[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY]

Implications of the Kinetics of Ionic Dissociation with Regard to Some Electrochemical Processes—Application to Polarography

BY PAUL DELAHAY

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Various implications of Onsager's theory of ionic recombination are discussed. The rate of dissociation of water is too low to account for experimental current densities in the electrolytic generation of hydrogen in neutral or alkaline solutions, and it is concluded that water is mainly the species which is reduced in these solutions. Implications with regard to studies on "hydrogen" overpotential are discussed. In general, dissociation of weak acids is sufficiently rapid to account for experimental current densities in the electrolytic production of hydrogen. Local variations of *p*H at the electrode surface are calculated for electrolytic processes carried out in presence of a buffer of the type HA/A⁻.

In studies of hydrogen overvoltage it is often assumed that hydronium ion is the species which is reduced at the electrode. In alkaline solutions the concentration of hydronium ion is extremely low, and the above assumption implies that the rate of dissociation of water into hydronium and hydroxyl ions is much larger than the rate of the electrolytic process. Similarly, in discussing electrolytic processes occurring in buffer solutions, it is generally assumed that the *p*H of the solution at the electrode surface is the same as the *p*H in the bulk of the solution. This implies that the rate of establishment of the equilibrium accounting for the action of the buffer mixture is much larger than the rate of consumption or liberation of hydronium ions at the electrode. The purpose of the present paper is to determine whether these hypotheses are compatible with the kinetics of the processes which are assumed to occur.

Reduction of Hydronium Ion *versus* Reduction of Water

Derivation of Current.—The current through a cell in which hydrogen gas is evolved can be divided into three components. (1) The current corresponding to the reduction of hydronium ions which are transferred from the bulk of the solution to the electrode: (2) the current corresponding to the reduction of hydronium ions which are formed by dissociation of water in the immediate vicinity of the electrode; (3) the current resulting from the reduction of water. The maximum current density corresponding to the first two components of the current is calculated here.

Consider a plane electrode on which hydronium ions are reduced. If the solution is unstirred, the change of concentration of hydronium ion between two planes at distance x and $x + dx$ from the electrode is

$$\frac{\partial C_{H_3O^+}}{\partial t} = D_{H_3O^+}\frac{\partial^2 C_{H_3O^+}}{\partial x^2} + k_d\, C^2_{H_2O} - k_r C_{H_3O^+} C_{OH^-} \quad (1)$$

in which the C's are the concentrations in moles per cm.³, $D_{H_3O^+}$ is the diffusion coefficient of H_3O^+ in cm.² sec.⁻¹, k_d and k_r are the rate constants for the dissociation of water and for the recombination of H_3O^+ and OH^- ions in sec.⁻¹ and (moles per cm.³)⁻¹ sec.⁻¹, respectively. The first term on the right-hand side of (1) represents the difference in the flux of ions H_3O^+ at x and $x + dx$; the second term represents the increase in concentration of H_3O^+ resulting from the dissociation of water according to the equation

$$2H_2O = H_3O^+ + OH^- \quad (2)$$

Activity coefficients are assumed to be equal to unity in equation (1).

In the following derivation it is assumed that concentrations C_{H_2O} and C_{OH^-} in (1) are constant. The validity of this approximation is examined below. By introducing the dissociation constant of water K ($K = k_d/k_r$) in (1) one obtains after transformations

$$\frac{\partial C_{H_3O^+}}{\partial t} = D_{H_3O^+}\frac{\partial^2 C_{H_3O^+}}{\partial x^2} + k_r C_{OH^-}(C^\circ_{H_3O^+} - C_{H_3O^+}) \quad (3)$$

