Hence

$$(\Delta H_{Act})_{max} = \frac{2.303RT_d^2}{100} (36.0) = 1.65T_d^2 \quad (8)$$

The validity of equation 8 is assessed in Table V, where experimental values of $(\Delta H_{Act})_{max}/T_d^2$ have been collected. The data are taken from papers I[2] and II.[3] The average value of $(\Delta H_{Act})_{max}/T_d^2$

TABLE V

RELATIONSHIP OF MAXIMUM APPARENT HEAT OF ACTIVATION AND DISTINCTIVE TEMPERATURE

Polymer	$(\Delta H_{Act})_{max}$, kcal.	T_d, °K.	$(\Delta H_{Act})_{max}/T_d^2$
Polymethyl methacrylate	300	384	2.03
Paracril 26	95.6	241.0	1.64
GR-S	85.0	220	1.75
60/40 Butadiene–styrene	101.9	237.1	1.81
50/50 Butadiene–styrene	99.0	250.8	1.57
30/70 Butadiene–styrene	140.4	285.1	1.73

is 1.74 (± 0.06). This suggests that the maximum value of $g(\Delta/T_d)$ may be slightly greater than 36.0, which is not unreasonable.

Discussion

If the viscoelastic properties of a wide variety of amorphous polymers in the transition region obey equation 2, it is clear that we have developed a kind of law of corresponding states for viscoelastic properties. In particular, the function Y should be identical for all polymers having the same T_d independent of the structure of the polymer. We believe that this will indeed be found valid for many normal amorphous polymers, but will not be true for incompatible copolymers or polyblends.

PRINCETON, NEW JERSEY


[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

The Polarography and Standard Potential of the Oxygen–Hydrogen Peroxide Couple

BY DAVID M. H. KERN

The generally accepted equation $O_2 + 2H^+ + 2e^- = H_2O_2$ for the first step in the polarographic reduction of oxygen has been confirmed in the pH range 6–14 by potentiometric null-point measurements with the dropping mercury electrode in buffered hydrogen peroxide–oxygen mixtures. The couple is completely reversible for $pH > 11$. The standard potential was determined both by the above technique, and by measurements of the oxygen half-wave potential in sodium hydroxide solutions in a cell without liquid junction. The result was $E^0 = +0.695 \pm 0.005$ v. The mechanism of the reduction is briefly discussed.

The recent work of Hacobian[1] on the a.c. polarography of oxygen has produced conclusive evidence of the reversibility of the first reduction step in unbuffered neutral and basic solutions. His observations were further confirmed by his discovery of an oxidation wave of hydrogen peroxide in dilute base. Heretofore, although reversible electron exchange between the oxygen molecule and the electrode has at times been postulated,[2] the over-all process has consistently been stated to be highly irreversible in all media.[3] This assumption was supported, at least in the pH range 1–10, by the observation[4] that the half-wave potential $(E_{1/2})$ of oxygen throughout this range is essentially independent of pH, while according to the accepted equation

$$2H^+ + O_2 + 2e^- \rightleftharpoons H_2O_2 \quad (1)$$
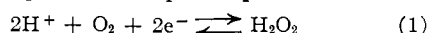
for the over-all electrode reaction, reversibility would have led to a shift of 60 mv. per unit change in pH. On the other hand, the standard potential of this couple has been given by Latimer[5] as +0.682 v. on the basis of data on reaction heats and

entropies, and a simple calculation shows that the overvoltage of the observed oxygen wave (generally placed at -0.05 v. vs. S.C.E.) rapidly diminishes as the solution becomes less acid until it disappears altogether in slightly basic solutions. Furthermore, Berl[6] has shown that the electrode reaction is reversible at activated carbon electrodes in strongly basic solutions. Practically, the reversibility of the oxygen wave in basic solutions has been exploited because of its steep shape and well developed diffusion plateau, but the appropriate thermodynamic conclusions had never been drawn.

Hacobian found that analysis of the oxygen wave in neutral unbuffered solution gave a linear log plot with a 62 mv. slope, indicating a one-electron process. The log plot analysis derives its validity from the thermodynamic current–voltage equation for the rising part of the wave, and this in turn is based on the assumption that the over-all electrode reaction is given by the expression

$$A + ne^- \rightleftharpoons B$$
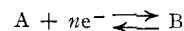
where n is determined by the slope of the log plot and A and B are the diffusing species. In one mechanism proposed by Hacobian, B has a coefficient of 3/2, and in the other the reaction involving the one electron is not the over-all process between the diffusing species. Consequently the slope of his plot cannot be used to support either mechanism. An attempt was made to reproduce the log plot of Hacobian in neutral 0.05 M Na$_2$SO$_4$

(1) S. Hacobian, *Australian J. Chem.*, **6**, 211 (1953). The same conclusion was very briefly reported by Kalousek, *Collection Czechoslav. Chem. Communs.*, **13**, 105 (1948), on the basis of observations made by a simpler technique.

(2) J. Heyrovsky, "Polarographie," Springer Verlag, Vienna, p. 78.

(3) *E.g.*, I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd Ed., Vol. II, Interscience Pubishers, Inc., New York, N. Y., p. 555; M. v. Stackelberg, "Polarographische Arbeitsmethoden," Walter de Gruyter and Co., Berlin, p. 320.

(4) I. Kolthoff and C. Miller, THIS JOURNAL, **63**, 1013 (1941).

