The high mobility of hydroxide ion would automatically lead to one of these fast moving boundaries in any suitably designed experiment to determine the mobility of $PO_4^{\equiv}$.

In addition to causing complications with strong electrolyte systems, moving boundaries across which no ion disappears may also complicate weak electrolyte and colloidal electrolyte systems. Consider the electrophoresis of a protein solution which has been dialyzed against a buffer containing an additional salt. In a particular case, the initial boundary system may be described as

$$\text{HA, Na}^+\text{, A}^-\text{, P}_1{}^{-x_2}\text{, P}_2{}^{-x_2}, \cdots, \text{P}_n{}^{-x_n}\text{, Cl}^-\ (\alpha) - \text{HA, Na}^+\text{, A}^-\text{, Cl}^-\ (\eta)$$

The uncharged weak acid type buffer is represented by HA, NaA, and the various negatively charged protein species are represented by $P_1{}^{-x_1}$, $P_2{}^{-x_2}$, ... $P_n{}^{-x_n}$. If, as might be expected, chloride is the fastest of these negatively charged species, there should be a moving boundary ahead of any boundary across which a protein constituent disappears. However, this boundary may be so small that the optical system will not detect it. It might, nevertheless, change appreciably the conductance upon which the protein mobility depends.

The basis for all of the foregoing discussion has been the assumption that the Dole polynomials provide two unequal values for the $V\sigma$ products associated with the faster boundary. However, it is perfectly reasonable that a system may be set up initially with compositions so that both of the roots associated with the faster moving boundary have the same value. In this highly specialized case the concentration ratio c^a/c^b is equal to unity for every species present in a phase adjacent to the particular boundary. This can only mean that the boundary is not a real one and that the number of moving boundaries for the system is diminished by one. However, it is not felt that any practical use can be made of this fact as a means of avoiding the difficulties which have been suggested. This is due to the fact that the lack of constancy of relative mobilities, even if accurate mobility data for some particular concentration were available, would prevent a rigorous application of the theory in order to determine the compositions of end phases which would allow the vanishing of the moving boundary across which no ion disappears.

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MADISON, WISCONSIN

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

Oxygen Induced Electroreduction of Hydrogen Peroxide and Reduction of Oxygen at the Rotated Gold Wire Electrode

BY I. M. KOLTHOFF AND JOSEPH JORDAN[1]

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The electroreduction of oxygen was studied voltammetrically at a rotated gold wire electrode in media of *p*H 4–13. Proportionality between diffusion current and concentration was found in an acetate buffer of *p*H 4, a phosphate buffer of *p*H 7 and in 0.1 *M* sodium hydroxide. The hydrogen overvoltage at the rotated gold electrode was determined in various supporting electrolytes and was found to be about 0.4 volt while the overvoltage at the rotated platinum electrode is negligible. Gold wire electrodes are more suitable than platinum for the amperometric determination of oxygen. Hydrogen peroxide greatly increases the limiting current of oxygen at the rotated platinum and gold electrodes. The electroreduction of oxygen induces the electroreduction of hydrogen peroxide at potentials at which the peroxide is not normally reduced. The exaltation of the oxygen wave by hydrogen peroxide and the induced electroreduction of the peroxide are accounted for by the sequence of reactions: $O_2 + e^- \rightarrow O_2^-$; $O_2^- + H_2O_2 \rightarrow OH^- + O_2 + OH^\cdot$; $OH^\cdot + e^- \rightarrow OH^-$. Use of the exaltation can be made in the determination of very small concentrations of oxygen.

In a preliminary communication[2] it was reported that the electroreduction of oxygen induces the reduction of hydrogen peroxide at rotated and stationary platinum electrodes. The exaltation of the oxygen wave by hydrogen peroxide was described and a reaction mechanism was postulated, involving primarily a two-step reduction of O_2 to O_2^{--}, with the intermediate formation of O_2^- (anion of HO_2). A chain reaction between O_2^- (or HO_2) and hydrogen peroxide, according to the Haber and Weiss mechanism[3] accounts for the exaltation of the oxygen wave.

In the present paper are presented and discussed the results of a detailed study of the electroreduction of oxygen at the rotated platinum and gold wire microelectrodes. The rotated gold wire electrode was found to be more suitable than platinum for the determination of oxygen in the *p*H range between 4 and 13. The exaltation of the oxygen wave by hydrogen peroxide has been investigated as a function of *p*H, concentration of hydrogen peroxide and of oxygen, and temperature. With our gold electrode the exalted limiting current in 10^{-3} *M* hydrogen peroxide solution was found to be proportional to oxygen concentration in the 10^{-7} to 10^{-6} *M* range. Analytical application of the exaltation to the determination of traces of oxygen is described.

