{kD_B}A_0 \tag{12}$$

If D_A and D_B are equal, eqs. 10, 11 and 12 reduce to eqs. 4, 5 and 8, respectively. Thus although we did not solve the partial differential equations when the diffusion coefficients were not equal, the steady state solution has given us an indication as to how the differing diffusion coefficients might enter into the solution of the partial differential equations at the non-steady state. However, this factor D_A/D_B will not be introduced into the following calculations because of the uncertainty of this ratio in the case of ferric and ferrous ions.

Since these results are for a plane electrode, some modifications must be made for the dropping electrode. The area of the dropping electrode is $s = 0.85\,m^{2/3}t^{2/3}$ where m is the rate of flow of mercury in grams/sec., and t is the time in seconds. In the case of pure diffusion there is a distortion of the diffusion gradient due to the expanding drop which increases the gradient by a factor of $\sqrt{7/3}$.[7] This factor will be assumed for the present to hold for the case of diffusion and reaction also. This is not rigorous, and a correction will be made later on the basis of the experimental results.

The current as a function of time is obtained by combining eqs. 6 and 8 to give

$$i = 0.85\sqrt{7/3}\,nFA_0\,m^{2/3}t^{1/6}\sqrt{D/\pi}\,(e^{-kt} + \sqrt{\pi kt}\operatorname{erf}(\sqrt{kt}) \tag{13}$$

In order to find the average current we will replace the function

$$e^{-kt} + \sqrt{\pi kt}\operatorname{erf}(\sqrt{kt}) \tag{14}$$

by the approximation

$$\sqrt{\pi kt} + \exp(2.4(kt)^{7/12}) \tag{15}$$

where $\exp(z) = e^z$. The approximation represents eq. 14 to 1% for small kt and at large kt it becomes more accurate. The approximation was obtained by trial and error.

The average current, i_{av}, as would be measured by a damped galvanometer for a drop of life time t_1 is

$$i_{av} = \frac{1}{t_1}\int_0^{t_1} i\,dt =$$
$$\frac{0.85}{t_1}\sqrt{7/3}\,nFA_0m^{2/3}\sqrt{D/\pi}\left[\int_0^{t_1}\sqrt{\pi k}t^{2/3}\,dt + \int_0^{t_1}\exp(-2.4(kt)^{7/12})dt\right]$$

The first integral in the brackets is just $(3/5)\sqrt{\pi k}t_1^{5/3}$. The second integral is evaluated by making the substitution $y = t^{7/12}$ which transforms it into the form $\int_0^t (12/7)y\exp(-2.4\,k^{7/12}y)\,dy$, which is easily integrated by parts. Combining constants and expressing m in milligrams/sec., t_1 in sec., A_0 in millimoles/liter, i in microamps, the average current is

$$i_{av} = 753\,nA_0m^{2/3}\sqrt{kD}t_1^{2/3} + 210\,nA_0m^{2/3}\sqrt{D}\left[\frac{1 - (1 + 2.4(kt_1)^{7/12})\exp(-2.4(kt_1)^{7/12})}{k^{7/12}t_1}\right] \tag{16}$$

When $k = 0$, the first term becomes zero, and the second term can be shown to reduce to the Ilkovic equation by expanding the exponentials in a power series. At large k, the first term predominates and the second term tends to zero.

Now it was assumed that the diffusion gradient was increased by a factor of $\sqrt{7/3}$ in the case of diffusion and reaction as well as for pure diffusion. The experimental results will be shown not to confirm this assumption. In order to get the best agreement with the experimental results, the arbitrary assumption will be made that instead of $\sqrt{7/3}$, the distortion of the diffusion gradient at the steady state of diffusion and reaction is $0.69\sqrt{7/3}$. This

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[6] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1940, p. 19.