(5) W. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 2nd ed., 1950, p. 43.

(6) W. Berl, *J. Electrochem. Soc.*, **83**, 253 (1943).

solution. (Hacobian worked in 0.1 M NaClO$_4$, but he states he obtained similar results in Na$_2$SO$_4$.) It is evident from Fig. 1 that the plot is not straight and only approximates a one-electron slope. Nevertheless, the reversibility of the electrode process could be confirmed by observing the effect of changing the mercury pressure; the current in every part of the wave was changed by the same ratio, as is characteristic of reversible but not of slow electrode reactions. Apparently the deformation of the log plot is caused by the varying concentration of hydroxide formed at the surface in different parts of the wave, which causes the potential of the system to vary continuously. In such a case it is difficult to draw conclusions from the log plot.
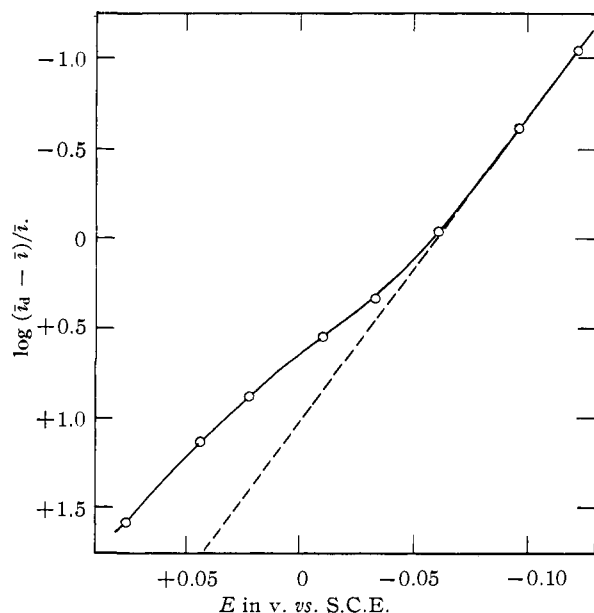

Fig. 1.—Log plot of the oxygen reduction waves in 0.05 M Na$_2$SO$_4$. The dashed line has a slope of 0.059, corresponding to a one-electron reduction.

In order to determine the conditions under which reversibility exists, to establish beyond doubt the validity of equation 1 for the over-all reaction, and to obtain a direct measurement of the reversible potential, the present investigation of this couple was undertaken in buffered media.

Experimental

The polarographic waves were recorded on a Sargent-Heyrovsky polarograph, but all work involving accurate voltage measurements was done with a manual apparatus. Reagent grade chemicals were used throughout. The cells were thermostated at 25 ± 0.1. Where necessary residual currents were measured in the solutions previous to the addition of depolarizer. Except where otherwise noted, the solutions used all had an ionic strength of 0.15. Hydrogen peroxide concentrations were determined by titration with permanganate. Other solutions were made up determinately from weighed material. The pH was measured with a Beckman pH meter. A trace of methyl red was added when necessary to suppress maxima.

General Polarographic Characteristics of the Couple.—The relationship between $E_{1/2}$ and pH found in various buffering media for oxygen and hydrogen peroxide waves is illustrated in Fig. 2. The oxygen $E_{1/2}$, initially independent of pH,

gradually merges with the pH-dependent peroxide $E_{1/2}$ until at pH > 11 the two are identical and follow the theoretical course predicted for the reversible couple of equation 1. In the pH range 7.5–10 borate buffers were found to give the best developed peroxide waves since in this medium, unlike ammonia and glycine buffers, the potential of the mercury dissolution wave is at its most positive value consistent with the hydroxide ion concentration, and so the largest possible voltage region is made available for the development of the diffusion current plateau.
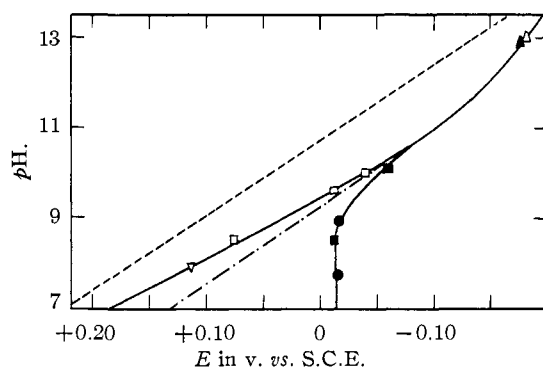

Fig. 2.—Half-wave potentials of O$_2$ (black) and H$_2$O$_2$ (open) waves as a function of pH: ▽, phosphate-citrate buffer; ☐, ammonia; O, borate; △, NaOH. The upper dashed line represents the potential of the mercury dissolution wave. The parallel below is the reversible half wave potential.