in which $C^\circ_{H_3O^+}$ is the bulk concentration of hydronium ions in moles per cm.³. If we assume that the potential of the electrode is such that the reduction of hydronium ion may be regarded as instantaneous in comparison with the dissociation process, the initial and boundary conditions are as follows: for $t = 0$, $C_{H_3O^+} = C^\circ_{H_3O^+}$; for $t > 0$ and $x = 0$, $C_{H_3O^+} = 0$. By solving (3) for the above conditions one obtains concentration $C_{H_3O^+}$ as a function of x and t. An equation similar to (3) is encountered in the theory of catalytic polarographic currents and the details of the derivation will be found in a previous paper from this Laboratory.[1] The current density is derived by multiplying $(\partial C_{H_3O^+}/\partial x)_{x=0}$ by $D_{H_3O^+}$ and by the faraday. The resulting equation can be simplified[1] when $k_r C_{OH^-}$ is larger than 100 sec.⁻¹—a condition which is fulfilled here (see below)—and the current density becomes

$$i_{C.D.} = FD_{H_3O^+}{}^{1/2}k_r{}^{1/2}C^\circ_{H_3O^+}C_{OH^-}{}^{-1/2} \quad (4)$$

The rate constant k_r in the above equation can be calculated from Onsager's theory of ionic recombination.[2,3] From the equation for k_r previously derived one obtains $k_r = 7.85 \times 10^{13}$ (moles per cm.³)⁻¹ sec.⁻¹ at 25°. The diffusion coefficients of H_3O^+ and OH^- ions used in this calculation of k_r were those listed by Kolthoff and Lingane.[4] Further transformation of (4) is obtained by noticing that the ionic product of water $C_{H_3O^+} \times C_{OH^-}$ is equal to 10^{-20} (moles per cm.³)². Finally $D_{H_3O^+}$ at 25° is 9.34×10^{-5} cm.² sec.⁻¹. Introducing these numerical data in (4) yields the equation

$$i_{C.D.} = 0.83C_{H_3O^+}{}^{1/2} \quad (5)$$

in which $i_{C.D.}$ is in amp. cm.⁻² and $C_{H_3O^+}$ in moles per cm.³.

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(1) P. Delahay and G. L. Stiehl, THIS JOURNAL, **74**, 3500 (1952).

(2) L. Onsager, *J. Chem. Phys.*, **2**, 599 (1934).

(3) P. Delahay and T. J. Adams, THIS JOURNAL, **74**, 1437 (1952).

(4) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 45.

Before deducing any conclusion from (5) the validity of the various assumptions made in the derivation will be discussed. (1) Equation (1) is written by assuming that the solution is unstirred and that the difference in flux at x and $x + dx$ from the electrode can be calculated on the basis of Fick's second law. However, when $k_r C_{OH^-}$ is larger than 100 sec.$^{-1}$, the current given by (4) and (5) is virtually controlled by the rate of dissociation of water according to (2). Therefore equations (4) and (5) are applicable whether or not the solution is stirred.

(2) Equation (4) is valid only when $k_r C_{OH^-}$ is larger than 100 sec.$^{-1}$. On the basis of the value $k_r = 7.85 \times 10^{13}$ (moles per cm.^{3})$^{-1}$ sec.$^{-1}$ at 25° the above condition is fulfilled when C_{OH^-} is larger than 1.3×10^{-12} mole per cm.^{3}, or 1.3×10^{-9} mole per liter. Thus the present derivation is applicable when the pH in larger than 5.1, *i.e.*, when the concentration of hydronium ions is so low that the contribution to the current resulting from the diffusion of hydronium ions is negligible.

(3) It was assumed that C_{OH^-} in (1) is independent of x and t, *i.e.*, that C_{OH^-} is simply the bulk concentration of hydroxyl ions. Actually because of the generation of hydronium ions by dissociation of water, C_{OH^-} in the immediate vicinity of the electrode is larger than the bulk concentration. As a result the last term on the right-hand side of (1) is larger than the value given by (1) and the current density given by (4) or (5) is too large. However, this is in favor of the explanation presented here (see below).