[7] D. Ilkovic, *Collection Czech. Chem. Commun.*, **6**, 498 (1934); *J. chim. phys.*, **35**, 192 (1938).

factor applies only to the first term and not to the second term of eq. 16, because if it did apply to the second term, eq. 16 would not reduce to the Ilkovic equation when $k = 0$. Thus eq. 16 becomes

$$i_{av} = 519\ nA_0m^{2/3}\sqrt{Dk}t_1^{2/3} + 210\ nA_0m^{2/3}\sqrt{D}\left[\frac{1 - (1 + 2.4(kt_1)^{7/12})\exp(-2.4(kt_1)^{7/12})}{k^{7/12}t_1}\right] \quad (17)$$

The ratio of the total current to the diffusion current (the current of the ferric ion with no hydrogen peroxide present) is found by dividing eq. 17 by the Ilkovic equation to give

$$\frac{i_{total}}{i_{diff.}} = 0.858\sqrt{kt_1} + 0.347\left[\frac{1 - (1 + 2.4(kt_1)^{7/12})\exp(-2.4(kt)^{7/12})}{k^{7/12}t_1}\right] \quad (18)$$

Comparison of Equations 16 and 17 with Kolthoff and Parry's Data.—The mechanism of the reaction between ferrous ion and hydrogen peroxide at the dropping mercury electrode has been discussed by Kolthoff and Parry.[1] The following simplifying assumptions and data will be used in the calculations. The extrapolation of the recent data of Barb, *et al.*,[8] gives a value of k_r = 75 liters/mole-sec. at 30° for the reaction

$$Fe^{+2} + H_2O_2 = Fe^{+3} + OH + OH^- \quad (V)$$

When the acrylonitrile is not present (neglecting the side reactions of Barb's mechanism or the Haber and Weiss[9] mechanism) the assumption will be made that the stoichiometry corresponds to eq. II, and therefore the rate of this reaction is just $2k_r$ = 150 liters/mole-sec.

In the presence of acrylonitrile, it will be assumed that all the hydroxyl radicals produced in the initiating step react with the acrylonitrile to form an acrylonitrile radical (which polymerizes and so is not reduced) instead of reacting with a second ferrous ion. Thus the stoichiometry of the reaction corresponds to one ferrous for each peroxide, and the rate constant is just 75 liters/mole-sec.

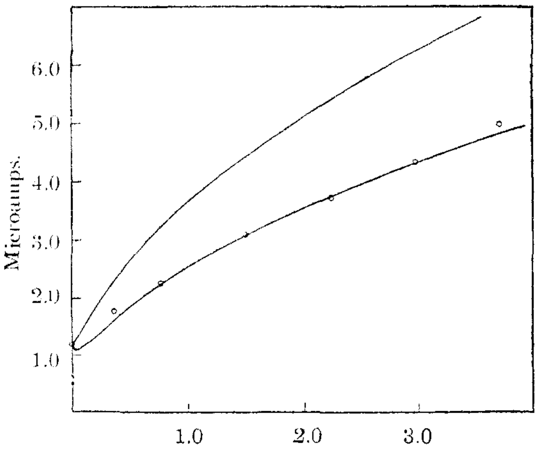

Fig. 1.—Total current of 2.0 × 10^{-4} *M* ferric ion in the presence of 0.25 *M* H_2SO_4, 0.005% gelatin, and varying concentrations of hydrogen peroxide at 30°. Upper curve calculated from eq. 16. Lower curve calculated from eq. 17. Points are experimental data of Kolthoff and Parry.

The diffusion coefficient of ferric ion is calculated from Parry's data[10] to be 29.8 × 10^{-6} cm.^{2} sec.$^{-1}$ at 30°. Although this seems quite large for a plus three ion, this value would have to be used in order to make the data consistent, as is seen from eq. 18, which shows that the ratio of the total current to the diffusion current does not depend on the diffusion coefficient. The diffusion coefficient of ferrous ion will be taken to be the same as ferric ion. The value of t_1 is 4.02 sec. and m is 1.680 mg./sec. The currents considered will be those in the presence of 0.005% gelatin as maximum suppressor, and the currents have been corrected for residual and hydrogen peroxide currents.