Mixtures of hydrogen peroxide and oxygen yielded a composite wave without inflection, as illustrated in Fig. 3, even in media of pH 8–10 in which the separate waves have distinctly different $E_{1/2}$'s. Thus a composite wave without observable
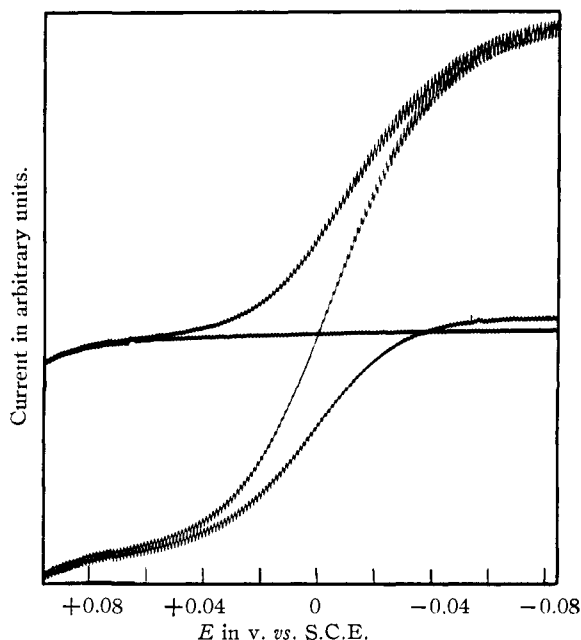

Fig. 3.—Polarograms of a borate buffer, pH 9.6, containing oxygen, hydrogen peroxide and a mixture of the two.

inflection does not necessarily indicate complete reversibility. The same conclusion is reached on the basis of the theory of semi-reversible waves presented by Koutecky,[7] in which the rate-determining step is assumed to be the electron transfer. In Fig. 4 are plotted the anodic and cathodic waves arising from a semi-reversible process with k_e (at $E = E^0$) $= 0.5 \sqrt{D/\tau}$ and $0.1 \sqrt{D/\tau}$ (as calculated from a combination of Koutecky's theory with the absolute rate theory) together with the corresponding composite waves, for a two-electron process with $\alpha = 0.5$. It is seen that even when the $E_{1/2}$'s are 50 mv. apart, there is no observable inflection in the composite, and only a small one when the separation amounts to 0.26 v.

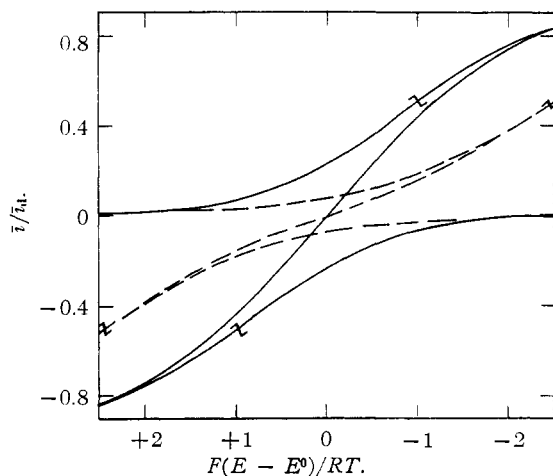Fig. 4.—Theoretical plot of the anodic, cathodic and composite waves for a two-electron process, $\alpha = \beta = 0.5$. Solid line, k_e (at $E = E^0$) $= 0.5 \sqrt{D/\tau}$; dashed line, $k_e = 0.1 \sqrt{D/\tau}$.

The Over-all Equation for the Electrode Reaction.—At the potential at which a composite wave crosses the residual current, no net current is being drawn from the depolarizer couple. Therefore, no net reaction occurs, and bulk conditions such as pH and depolarizer concentration prevail right up to the surface. Consequently, if equation 1 accurately describes the over-all electrode process, the crossing point potential should obey the relationship

$$E_c = E^0 + \frac{RT}{2F} \ln \frac{(O_2)\gamma_{O_2}}{(H_2O_2)\gamma_{H_2O_2}} - \frac{RT}{F}pH \quad (2)$$

regardless of whether the couple is reversible or irreversible.[8] Under these conditions the d.m.e. is acting as a null point electrode, as does the platinum wire in conventional potentiometric measurements. However, although numerous attempts have been made to measure this couple at platinum electrodes,[9] it has been found impossible to obtain stable potentials.

Preliminary tests[10] of equation 2 were carried out

(7) J. Koutecky, Collection Czechoslov. Chem. Communs., 18, 597 (1953).

(8) The reasoning has been amplified by R. Goto and I. Tachi, "Proc. of the Int. Polarographic Cong. in Prague," Part I, p. 69; N. Tanaka and R. Tamamushi, ibid., p. 486.

(9) E.g., K. Bornemann, "Nernst Festschrift," Knapp, Halle, 1912, p. 118.

(10) These were reported in THIS JOURNAL, 76, 1455 (1954).

on mixtures of oxygen and hydrogen peroxide in borate buffers of pH 7.5–10 and NaOH–KNO$_3$ solutions up to pH 13. Comparison of the composite waves with the residual current in the deaerated solutions yielded the crossing point potential. The molar ratio of oxygen and hydrogen peroxide was taken as the ratio of the cathodic and anodic diffusion currents. Representative plots of E_c vs. log $(O_2)/(H_2O_2)$ are shown in Fig. 5. It is clear that the slopes are in satisfactory agreement with the theoretical value.
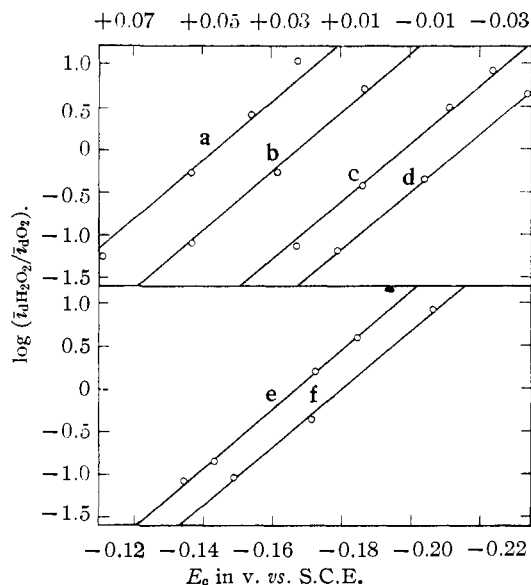

Fig. 5.—E_c as a function of the diffusion current ratio of O_2 and H_2O_2 in various borate (above) and NaOH–KNO$_3$ (below) buffers: a, pH 8.4; b, 9.0; c, 9.4; d, 9.7; e, 12.6; f, 13.0. The slopes are theoretical for a two-electron process.