Electrolysis of Water. Equation (5) gives the maximum current density which could be observed in the electrolytic production of hydrogen if only hydronium ions were to be reduced at the electrode at the exclusion of water. It can be seen that (5) yields values of $i_{\text{C.D.}}$ in the alkaline range, which are much lower than experimental current densities. For example in a 0.1 N sodium hydroxide solution, $i_{\text{C.D.}}$ maximum would be 2.6×10^{-9} amp. cm.$^{-2}$, whereas it is well known that hydrogen can be prepared industrially by electrolysis of a sodium hydroxide solution. Therefore, it is not possible to account for the experimental current densities by assuming that water is dissociated into H_3O^+ and OH^- ions *before* reduction. The only alternative is that water is reduced in neutral and alkaline solutions. This is an assumption which was made by Eyring, Glasstone and Laidler[5] on the basis of considerations entirely different from those presented here. The present derivation shows conclusively the validity of the assumption made by these authors as far as neutral or alkaline solutions are concerned. This present treatment is not valid for acid solutions, but it is logical to assume that water is also reduced in acid solutions. Thus, in alkaline solutions, the current virtually corresponds to the reduction of water. In acid solutions the reduction of hydronium ion should also be taken into account (see below).

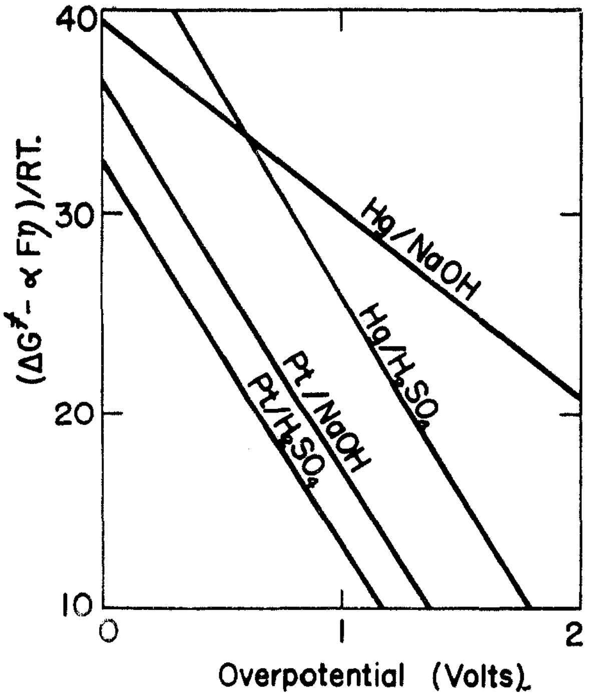

Fig. 1.—Variations of $(\Delta G^{\ddagger} - \alpha F\eta)/RT$ with overpotential for bright platinum and mercury electrodes in 0.2 N sodium hydroxide and 0.2 N sulfuric acid. Ordinate values are in kcal.

Overpotentials.—The equilibrium potentials for the reduction of water or hydronium ion are the same, but the overpotentials for a given current density may not necessarily be the same. This can be shown in the following manner.

The current density for the reduction of hydronium ion and water is given by the equation[6]

$$i_{\text{C.D.}} = \frac{kT}{h} Fa_{w}\delta_{w} \exp[-(\Delta G_{w}^{\ddagger} - \alpha_{w}F\eta)/RT] + \frac{kT}{h} Fa_{H_3O^+}\delta_{H_3O^+} \exp[-(\Delta G_{H}^{\ddagger} - \alpha_{H}F\eta)/RT] \quad (6)$$

in which $\Delta G_{w}^{\ddagger}$ and $\Delta G_{H}^{\ddagger}$ are the free energies of activation for the reduction of water and hydronium ion, respectively; the α's are the transfer coefficients; δ_w is the average distance of two molecules of water, and $\delta_{H_3O^+}$ the average distance between two hydronium ions; η is the overpotential which is the same for the reduction of hydronium ion or water; the a's are the activities, F is the faraday and the other symbols are conventional.

Experimental values of $(\Delta G^{\ddagger} - \alpha F\eta)/RT$ are plotted against overpotential in Fig. 1 for platinum and mercury electrodes. Figure 1 was constructed by applying the treatment embodied in equation (6)[5] to the data compiled by Bowden and Agar.[7] It was shown in the previous section that in alkaline solutions, the reduction of water virtually accounts for the current. Thus the data of Fig. 1 for sodium hydroxide correspond to the reduction of water on platinum or mercury. At appreciable current densities the data obtained with sulfuric acid and a mercury cathode can be interpreted as corresponding to the reduction of hydronium ion

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(5) H. Eyring, S. Glasstone and K. J. Laidler, *J. Chem. Phys.*, **7**, 1053 (1939).