The comparisons of Kolthoff and Parry's experimental data and the theoretical results are shown in Figs. 1, 2 and 3. In the three figures the points are the experimental results of the total current, the upper solid curve is calculated from eq. 16, and the lower solid curve is that calculated from eq. 17.

In Fig. 1 the points represent the total current of 2.0 × 10^{-4} *M* ferric ion in the presence of varying concentrations of hydrogen peroxide. In Fig. 2 the points represent the total current of 2.0 × 10^{-4} *M* ferric ion in the presence of varying concentrations of hydrogen peroxide with 0.06 *M* acrylonitrile present. In Figs. 1 and 2 the agreement of eq. 16 with the experimental results is correct in form for the larger concentrations of hydrogen peroxide, and the agreement of the data with eq. 17 is within the experimental error. The dip near zero peroxide concentration in the curve calculated from eq. 17 is due to the nature of the approximation function (eq. 15) and to the arbitrary setting of 0.69 $\sqrt{7/3}$ as the factor for the diffusion gradient distortion. If eq. 16 is applied to calculate the rate con-

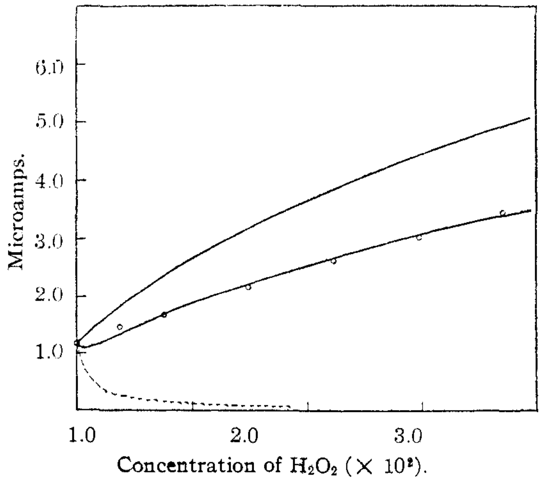

Fig. 2.—Total current of 2.0 × 10^{-4} *M* ferric ion in the presence of 0.25 *M* H_2SO_4, 0.06 *M* acrylonitrile, 0.005% gelatin, and varying concentrations of hydrogen peroxide. Upper curve calculated from eq. 16. Lower curve calculated from eq. 17. Points are experimental data. Broken curve is contribution of current from second term of eq. 16 or 17.

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[8] W. G. Barb, J. H. Baxendale, P. George and K. R. Hargrave, *Nature*, **163**, 692 (1949); *Trans. Faraday Soc.*, **47**, 462 (1951).

[9] F. Haber and J. Weiss, *Naturwissenschaften*, **20**, 948 (1932); *Proc. Roy. Soc.* (*London*), **A147**, 332 (1934).

[10] E. P. Parry, Ph.D. Thesis, Univ. of Minnesota, 1950.

stants from the experimental data, the value of k_r will be 0.50 times the known value. This is to be compared with the factor of 10^4 from the Brdicka and Wiesner treatment.[1]

The dashed curve in Fig. 2 gives the contribution of the second term of eq. 16 and 17. This shows how quickly this term falls off, and indicates that steady state solutions in cases of non-linear differential equations might be helpful in solving for the currents as was done with eq. 9.

In Fig. 3 the dependence of the total current on the concentration of ferric in 0.04 *M* hydrogen peroxide is shown. The observed linear dependence of the current on the concentration of ferric ion is predicted from eqs. 16 and 17. The agreement with eq. 17 is not as good as in Figs. 1 and 2, but is almost within the experimental error.

Further support for the treatment is found in the independence of the total current on the mercury column height[11] which is predicted if the current varies as $(mt)^{2/3}$. This is approximated by eq. 17.