A plot of E_c vs. pH for solutions in which the anodic and cathodic diffusion currents are equal, as read from Fig. 5, yields a value for the standard oxygen–hydrogen peroxide potential $E^0_{O_2,H_2O_2}$ that is in fair agreement with Latimer's figure, but the agreement is due in part to a fortuitous cancellation of errors. First, the diffusion coefficients of oxygen and hydrogen peroxide are rather different (see below) so that equating the ratio of diffusion currents with the molar ratio introduces a small negative error. (Either ratio can, however, be used to test the coefficient of the O_2/H_2O_2 term in equation 2, as described above, since they differ by a constant.) More important, hydrogen peroxide complexes weakly with borate ion,[11] causing the potential of the couple to appear too positive. The author was made aware of this fact by the marked difference in the apparent diffusion coefficient of hydrogen peroxide in borate and ammonia buffers. A similar phenomenon was observed just recently by Elving[12] in the polarography of glyoxal in borate buffers. The effect of borate on the oxygen, hydrogen peroxide couple is under study, and will be the subject of a future communication.

The pH dependence of the potential of the couple

(11) H. Menzel, Z. physik. Chem., 105, 427 (1923).

(12) P. Elving and C. Bennett, THIS JOURNAL, 76, 1412 (1954).

was investigated in citrate–phosphate and NH_3–NH_4NO_3 buffers over the pH range 6–10. The anodic diffusion plateau is not accessible in these solutions. The concentration ratio was obtained by adding known amounts of H_2O_2 to the air saturated solutions. One null point measurement in each buffer solution was sufficient. The potential E' plotted in Fig. 6 was obtained from E_c by the relation

$$E' = E_c - 0.0296 \log P_{O_2}/\Sigma_{H_2O_2}$$

where P_{O_2} was taken as the partial pressure of oxygen in the atmosphere at 760 mm. The atmospheric pressure differed from this value during the course of the experiments, but the accuracy of the experiments was not such as to warrant a correction. In several cases the solutions were freshly air saturated before use, but no difference in the potential was ever observed. $\Sigma_{H_2O_2}$ refers to the stoichiometric hydrogen peroxide concentration, without correction for dissociation. Assuming the validity of equation 1, E' should be related to the standard potential $E^0_{O_2, H_2O_2}$ by the equation

$$E' = E^0_{O_2.H_2O_2} - 0.0296 \left[\log \gamma_{H_2O_2} + \right.$$
$$\left. \log \frac{a_{H^+}}{K_a'}\left(1 + \frac{a_{H^+}}{K_a'}\right)^{-1}\right] - 0.0591 \, pH \quad (3)$$

where $K_a' = K_a\gamma_{H_2O_2}/\gamma_{HO_2^-}$ and $K_a = 2.25 \times 10^{-12}$ at 25° for H_2O_2.[13]

In solutions in which $a_{H^+} >> K_a'$, the last term inside the bracket, which accounts for the dissociation of hydrogen peroxide, drops out: the linear asymptotic relationship between pH and E' has a slope of 0.0591. In Fig. 6, the solid line has the theoretical slope. Extrapolation to $pH = 0$ yields the result

$$E^0_{O_2.H_2O_2} = 0.460 \text{ v.} + 0.0296 \log \gamma_{H_2O_2} \text{ vs. the S.C.E. (4)}$$

The reference anode consisted of a saturated calomel electrode divided from the buffer solution by saturated KNO_3 solution. The effective potential of this combination was found by adding quinhydrone to borate buffers of pH 7.65 and 7.83 and determining the potential against the reference combination. The reference half cell potentials obtained in this calibration were 0.236 and 0.235 v. vs. the S.H.E., respectively. Combining this result with equation 4

$$E^0_{O_2.H_2O_2} = 0.6955 \text{ v.} + 0.0296 \log \gamma_{H_2O_2} \text{ vs. the}$$
$$\text{S.H.E., } \mu = 0.15 \quad (5)$$

Beyond pH 11 the last bracketed term in equation 3 becomes important. The theoretical value of E' as obtained from the equation in its complete form is represented by the dashed line in Fig. 6. According to Evans and Uri[13] at 20° in $NaClO_4$

$$pK_a' = pK_a - 0.5\sqrt{\mu} + 0.08\mu \quad (6)$$

solutions up to 2 M containing 0.5 M H_2O_2 and 0.05 M HO_2^-. Assuming this equation holds in NaOH–KNO_3 solutions at 25°, we find $pK_a' = 11.47$ for $\mu = 0.15$. This value was used in calculating the dashed line. Crossing point potential measurements were made in three solutions containing 8, 50 and 150 mM NaOH and an appropriate amount of KCl to maintain the ionic strength at 0.15. The activity coefficient of the OH^- was taken as 0.75

(13) M. Evans and N. Uri, Trans. Faraday Soc., 45, 224 (1949).