Experimental

Materials.—C.P. chemicals and conductivity water (redistilled in an all-Pyrex still) were used throughout. Dilute

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(1) On leave from the Hebrew University, Jerusalem, Israel.

(2) I. M. Kolthoff and J. Jordan, THIS JOURNAL, **74**, 570 (1952).

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

solutions of hydrogen peroxide were prepared from an unstabilized Baker product and standardized with ceric sulfate at frequent intervals.

Apparatus.—Current–voltage curves were recorded with a Sargent Model XXI polarograph. For some measurements of limiting currents a manual setup[4] was used. The electrolysis cell and the reference electrode have been described in a previous paper.[5] A synchronous motor was used to rotate the electrodes at 600 r.p.m.

Electrodes.—Results reported in this paper were obtained at platinum, gold, silver, as well as at gold amalgam and silver amalgam electrodes.

The rotated platinum electrode was made of an annealed wire, 0.5 mm. in diameter and 4 mm. in length. In one type of electrolysis experiments a large cylindrical cathode, made of perforated platinum foil, was used. Its total exposed area was approximately 110 sq. cm. The gold electrode was made of pure gold wire, 0.3 mm. in diameter and 6 mm. in length. Since gold dissolves in mercury, the wire was soldered to a copper wire. The copper–gold joint was sealed into a glass tube, the copper end protruding upwards into the tube. Electrical contact to the copper was made with the aid of mercury.

In a few qualitative experiments silver, silver amalgam and gold amalgam electrodes were used. They consisted of wires 0.5 mm. in diameter and 5 mm. in length, dipped into mercury for various intervals (15 minutes to 24 hours).

Procedure.—All experiments were carried out in a water thermostat at 25 ± 0.02°.

To prepare air-saturated solutions, air was bubbled through with a fritted glass disk[6] of medium porosity. Saturation was obtained within 2 minutes. Oxygen-free solutions were prepared by deaerating with Linde nitrogen washed through vanadous perchlorate.[7] Whenever it was desired to maintain a known oxygen concentration at a level below the partial pressure of oxygen in the atmosphere, a measured volume of the supporting electrolyte was first completely deaerated; then—while nitrogen was led *over* the surface of the solution—a known volume of air-saturated supporting electrolyte was injected with a calibrated syringe. For instance, 1 ml. of air-saturated 0.1 *M* potassium chloride solution (which is 2.62×10^{-4} *M* in oxygen at 25° and at a barometric pressure of 740 mm.) injected into 50 ml. of deaerated 0.1 *M* potassium chloride, yields a solution which is 5.24×10^{-6} *M* in oxygen. By adjusting the nitrogen stream over the solution, it was possible to maintain the dissolved oxygen level constant up to one hour. Hydrogen peroxide was injected in the form of an air-free solution immediately before the current–voltage curves were determined. Under these conditions the hydrogen peroxide concentration remained constant throughout the duration of a current–voltage recording experiment. Upon longer periods of contact with the metal electrode—especially gold—appreciable decomposition of the peroxide may occur.

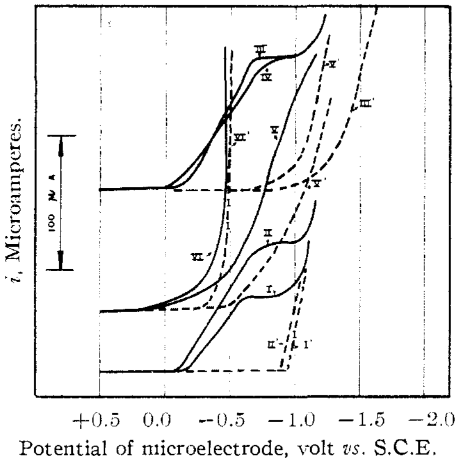

Fig. 1.—Current–voltage curves of oxygen in air-saturated solutions at the rotated platinum electrode: I, in 1 *M* NaOH; II, in 0.1 *M* NaOH; III, in 0.1 *M* $NaClO_4$; IV, in phosphate buffer of *p*H 7; V, in acetate buffer of *p*H 4; VI, in 0.1 *M* perchloric acid. Curves I′–VI′ (dotted lines) indicate corresponding residual currents of oxygen-free supporting electrolytes. Curves are shifted arbitrarily along vertical axis.