The Estimation of the Effective Reaction Layer Thickness.—The problem of the estimation of the reaction layer thickness, μ, deserves some discussion. μ has always been assumed to be 10^{-7} cm.[12] There is, however, no evidence to always use this arbitrary choice.

Let us consider more closely the meaning of μ as formulated by Brdicka and Wiesner.[2] Assuming a bimolecular rate law, the magnitude of the catalytic current is determined by the number of equivalents of ferric formed in the volume close to the drop due to this bimolecular reaction. This reaction volume is equal to μs where s is the area of the electrode, and μ is the thickness of the reaction volume as measured from the surface of the electrode. The kinetic current is thus given by the amount of reducible material formed in this reaction volume times nF, so

$$i_k = nF\,10^{-3}\mu k_r\,(H_2O_2)_0\,(Fe^{+2})_0 \qquad (19)$$

where $(H_2O_2)_0$ and $(Fe^{+2})_0$ represent the concentrations of the respective substances at the interface of the electrode. The factor of 10^{-3} enters because concentrations are expressed in moles/liter and μs is expressed in milliliters. The value of n is 2 because two ferric ions result from each hydroxide that is reduced. This equation implies that all the ferric produced inside this volume is reduced, and any ferric outside this volume (beyond a distance μ from the electrode) is not reduced.

This state of affairs certainly does not exist, because the ferric ions in their random motions would cross this boundary in both directions. In other words, the diffusion gradient extends far out into the solution, and does not stop at an arbitrary point. Therefore μ must be considered to be an arbitrary parameter, having no precise physical meaning, but rather that distance from the electrode which if all ferric in this volume were reduced and no other, the current would be the current actually observed.

By considering μ as an arbitrary parameter, statistical derivations of μ have been made by Wiesner[13] for the acid dissociation case, and by Kern[3] for the disproportionation case.

That μ is often much larger than 10^{-7} cm. is shown by the following examples. The value of μ for the case of pure diffusion can be calculated as follows. The concentration gradient of A at the surface of a plane electrode is given by eq. 7. The number of moles of material reaching the electrode per second per square centimeter, dN/dt, is given by Fick's first law of diffusion and from eq. 7.

$$dN/dt = D(\partial A/\partial x)_{x=0} = A_0\sqrt{D/\pi t}$$

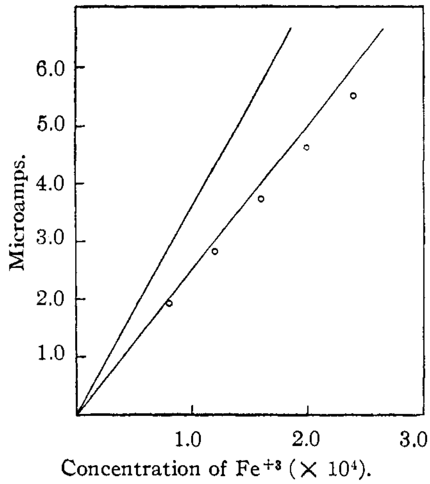

Fig. 3.—Total current of varying concentrations of ferric ion in the presence of 0.04 *M* hydrogen peroxide, 0.25 *M* H_2SO_4, 0.005% gelatin at 30°. Upper line calculated from eq. 16. Lower line calculated from eq. 17. Points are experimental data.

The total moles of reducible material that will have arrived at the electrode after time t is

$$N = \int_0^t A_0\sqrt{D/\pi t}\,dt = 2A_0\sqrt{Dt/\pi}$$

Thus if we were to construct the oversimplified model of the pure diffusion process involving the arbitrary reaction volume of thickness μ such that all the material within a distance μ reached the electrode, and any outside this distance did not, we would choose the value of $2\sqrt{Dt/\pi}$ for μ. In this case, then, μ is a function of D and t and is not constant.