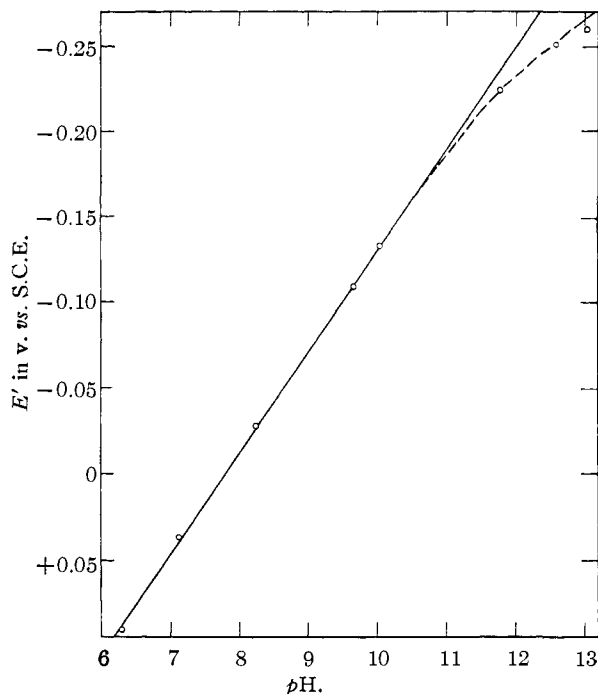in all three solutions, this being the value in pure 0.15 M NaOH.[14]

Fig. 6.—E' as a function of pH in phosphate citrate ammonia and NaOH–KNO_3 buffers. The solid line has the slope 0.05915. The dotted line represents the correction for H_2O_2 dissociation.

It is seen that the validity of equation 3 extends into strongly basic solutions, after correction for H_2O_2 dissociation. The downward drift in the most basic solution is real, and is probably due to an increased junction potential arising from the relatively great mobility of the OH^- ion.

Potential Measurements in Cells without Liquid Junction.—In an attempt to escape the uncertainty introduced by the junction potential, measurements were made in a cell without liquid junction, the unpolarizable anode being a mercuric oxide–mercury half-cell separated from the cathode compartment by a glass frit. The half reaction is
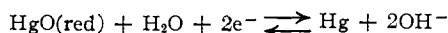
$$HgO(\text{red}) + H_2O + 2e^- \rightleftarrows Hg + 2OH^-$$
$$E^0_{HgO.Hg} = +0.0984$$

The same air-saturated carbonate-free NaOH solution was introduced into both compartments, and the $E_{1/2}$ of the oxygen wave measured.

The $E_{1/2}$ can be used as a measure of the standard potential of a couple only if complete reversibility has been established. In Fig. 7 are reproduced the log plots of the anodic peroxide wave and the cathodic oxygen wave in 0.15 M NaOH. The slope has the theoretical value for a two-electron process. The coincidence of the two plots is absolute proof of polarographic reversibility. Even at pH 10 the $E_{1/2}$'s are separated by only ten millivolts. It can be concluded that complete reversibility prevailed in the solutions investigated, which

(14) Interpolated from values reported by H. Harned and J. Hecker, THIS JOURNAL, 55, 4838 (1933).
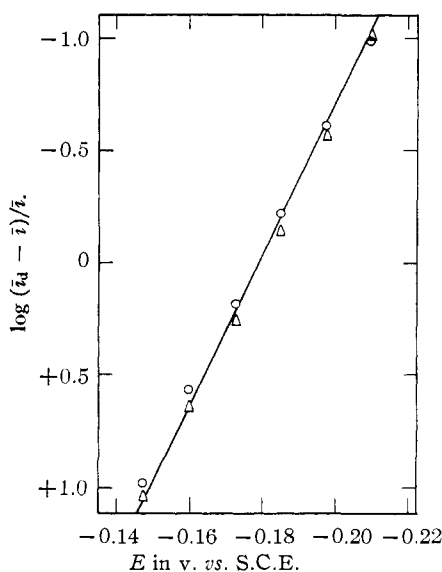
Fig. 7.—Log plot of hydrogen peroxide (triangles) and oxygen (circles) wave in 0.15 M NaOH. The line has the theoretical slope for a two-electron process.

were 8, 80 and 800 mM NaOH. The following relationship applies

$$E^0_{O_2,H_2O_2} = E_{1/2} + E^0_{HgO,Hg} - 0.0296 \, [\log K_a'/K_w +$$
$$\log a_{OH^-} - 1/2 \log D_{O_2}/D_{H_2O_2} - \log \gamma_{H_2O_2} + \log \gamma_{O_2} +$$
$$\log (1 + a_{H^+}/K_a')] \quad (7)$$

Here $E^0_{O_2,H_2O_2}$ represents the standard potential of the couple when the unit of activity of both oxygen and hydrogen peroxide is taken as the mole. The solubility of oxygen in water at one atmosphere is 1.27 mM. Hence a correction of $RT/2F \ln 1.27 \times$

$E_{1/2}$	(1)	(2)	(3)
−0.0813	0.8457	0.0078	0.0046
− .1135	.8531	.0357	.0044
− .131	.8562	.0632	.0038

$10^{-3} = -86.0$ mv. must be applied to obtain the conventional standard potential.