Results

The Reduction of Oxygen at Various Rotated Microelectrodes.

(a) **Platinum.**—Laitinen and Kolthoff[4] studied current–voltage curves of oxygen at the rotated platinum wire electrode in 0.1 *M* potassium chloride solution. We ran polarograms of oxygen at different *p*H. From Fig. 1 it is seen that well-defined diffusion currents were obtained in solutions of *p*H 7 or greater. In acid solution hydrogen evolution interferes. The half-wave potential was reasonably constant (−0.4 v. *vs.* S.C.E.) and independent of *p*H. In 0.1 *M* sodium hydroxide, in 0.1 *M* sodium perchlorate and in a phosphate buffer of *p*H 4 the diffusion current was 100 ± 2μa. The concentration of oxygen in these solutions, in equilibrium with the ambient atmosphere, was 2.62×10^{-4} *M*. In 0.1 *M* sodium hydroxide and at the same electrode the value of i_d/c for the thallous–thallic oxidation was found to be 281 ± 6μa millimole/liter. Assuming that diffusion currents at the rotated platinum electrode to be proportional to diffusion coefficients and taking the diffusion coefficient of thallium[8] in the given medium equal to 2.00×10^{-5} cm.^{2} × sec.$^{-1}$, we calculate a diffusion coefficient of oxygen of $(2.72 \pm 0.05) \times 10^{-5}$ cm.^{2} × sec.$^{-1}$ in 0.1 *M* alkali at 25°. This compares with a value of 2.6×10^{-5} derived from measurements with the dropping electrode in 0.1 *M* potassium nitrate,[9] of 2.4×10^{-5} reported by Laitinen and Kolthoff[4] in 0.1 *M* potassium chloride (stationary platinum electrode) and of 2.39×10^{-5} found by Carlson from direct diffusion measurements in 0.17 *M* sodium chloride.[10] The diffusion current of oxygen in 1 *M* sodium hydroxide was found to be only 58% of that in 0.1 *M* alkali. This small value is accounted for mainly by the decreased solubility of oxygen and to a minor extent by the viscosity effect.

For the determination of oxygen at the rotated platinum electrode 0.1 *M* sodium hydroxide and 0.1 *M* sodium perchlorate appear to be best suited. We checked the proportionality between oxygen concentration and diffusion current in these two supporting electrolytes, for concentrations between 5×10^{-6} and 2.6×10^{-4} *M*: i_d/c was (382 ± 7) μa./millimole/liter. The diffusion current should be measured in the −0.85 to −0.90 v. region (*vs.* S.C.E.). The narrowness of this region is a great disadvantage in the use of the rotated platinum electrode.

(b) **Gold.**—Experiments with the rotated gold wire electrode as indicator electrode appeared promising because it was found that the hydrogen overvoltage at this electrode is considerably greater

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[10] J. Carlson, *ibid.*, **33**, 1027 (1911).

than at the rotated platinum electrode. The gold electrode yielded reproducible residual currents provided it was washed in 10 M nitric acid and subsequently prepolarized at -2.0 v. for 10 minutes. The cathodic decomposition potentials (*i.e.*, the potentials at which the air-free supporting electrolytes yield a hydrogen current in excess of one microampere) at the rotated gold wire electrode are summarized in Table I. The corresponding values at the rotated platinum electrode and the thermodynamic equilibrium potentials for hydrogen evolution are listed for comparison. The data in the unbuffered perchlorate solution are given in parentheses; they have no exact significance. While the hydrogen overvoltage in the buffered solutions is negligible on platinum it is seen that between pH 4 and 13 the overvoltage at the rotated gold electrode is of the order of 0.4 to 0.5 v. On the basis of these results it was anticipated that the constant diffusion current region of oxygen would extend to more negative potentials at the rotated gold electrode than at the platinum wire electrode. This is seen to be true from some typical current–voltage curves presented in Fig. 2.

TABLE I

HYDROGEN OVERVOLTAGE (*vs.* S.C.E.) AT ROTATED MICRO-CATHODES

Supporting electrolyte	pH	Thermodynamic hydrogen potential	Observed decomposition potentials Platinum	Gold
0.1 M perchloric acid	1.0[c]	-0.31	-0.31	-0.37
Acetate buffer[a]	4.0	$-$ .49	$-$ .50	-0.88
0.1 M sodium perchlorate	(7.0)	($-$ .66)	($-$ .85)	(-1.13)
Phosphate buffer[b]	7.0	$-$ .66	$-$ .70	-1.19
0.05 M borax	9.2	$-$ .79	$-$ .80	-1.25
0.1 M sodium hydroxide	12.9[c]	$-$ .90	$-$ .91	-1.28

[a] Total concentration in sodium acetate + acetic acid = 0.1 M. [b] M/30 in total phosphate. [c] pH calculated using Latimer's activity coefficients.