Using a value for D of 7×10^{-6} and a value of t of 4 sec., μ is calculated to be 6.0×10^{-3} cm. Using this value of μ instead of 10^{-7} cm. the rate constants calculated from Kolthoff and Parry's data are of the right order of magnitude. Antweiler's photographic studies of the diffusion layer have shown it to be on the order of 5×10^{-3} cm. thick.[14] Although the "photographic thickness" is not the same as the effective thickness, the values should be about the same. This is confirmed by the above figures.

In the case of the kinetic waves of ferric and hydrogen peroxide, μ would be $\sqrt{D/k}$ as is seen from eq. 8 and 19. μ is then calculated to be 1.9×10^{-3} cm. using D as 7×10^{-6} and k as 2 per sec. The faster the reaction is, the smaller the reaction volume, which corresponds to the picture that the faster the ferrous ions produced by the electrode react with the hydrogen peroxide, the shorter time it has to diffuse out into the solution, and so the smaller the reaction volume.

In the disproportionation case, Kern[3] has shown that $\mu = 0.30\sqrt{Dt}$. Using D as 7×10^{-6} and t of 4 sec., μ becomes 1.6×10^{-3} cm.

In the acid dissociation case where the acid is reduced at a more positive potential than its anion and the current is determined by the rate of recombination of the anion with hydrogen ion, the value of μ is approximately $\sqrt{D/kK}$[14,15] where k is the rate of recombination of the anion, and K is the equilibrium constant for the acid. The previous cases have dealt with kinetic currents that have resulted from chemical reactions involving species produced by the electrode while in the acid dissociation case, the kinetic current is due to a reaction of a species that does not enter into the electrode reaction. Due to the large values of k needed to produce a significant kinetic current, the values of μ will be smaller, and closer to the usually assumed value of 10^{-7} cm. but still depending on the rate constant, diffusion coefficient and equilibrium constant.

Therefore we see that μ is not a quantity that is the same

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[11] Reference 1, Table III.

[12] References 1 and 2. R. Brdicka and K. Wiesner, *Collection Czech. Chem. Commun.*, **12**, 212 (1947); I. M. Kolthoff and A. Liberti, THIS JOURNAL, **70**, 1885 (1948); K. Wiesner, *Z. Elektrochem.*, **49**, 164 (1943).

[13] K. Wiesner, *Chem. Listy*, **41**, 6 (1947).

[14] H. J. Antweiler, *Z. Elektrochem.*, **44**, 719, 831, 888 (1938).

[15] J. Koutecky and R. Brdicka, *Collection Czech Chem. Commun.*, **12**, 337 (1947).

for all cases, but generally becomes smaller for a faster reaction and smaller diffusion coefficient. However, values of μ from 10^{-2} to 10^{-3} cm. will at least predict the order of magnitude of the rate constants for the cases where the reaction involves a reduction product of the electrode, and values closer to 10^{-7} cm. for reactions that precede the electrode reduction.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KENTUCKY]

Properties of Dilute Solutions of Magnesium Halides in Ethanol at 20° from Conductance Measurements[1,2]

BY LYLE R. DAWSON AND MICHAEL GOLBEN

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The electrical conductances of dilute solutions of magnesium chloride, bromide and iodide in ethanol at 20° have shown these halides to be incompletely dissociated electrolytes increasing in strength in the order named. The data gave evidence of second stage dissociation in the dilute range. A mass law expression has been derived for the secondary dissociation of a bi-univalent electrolyte for the special case in which the primary dissociation is substantially complete. An expression has been developed for the secondary dissociation which corrects the mass law expression for ion retardation and deviation from ideality in the manner of Fuoss and Shedlovsky. Limiting equivalent conductances, actual and theoretical slopes, classical and thermodynamic dissociation constants have been computed for the magnesium halides in ethanol at 20°.

Recent conductance work with ethanol solutions of bi-univalent salts has been confined largely to solutions in the mixed solvent ethanol–water of different ratios rather than in ethanol alone.[3–5] An exception is the work of Olmer,[6] who measured the conductance of magnesium chloride in ethanol and obtained an improbably low value of Λ_0, indicating that his measurements were not carried to a dilution necessary to show a rapid change in equivalent conductance in the very dilute range.