The activity coefficients for NaOH were obtained from the measurements of Harned,[14] those for O_2 from its solubility in NaOH solutions.[15] The potential was corrected for the IR drop, which amounted to 7.5 mv. in the most dilute solution. Even at the lowest hydroxide ion concentration, hydroxide ion formed at the surface by reduction was not sufficient to alter the pH significantly, nor was transport by the HO_2^- sufficient to affect its concentration at the electrode.

The Diffusion Coefficients of H_2O_2 and HO_2^-.[15a]— The apparent diffusion coefficient of hydrogen peroxide varies in different NaOH concentrations depending upon the degree of dissociation. In general, if A and B are two substances in rapid equilibrium and (A) = K(B), then the effective diffusion coefficient is the weighted mean, or (KD_a + D_b)/(K + 1). The diffusion coefficient of H_2O_2 was measured in a phosphate buffer of pH 5 at −1.35 v. $vs.$ S.C.E. by adding known increments

(15) Interpolated from values reported in I.C.T., Vol. 3, p. 271.
(15a) The diffusion coefficients in this section were calculated by means of the simple Ilkovic equation. See Ref. 3, Vol. I, p. 43.

of H_2O_2. The result was $D_{H_2O_2} = 1.71 \times 10^{-5}$ cm.^{2}/sec.

The diffusion coefficient of HO_2^- was measured in 0.08 M NaOH. In this medium 5% of the peroxide exists in the acid form. The method used was an amperometric titration of the anodic peroxide wave with arsenite ion, at −0.11 v. $vs.$ S.C.E. At this pH the reaction is virtually instantaneous. (The reaction was found to be slow at pH 9.4.) The peroxide wave first subsides because of the removal of H_2O_2, then builds up again in the presence of excess arsenite on account of the formation of an insoluble mercurous arsenite. Excellently reproducible results were obtained, yielding the value 1.30 × 10^{-5} cm.^{2}/sec. Corrected for the small amount of H_2O_2 present, $D_{HO_2^-} = 1.28 \times 10^{-5}$. In 8 m$M$ NaOH one calculates that (H_2O_2) = 0.58·· (HO_2^-) and the average diffusion coefficient is thus 1.43 × 10^{-5} cm.^{2}/sec. The measured value at −1.20 v. $vs.$ S.C.E. was 1.34 × 10^{-5}.

The value of D_{O_2} used was that reported by Kolthoff and Miller[4] in 0.1 M KCl solution, 2.6 × 10^{-5} cm.^{2}-sec.

Since $K_a' = K_a\gamma_{H_2O_2}/\gamma_{HO_2^-}$ and is further related to K_a by equation 6, the activity ratio can be found as a function of μ. If the assumption is made that $\gamma_{HO_2^-}$ is equal to $\gamma_\pm$ of NaOH in the same solution, $\gamma_{H_2O_2}$ can be calculated. It is found that $\gamma_{H_2O_2}$ increases slightly with increasing ionic strength.

The Standard Potential of the O_2–H_2O_2 Couple.— The data needed to calculate E^0 are tabulated below. The numbers at the head of the columns refer to the bracketed terms in equation 7 in the order in which they appear there, after multiplication by −0.0296.

(4)	(5)	(6)	E^0
0.0062	−0.0042	0.0000	0.779
.0006	− .0009	.0007	.779
.0000	− .000	.0038	(.786)

The measurement in the most dilute solution is unreliable because of a stubborn maximum that somewhat distorted the shape of the wave. Applying the 86.0 mv. correction, we find, omitting the third measurement

$$E^0_{O_2,H_2O_2} = 0.693 \text{ v. } vs. \text{ the S.H.E.}$$

If the value of $\gamma_{H_2O_2}$ at $\mu = 0.15$, calculated as above, is substituted into equation 5, the result is

$$E^0_{O_2,H_2O_2} = 0.697 \text{ v. } vs. \text{ the S.H.E.}$$

Probably the most significant error in these measurements is that introduced by the estimates of the activity coefficients, which might well amount to ±5 mv.[16] It is unlikely, however, that it accounts for the +13 mv. difference between the average +0.695 and Latimer's value[5] + 0.682 v. Berl[6] found the value +0.715 v.,[17] but it should be

(16) Latimer, ref. 5, cites K_a = 2.4 × 10^{-12}, a value based on the work of Joyner, $Z.$ $anorg.$ $Chem.$, **77**, 103 (1912). It is the average of results obtained by several different methods, all in solutions of ionic strength 0.05–0.2 without correcting for the activity coefficients. If K_a', is assigned this same value in all media that were investigated, and used throughout the calculations, the result is E^0 − 0.0296 log $\gamma_{H_2O_2}$ = 0.697 and 0.695 v. in 0.8 and 0.08 M NaOH, respectively, in good agreement with equation 5, which refers to solutions of μ = 0.15.
(17) This figure was erroneously given as +0.684 v. in ref. 10.

pointed out that his work was done in part in concentrated KOH solutions and no correction was made for the junction potential.