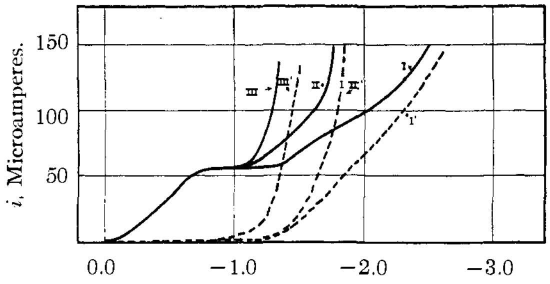

Fig. 2.—Current–voltage curves of 2.62×10^{-4} M oxygen at the rotated gold wire electrode: I, in 0.1 M NaOH; II, in phosphate buffer of pH 7; III, in acetate buffer of pH 4. Curves I', II', III' (dotted lines) indicate residual currents of oxygen-free supporting electrolytes.

In 0.1 M alkali the diffusion current of oxygen can be measured at any potential between -0.8 and -1.25 v. (*vs.* S.C.E.), between -0.8 and -1.1 v. at pH 7, and between -0.8 and -1.0 at pH 4. The ratio i_d/c was constant at oxygen concentrations between 5×10^{-6} and 2.6×10^{-4} M and found to be equal to (221 ± 4) μa./millimole/liter with our electrode. The rotated gold wire electrode is ideally suited for the determination of oxygen in the pH range 4–13.

Curve I in Fig. 2 indicates the appearance of a very poorly developed second wave in alkaline solution, corresponding to the electroreduction of hydrogen peroxide

$$H_2O_2 + 2e^- \longrightarrow 2OH^-$$

This wave was slightly better defined at a rotated amalgamated gold electrode, which, however, yields irreproducible results. A well-defined double-wave was obtained in air-saturated sodium perchlorate solution at a rotated amalgamated silver electrode, but the results were poorly reproducible. An unamalgamated silver wire electrode did not yield any hydrogen peroxide wave.

The Effect of Hydrogen Peroxide on the Oxygen Wave.—A brief description of the exaltation of the oxygen wave by hydrogen peroxide at rotated and stationary platinum wire electrodes has been given previously.[2] In the present paper are reported results of a systematic study of the various factors which affect the exaltation at the rotated gold wire electrode. Gold, because of the hydrogen overvoltage, is much more suitable for this investigation than platinum. However, qualitatively the platinum electrode yields results similar to those found with gold.

Current–voltage curves of oxygen-free 0.1 M sodium hydroxide solutions containing varying amounts of hydrogen peroxide are shown in Fig. 3.

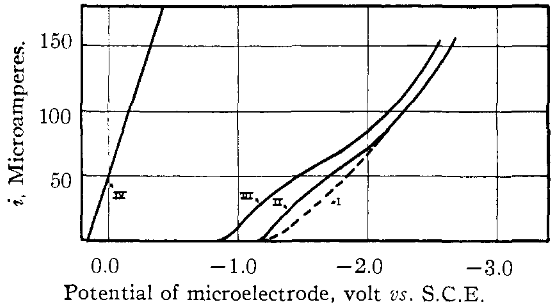

Fig. 3.—Current–voltage curves of oxygen-free 0.1 M sodium hydroxide at the rotated gold wire electrode: I, no H_2O_2; II, 10^{-4} M H_2O_2; III, 10^{-3} M H_2O_2; IV, 10^{-2} M H_2O_2.