(6) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 584–589.

(7) F. P. Bowden and J. N. Agar, *Ann. Rep. Chem. Soc.*, **35**, 90 (1938). See also ref. 6.

exclusively, since $(\Delta G^{\ddagger} - \alpha F\eta)/RT$ is much smaller for the reduction of hydronium ion than for the reduction of water (Fig. 1). Therefore, it can be concluded that the overpotential for the reduction of hydronium ion on mercury at a given current density is much smaller than the overpotential for the reduction of water in the same conditions.

With platinum electrodes the values of $(\Delta G^{\ddagger} - \alpha F\eta)RT$ are approximately the same for sodium hydroxide and sulfuric acid (Fig. 1) and the current for the reduction of water cannot be regarded as negligible *a priori* in comparison with the current for the reduction of hydronium ion. Therefore, the data on "hydrogen" overpotential obtained with platinum cathodes actually represent the combined effects of the reduction of water and hydronium ion. This is a point which cannot be disregarded in studies on hydrogen overpotentials.

Application to Polarography.—The possibility of using the dropping mercury electrode up to very negative potentials (approximately −2.7 volts *vs.* S.C.E.) is generally explained by the high "hydrogen" overpotential for mercury. From the present discussion it is readily seen that actually a high overpotential for the *reduction of water* accounts for this phenomenon. If one considers that the current density at which the effect of the reduction of water becomes noticeable, is approximately 5×10^{-5} amp. cm.^{2} (*i.e.*, $i = 10^{-6}$ amp. for an electrode area of 0.02 cm.^{2}), one calculates from (6) and from the data of Fig. 1, that η is 0.96 volt (using $\delta_w = 3.1 \times 10^{-8}$ cm.). Since the OH^- ions resulting from the reduction of water are accumulated at the surface of the electrode it can be assumed that the local *p*H at the electrode surface is much higher than 7, say 14 for example. On the basis of the latter *p*H one calculates a reversible potential for the reduction of water of −1.08 volts (*vs.* S. G. E.), and the potential for which $i_{\text{C.D.}} = 5 \times 10^{-5}$ amp. cm.^{2} is −2.04 volts (*vs.* S. C.E.) This potential is not too different from the value obtained by Ilkovic[8] who observed that the current for the reduction of water becomes noticeable in the neighborhood of −2.7 volts (*vs.* S.C.E.). It should be added that the present calculation on η is approximate because the value of the transfer coefficient α varies with the nature of the solution; also, the current density at the dropping mercury electrode varies during the drop life.

The previous treatment is also applicable to platinum electrodes, and it can be seen from Fig. 1 that at equal current densities, the overpotentials for the reduction of hydronium ion and water are of the same order of magnitude. Furthermore, the overpotentials for platinum electrodes are smaller than in the case of mercury. As a result platinum electrodes cannot be used in voltammetry at very negative potentials.

Reduction of Weak Acids

The foregoing treatment can easily be transposed to the electrolysis of a solution of a weak acid. By proceeding as in the previous section one obtains

$$i_{\text{C.D.}} = FD_{H_3O}{}^{1/2}k_r{}^{1/2}C^{\circ}_{H_3O^+}C^{\circ}_{A^-}{}^{1/2} \qquad (7)$$

in which $C^{\circ}_{H_3O^+}$ and C_{A^-} are the bulk concentrations of ions H_3O^+ and A^- in moles per cm.^{3}, and k_r is the rate constant in (moles per cm.^{3})$^{-1}$ sec.$^{-1}$ for the recombination of hydronium with ion A^-. Activity coefficients are assumed to be equal to one in (7). Since HA is a weak acid the concentrations $C^{\circ}_{H_3O^+}$ and $C^{\circ}_{A^-}$ are given by the equation