The Mechanism of Oxygen Reduction at the d.m.e.—Most of the information that has been gathered on the oxidation–reduction chemistry of oxygen has arisen from kinetic studies in homogeneous solutions.[18] There has been relatively little speculation in the literature on the mechanism of oxygen reduction at a cathode. Hickling[19] deduces from the reversibility of the oxygen–peroxide couple in strongly basic solutions established by Berl that the discharge of $OH^- \rightarrow OH + e^-$ is a rapid process, the over-all half reaction being given by

$$2e^- + O_2 + H_2O \rightleftharpoons HO_2^- + OH^-$$
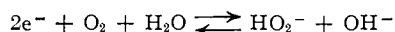
It would appear more reasonable to the present author to suppose that the HO_2^- is discharged, and that the hydroxide ion merely acts as a proton acceptor. In this way the energy consuming resolution of the oxygen molecule into its constituent atoms is avoided. Hacobian[1] supports an atomic oxygen mechanism, but only in an attempt to explain his evidence for a one-electron reduction. Heyrovsky,[2] on the other hand, favors a direct reduction of the oxygen molecule.

In the course of the investigation described in this article, it was not possible to resolve this problem, but certain phenomena were observed that may eventually throw light on the mechanism.

1.—In acid solutions, in which the reverse rate (oxidation of H_2O_2) is definitely negligible, the reduction wave of oxygen does not satisfy the requirements for a slow electrode reaction mechanism recently derived by Koutecky.[7] This theory, combined with absolute reaction rate theory, requires that the log plot of the wave be a straight line with slope $0.059/an$, where $0 < \alpha < 1$. In Fig. 8 is shown the log plot of oxygen in 0.15 M HClO$_4$ acid solution. The line has a definite break in it. This break occurs in all solutions in which the reduction is irreversible, and is a reflection of the drawn out nature of the wave in its upper portion,
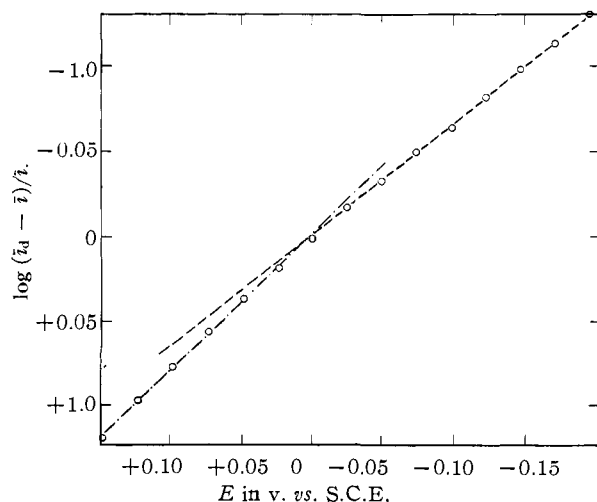

Fig. 8.—Log plot of oxygen in 0.15 M HClO$_4$.

(18) N. Uri, *Chem. Revs.*, **50**, 375 (1952).
(19) A. Hickling, *Quart. Revs.*, **3**, 95 (1949).

which is so marked that it is difficult in these solutions to obtain a reliable i_d value before the second reduction step begins.

2.—Waves in a series of acid buffers (citrate–phosphate) are presented in Fig. 9. As reported by Kolthoff and Miller,[4] the $E_{1/2}$ of the waves changes little in this range of pH. However, it will be noted that the wave shape becomes progressively more drawn out in its lower portion as the solution becomes more acid, resulting in a more symmetrical wave and a straighter log plot. The exact shape of the wave and value of the $E_{1/2}$ potential was somewhat dependent on the buffer, as observed previously,[4] but the effect of acidity on the lower portion of the wave was general.
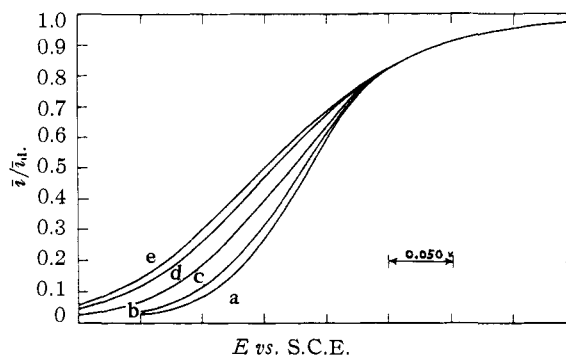

Fig. 9.—The first oxygen reduction wave in phosphate–citrate buffers: a, pH 6.1; b, 5.1; c, 4.1; d, 3.0; e, 0.15 M HClO$_4$.

3.—In the pH region in which the reduction wave changes from an irreversible to a reversible wave, a peculiar phenomenon was observed which is illustrated in Fig. 10. At pH 8 and 9 the wave retains the characteristics observed in acid solution. But as it approaches reversibility, the wave steepens and cuts through the irreversible waves. Thus in the upper portion oxygen is being reduced at a more positive potential, even though the solution is more basic (pH 10). As the basicity is increased further, the wave moves off to more negative potentials in accordance with thermodynamic expectations for the reversible couple.
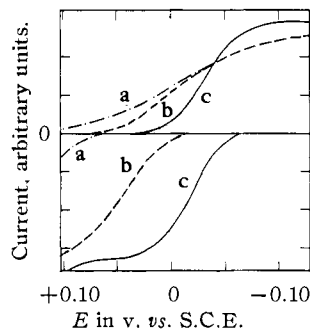

Fig. 10.—Oxygen and hydrogen peroxide waves in borate buffers: a, pH 7.75; b, 8.97; c, 9.87.