Paucity and variability of existing conductance data for ethanol solutions of polyvalent electrolytes are due partly to difficulties of experimentation and interpretation. Solvent and salts must be anhydrous. The true trend of a multi-step dissociation may not be revealed in non-aqueous solutions except at dilutions where experimental error tends to increase rapidly. Sometimes solute–solvent relationships complicate the interpretation of data.

In the studies reported here the magnesium halides in dilute ethanol solution were found to be weak electrolytes undergoing second-stage dissociation. A dilution law has been developed for the secondary dissociation, as well as an equation corrected for interionic effects in a manner similar to that of Fuoss and Kraus[7] and Shedlovsky[8] for weak uni-univalent electrolytes. This equation has been applied to the data by plotting parameters which would show linearity if the assumed relationships were correct.

Experimental

Preparation of Anhydrous Ethanol.—Ethanol of low specific conductance and high purity was prepared from commercial absolute alcohol by azeotropic distillation with small amounts of benzene, adding alkaline silver oxide to remove aldehyde, then refluxing briefly with aluminum amalgam and activated alumina. The mixture was distilled slowly, retaining the middle portion for conductance work. The average specific conductance of the samples used was 3×10^{-8} ohm^{-1}.

Preparation of Solutions.—Anhydrous solutions of the magnesium halides were prepared by dissolving best grade commercial salts in anhydrous ethanol and removing the water by azeotropic distillation, first using dry redistilled benzene, then dry redistilled ether.

Substantially the same conductance results were obtained by an alternate method of preparing anhydrous magnesium chloride, involving careful preparation of a magnesium chloride-pyridine complex and heating under vacuum to remove the pyridine.[9] The ethanol solutions were tested for water by density measurements and a modified Weaver test.[10] The halide concentration of each was determined by potentiometric titration with 0.01 *N* silver nitrate, using a Fisher titrimeter with silver and calomel electrodes.

A Dike bridge,[11] incorporating features recommended by Jones and Josephs[12] and Shedlovsky,[13] was used. The conductivity cell was held in a kerosene-bath thermostated at 20 ± 0.001°.

Experimental Technique.—The "solution addition" technique[14] was adopted. After calibration the buret was filled through the tip from a stock solution by means of air pressure, 30 to 40 g. of freshly distilled ethanol was transferred to the conductance cell, and the unit assembled. The conductance of the solvent was obtained *in situ* upon reaching temperature equilibrium after several passes between cell and mixing chamber. Each subsequent addition of stock solution from the buret was followed by mixing in the mixing chamber, then several passes between chamber and cell until the resistance readings became constant.

An Expression for the Secondary Dissociation of Bi-univalent Salts

Preliminary values for the limiting equivalent conductances of the magnesium halides in ethanol solution as obtained by extrapolation of the Kohlrausch plots gave evidence that secondary dissociation occurred in dilute solution. Treatment of these solutions as electrolytes for which primary and secondary dissociations occur simultaneously,

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[1] Abstracted from a Ph.D. dissertation submitted by Michael Golben.

[2] Support for part of this work was received from a research contract with the U. S. Army Signal Corps.

[3] I. C. Connell, R. T. Hamilton and J. A. V. Butler, *Proc. Roy. Soc. (London)*, **A147**, 418 (1934).

[4] B. Norberg and C. J. Clemedson, *Arkiv Kemi, Mineral. Geol.*, **A16**, No. 4 (1942); ref. *Chem. Zentr.*, **114**, I, 130 (1943).

[5] R. L. Bateman, University Microfilms (Ann Arbor, Mich.), Publication No. 668.

[6] F. Olmer, *Bull. soc. chim. France*, [5] **5**, 1178 (1938).

[7] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 2387 (1933); **57**, 1 (1935).

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