$$C^{\circ}_{H_3O^+} = C^{\circ}_{A} \approx (KC^{\circ})^{1/2} \qquad (8)$$

in which K is the dissociation constant of acid HA in moles per cm.^{3}, and C^0 is the bulk concentration of acid HA in moles per cm.^{3}. Further transformation of equation (8) is obtained by introducing the numerical value of F, and that of $D_{H_3O^+} = 9.34 \times 10^{-5}$ cm.^{2} sec.$^{-1}$. Finally one calculates $k_r = 5.3 \times 10^{13}$ (moles per cm.^{3})$^{-1}$ sec.$^{-1}$ on the basis of Onsager's theory of ionic recombination,[2-3] using the approximate diffusion coefficient $D_{A^-} = 0.6 \times 10^{-5}$ cm.^{2} sec.$^{-1}$. After transformation one obtains for 25° the maximum current density

$$i_{\text{C.D.}} = 6.8 \times 10^{9}\, K^{3/4}\, C^{\circ 1/4} \qquad (9)$$

Equation (9) shows that the dissociation of weak acids is sufficiently rapid to account for experimental current densities. For example for $K = 10^{-9}$ mole per liter, *i.e.*, 10^{-12} mole per cm.^{3}, and $C^{\circ} = 10^{-4}$ mole per cm.^{3}, equation (9) yields $i_{\text{C.D.}} = 6.8 \times 10^{-3}$ amp. cm.$^{-2}$. Of course, the present derivation does not prove that dissociation actually precedes the reduction, but merely indicates that this is a possibility. For very weak acids as $i_{\text{C.D.}}$ becomes too low it may be necessary to assume that undissociated molecules of HA are directly reduced as in the case of water.

Buffering Action in Electrolytic Processes

Consider an electrolytic process in which m hydronium ions and n faradays are consumed per mole of substance reacting at the electrode. The reaction is carried out in presence of a buffer composed of a weak acid HA and a salt of HA and a strong base. If one assumes that the hydronium ions consumed by the electrode process are supplied by the dissociation of acid HA one has

$$\frac{mi_{\text{C.D.}}}{nF} = (k_d)_h\, C_{HA} - (k_r)_h C_{H_3O^+}C_{A^-} \qquad (10)$$

in which the C's are the concentrations in moles per cm.^{3}, and $(k_d)_h$ and $(k_r)_h$ are the rate constants for the dissociation of HA and the recombination of ions H_3O^+ and A^- *at the electrode surface;* the rate constants $(k_d)_h$ and $(k_r)_h$ for heterogeneous processes are in cm. sec.$^{-1}$ and cm. (moles per cm.^{3})$^{-1}$ sec.$^{-1}$, respectively. Activity coefficients are assumed to be equal to one in (10). By introducing the dissociation constant K of acid HA ($K = (k_d)_h/(k_r)_h$ moles per cm.^{3}), equation (9) is transformed into

$$C_{H_3O^+} = K\frac{C_{HA}}{C_{A^-}} - \frac{mi_{\text{C.D.}}}{nFC_{A^-} - (k_r)_h} \qquad (11)$$

The first term on the right-hand side of (10) is the equilibrium value of $C_{H_3O^+}$. Therefore, the second term is the change $\Delta C_{H_3O^+}$ caused by the consumption of hydronium ions at the electrode. The value of $\Delta C_{H_3O^+}$ is obtained by replacing $(k_r)_h$ by its value in terms of the conventional rate con-

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[8] D. Ilkovic, *Collection Czechoslov. Chem. Communs.*, **4**, 480 (1932).

stant k_r. The following relationship recently derived[9] will be applied

$$(k_r)_h = (D_{HA}^{1/2}/K^{1/2})k_r^{1/2} \quad (12)$$

By combining (11) and (12) one obtains

$$\Delta C_{H_3O^+} = -\frac{mK^{1/2}i_{C.D.}}{nFD_{HA}^{1/2}C_A k_r^{1/2}} \quad (13)$$

Equation (13) can be simplified by introducing the value $k_r = 5.3 \times 10^{13}$ (moles per cm.^{3})$^{-1}$ sec.$^{-1}$ calculated in the previous section, and the approximate value $D_{HA} = 0.6 \times 10^{-5}$ cm.^{2} sec.$^{-1}$.