4.—Borate was the only buffer medium investigated in which the peroxide wave was well developed. Because of the complexation mentioned above it would presumably be hazardous to draw

conclusions from the $E_{1/2}$ of the peroxide wave in this medium, and possibly from the log plot also. The peroxide branch of the diagram in Fig. 2 was obtained from the first half of the wave, which can be observed fairly well in ammonia and in phosphate solution (pH 8) before the mercury dissolution wave completely obscures it. In general the wave appeared to be symmetrical in shape, with an apparent n value (on the basis of a reversible wave) of about 1.5. There is unfortunately only a narrow range of pH in which the peroxide wave can be observed in a truly irreversible state.

Discussion.—It may be worthwhile to discuss a simple model for the oxygen mechanism and compare the consequences with the experimentally observed facts. Thus the specific effects of pH and buffer components on the oxygen wave in acid and neutral medium may be dismissed as absorption effects, and the electron transfer be taken as the rate-determining step. The essential pH-independence of the reduction $E_{1/2}$ would require the following mechanism

$$O_2 + ne^- \longrightarrow O_2^{-n} \text{ (rate-determining)}$$
$$2H^+ + O_2^{-n} + (2 - n)e^- \rightleftarrows H_2O_2$$
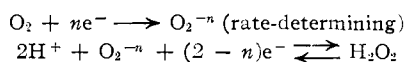
where $n = 1$ or 2. By the same token the $E_{1/2}$ of the peroxide wave would be pH dependent, as is observed experimentally, since the rate-determining electron transfer would be preceded by an equilibrium involving the hydrogen ion. On the basis of absolute rate theory, for a unit change in pH the $E_{1/2}$ would be expected to shift $0.059/\beta$ v. for $n = 2$, and $0.059/1/2(1 + \beta)$ for $n = 1$, where β is the transfer coefficient for the oxidation reaction. From the data available it would appear that the actual shift lies somewhere between 0.059×1 and $0.059 \times$

2, a condition that could be satisfied by either value of n.

According to the same theory,[20] the apparent n value n_b of the oxidation reaction, as determined from the log plot, should be 2β and $1 + \beta$ for $n = 1$ and $n = 2$, respectively. If it is assumed that $\alpha = 1 - \beta$, it follows that the relation $n_b = 2 - n_a$ should hold regardless of the value of n. As stated above, $n_b = ca.$ 1.5, hence the apparent n value n_a of the oxygen reduction wave should be $ca.$ 0.5. It has been shown that a reliable value for n_a cannot be measured, because of the deformation of the oxygen wave in different media. However, if the average of the two slopes in Fig. 7 is used, one obtains $n_a = 0.47$. In view of the uncertain value of both n_a and n_b, one must be cautious in attaching significance to this agreement.

The behavior mentioned in paragraph 3 is not consistent with the simple model discussed above. As the pH reaches values at which the reverse reaction (peroxide oxidation) becomes important, one would expect the reduction wave to move to more negative potentials along its entire length, and not have one part of the wave move backward while the other moves forward. The observed behavior suggests a radical change in the mechanism of reduction as the reaction approaches reversibility. It is conceivable, though unlikely, that the presence of HO_2^- in the solution in significant quantities might be connected with such a change in mechanism.

(20) D. M. H. Kern, THIS JOURNAL, **76**, 4234 (1954).

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Polarography of Nitrate Ion

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The reduction of nitrate ion in the presence of certain catalysts has been studied by the method of controlled potential coulometric electrolysis at a large mercury cathode. Electricity consumption and chemical analyses show that in the presence of uranyl ion nitrate is reduced chiefly to hydroxylamine, while in the presence of lanthanum or cerous ions the predominant reduction products are hydroxylamine and ammonia. Reasons are given why these products should also obtain at the dropping mercury electrode. Polarographic reduction of nitrate ion in acid medium without any specific catalyst present has been discovered. Under these conditions nitrite is a major, although probably not the only, product.

Introduction

That nitrate and nitrite produce polarographic waves in certain supporting electrolytes is well known,[1] but there is no agreement among previous investigators on the nature of the reduction products.

From the relative heights of the cadmium ion and nitrate ion waves in the presence of multi-charged cations Tokuoka and Ruzicka[2] concluded that reduction proceeds all the way to ammonia. This conclusion rests on the assumption of equal diffusion coefficients for nitrate and cadmium ions, whereas

in fact the diffusion coefficient of nitrate ion is more than twice as large as that of cadmium ion.

Kolthoff, Harris and Matsuyama[3] pointed out that the observed diffusion current constants, coupled with the assumption that the diffusion coefficient of nitrate ion in the test solutions is the same as at infinite dilution, indicates hydroxylamine as the reduction product in lanthanum chloride solution and elemental nitrogen in acidic uranyl solutions. This is, however, only a tentative conclusion. The fact that the true diffusion coefficient of nitrate ion in the actual solutions is uncertain makes impossible a more definite conclusion than that the n-value is close to 5 or 6, and probably not as large as 8.

(1) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 2nd ed., 1952, p. 533.

(2) M. Tokuoka, *Collection Czech. Chem. Communs.*, **4**, 444 (1932); M. Tokuoka and J. Ruzicka, *ibid.*, **6**, 339 (1934).

(3) I. M. Kolthoff, W. E. Harris and G. Matsuyama, THIS JOURNAL, **66**, 1782 (1944).