A cathodic current starting at -1.2, -0.9 and $+0.2$ v. in 10^{-4}, 10^{-3} and 10^{-2} M hydrogen peroxide, respectively, is observed. This current (probably corresponding to the reduction of the peroxide) merges gradually with the residual current (due to hydrogen evolution) of the supporting electrolyte. The "decomposition potentials" observed in the presence of hydrogen peroxide were found to be independent of pH, between pH 4 and 13. From the above it is evident that 10^{-3} M is about the upper limit of the hydrogen peroxide concentration at which the limiting current (i_l) of the oxygen wave can still be measured. Exalted waves obtained at pH 4 and 13 are plotted in Fig. 4. The constant current regions end at about 0.2

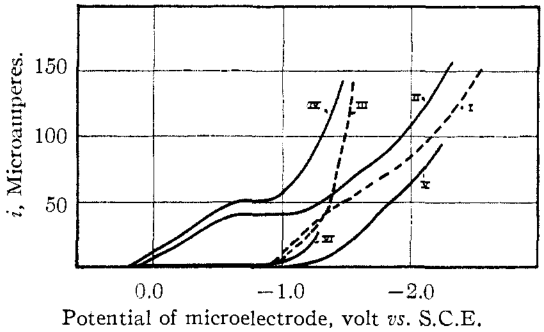

Fig. 4.—The exalted oxygen wave at the rotated gold wire electrode: I, 0.1 M NaOH, O_2-free, 10^{-3} M H_2O_2; II, 0.1 M NaOH, 2.62 × 10^{-6} M O_2, 10^{-3} M H_2O_2; III, acetate buffer of pH 4, O_2-free, 10^{-3} M H_2O_2; IV, acetate buffer of pH 4, 2.62 × 10^{-6} M O_2, 10^{-3} M H_2O_2; V, 0.1 M NaOH, 2.62 × 10^{-6} M O_2, no H_2O_2; VI, acetate buffer of pH 4, 2.62 × 10^{-6} M O_2, no H_2O_2.

v. more positive potentials than the "normal" (unexalted) oxygen waves do (*cf.* Fig. 2). The ratio $i_l/i_{d_{O_2}}$, between the limiting current of a given oxygen solution in the presence of hydrogen peroxide and its diffusion current obtained in the absence of peroxide, is defined as the "exaltation." The exaltation appears to be independent of pH in the region between 4 and 9 but it decreases markedly at increasing concentrations of free alkali. A few representative data are given in Table II. The exalted wave provides a sensitive method for the determination of microquantities of oxygen, 0.1 M sodium hydroxide being a suitable supporting electrolyte. The limiting current can be measured manually at −0.8 v. *vs.* S.C.E. As seen in Fig. 5 proportionality between limiting current and concentration in 10^{-3} M hydrogen peroxide is found for oxygen concentrations of 1 × 10^{-7} to 5 × 10^{-6} M. At higher concentrations the i_l/c_{O_2} ratio decreases rapidly, probably because of the marked depletion of the peroxide concentration at the electrode surface as a result of its induced decomposition. Figure 6 indicates that i_l is proportional to the concentration of hydrogen peroxide, provided that its molar concentration is at least two hundred times greater than that of oxygen.

TABLE II

EXALTATION IN VARIOUS MEDIA

O_2 = 2.62 × 10^{-6} M; H_2O_2 = 10^{-3} M

Supporting electrolyte	pH	Exaltation
Acetate buffer[a]	4.0	90
Phosphate buffer[b]	7.0	90
0.05 M borax	9.2	85
0.1 M NaOH	12.9[c]	69
1 M NaOH	13.8[c]	30

[a,b,c] See same notations in Table I.

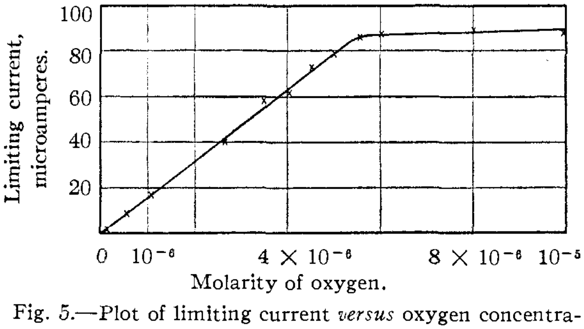

Fig. 5.—Plot of limiting current *versus* oxygen concentration (gold electrode); 10^{-3} M H_2O_2 in 0.1 M sodium hydroxide.

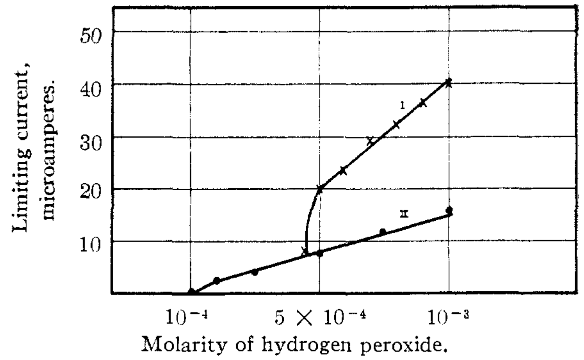

Fig. 6.—Plot of limiting current *versus* hydrogen peroxide concentration in 0.1 M sodium hydroxide (gold electrode): I, 2.62 × 10^{-6} M oxygen; II, 1.00 × 10^{-6} M oxygen.