Thus after numerical transformations

$$\Delta C_{H_3O^+} = -5.8 \times 10^{-6} \frac{mi_{C.D.}K^{1/2}}{nC_A} \quad (14)$$

From (14) one calculates a relative variation in the concentration of hydronium ions at the surface of the electrode

$$(\Delta C_{H_3O^+})_{\%} = -5.8 \times 10^{-8} \frac{mi_{C.D.}}{nK^{1/2}C_{HA}} \quad (15)$$

which is expressed in per cent. of concentration $C_{H_3O^+}$.

Values of $(\Delta C_{H_3O^+})_{\%}$ obtained from (15) are by no means negligible when HA is a very weak acid. Consider for example the following case: $m = n$, $K = 10^{-12}$ mole per cm.^{3}, *i.e.*, $K = 10^{-9}$ mole per liter, $C_{HA} = 10^{-4}$ mole per cm.^{3}; under these conditions $(\Delta C_{H_3O^+})_{\%}$ is equal to $-580\ i_{C.D.}$ per cent. of C_{H_3O}. If $i_{C.D.}$ is for example 10^{-2} amp. cm.$^{-2}$—a fairly low current density in electrolysis—$(\Delta C_{H_3O^+})_{\%}$ is 5.80%. Even larger errors would be obtained for lower values of the dissociation constant K. It should be emphasized that the influence of concentration polarization of HA or A^- was not taken into account in the present treatment, and consequently that even larger errors than these calculated from (15) could possibly be observed.

In the case of polarographic electrolyses the current densities are of the order of 10^{-3} to 10^{-5} amp. cm.^{2} and the resulting $(\Delta C_{H_3O^+})_{\%}$ is negligible (see (15)).

From the present treatment it is not possible to decide whether the hydronium ion concentration actually varies at the electrode surface. But, it can be concluded that if the pH does not vary at the electrode surface as predicted from (15) it is likely that dissociation of acid HA does not precede the electrode process, and that molecules of HA are directly consumed in the electrode process. Dissociation would then occur in some subsequent step of the electrode process. On the other hand, if undissociated molecules of HA are not directly used in the electrode process, one can predict on the basis of equation (15) that the pH at the electrode surface is different from that in solution. The difference in pH is appreciable (see above) when HA is very weak ($K = 10^{-9}$ mole per liter) and the current density is not too low (10^{-2} amp. cm.$^{-2}$ or above).

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BATON ROUGE, LA.

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[9] P. Delahay, THIS JOURNAL, **74**, 3506 (1952).

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Theory of Catalytic Polarographic Currents

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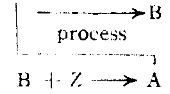
The theory of polarographic currents controlled by diffusion and by the rate of a catalytic process which regenerates the substance reacting at the dropping mercury electrode is developed. The properties of catalytic currents are derived and a graphic method for the determination of rate constants from experimental currents is reported. The theory is applied to the catalytic currents observed in the reduction of ferric ion in presence of hydrogen peroxide. Calculated and experimental data are in good agreement.

Introduction

In previous publications[1-3] from this Laboratory the theory of polarographic currents controlled by diffusion and by the rate of an heterogeneous reaction was developed and applied to various electrode processes. This theory is applicable to cases in which the chemical process, partially controlling the current, occurs essentially at the surface of the electrode. This condition is fulfilled for many so-called kinetic waves, but there are cases in which the current is controlled by diffusion and by the rate of a reaction occurring at the surface of the electrode and in the vicinity of the electrode. The theory of these so-called catalytic currents is developed in the present paper for cases in which the regeneration process is a second order reaction.

The nature of catalytic polarographic currents can be explained by considering an electrode process in which a substance A is reduced to another substance B at the dropping mercury electrode (reaction (1)). The solution also contains a substance Z which is not reduced at the dropping mercury electrode at the potential at which the limiting current for A is observed.



(1)

$$B + Z \longrightarrow A \quad (2)$$

Furthermore, Z reacts with B to regenerate substance A (reaction (2)). Because of this "cat-

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

[2] P. Delahay and J. E. Strassner, *ibid.*, **73**, 5219 (1951).

[3] P. Delahay and T. J. Adams, *ibid.*, **74**, 1437 (1952).