Effect of Temperature on the Exalted Oxygen Wave.—The values of the limiting current at 25° in 0.1 M sodium hydroxide and 10^{-3} M hydrogen peroxide were 40 μa. in a 2.62 × 10^{-6} M oxygen solution and 78 μa. in a 5.00 × 10^{-6} M solution. At 35° these values were 57 and 111 μa., respectively. Hence the temperature coefficient of the exalted wave is equal to 4.2% per degree in this interval.

The Induced Decomposition of Hydrogen Peroxide at a Large Platinum Cathode (area 110 sq. cm.).—In 300 ml. of a deaerated phosphate buffer of pH 7 (1/6 M in total phosphate), which was 0.01000 M in hydrogen peroxide, no measurable current was observed with a milliammeter at a cathode potential of −0.1 v. *vs.* S.C.E. The cathode potential was maintained for 60 hours at this value, with nitrogen bubbling continuously through the solution. At the end of this period the concentration of hydrogen peroxide was 0.01005 M.

An air saturated solution of identical composition was now electrolyzed for 60 hours at −0.1 v. *vs.* S.C.E. with air bubbling through the cell continuously. An average current of 0.25 μa. was observed (0.27 μa. at the beginning of the electrolysis, 0.24 μa. at the end). During the electrolysis the concentration of hydrogen peroxide dropped from 0.01000 to 0.00850 M. If the current would have resulted in a reduction of oxygen to hydrogen peroxide the concentration of the latter should have *increased* by about 10% at 100% current efficiency.

Discussion

The reduction of oxygen at the dropping mercury electrode[9,11] and at the platinum wire electrode[4] is irreversible. The first wave at the dropping electrode corresponds to the one wave obtained at platinum and rotated gold wire electrodes. Hydrogen peroxide is produced, according to the over-all stoichiometry.

$$O_2 + 2e^- + 2H^+ \longrightarrow H_2O_2$$

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(11) J. Heyrovsky, *Trans Faraday Soc.*, **19**, 785 (1924).

We assume that the electroreduction of oxygen occurs in the two steps[2]

$$O_2 + e^- \longrightarrow O_2^- \qquad (1)$$

$$O_2^- + e^- \longrightarrow O_2^{=} \qquad (2)$$

The characteristics of the reduction waves of oxygen at the dropping mercury and rotated noble metal electrodes are independent of pH; thus it may be concluded that hydrogen ions are not potential determining in reactions (1) and (2).

The existence of O_2^- (and of the corresponding acid HO_2) has been postulated by various authors.[12-15] Spectroscopic evidence that this species is formed in the reaction $O_3 + OH^- \rightarrow O_2^- + HO_2$ was provided by Weiss.[16] Newman[17] concluded from magnetic susceptibility measurements that the structure of the anion in KO_2 corresponds to $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:\underset{\cdot\cdot}{\overset{\cdot}{O}}:^-$. This was recently substantiated by Astakhov and Getsov[18] in a study of the properties of CaO_4.

The exaltation of the oxygen wave by hydrogen peroxide can be accounted for by assuming that O_2^- (or HO_2, *v.i.*), formed intermediately in the reduction of oxygen, reacts faster with hydrogen peroxide than it is reduced according to equation (2). In the reaction of O_2^- and HO_2 with hydrogen peroxide by the Haber and Weiss mechanism[3] oxygen is regenerated continuously

$$O_2^- + H_2O_2 \longrightarrow OH^- + O_2 + OH^{\cdot} \qquad (3a)$$

or

$$HO_2 + H_2O_2 \longrightarrow H_2O + O_2 + OH^{\cdot} \qquad (3b)$$

The free radicals can react with hydrogen peroxide with regeneration of HO_2

$$OH^{\cdot} + H_2O_2 \longrightarrow H_2O + HO_2 \qquad (4)$$

or they can be reduced at the electrode

$$OH^{\cdot} + e^- \longrightarrow OH^- \qquad (5)$$

or both reactions (4) and (5) might occur simultaneously. From the fact that substances like methanol, ethanol, glycerol, allyl alcohol, allyl acetate, acrylonitrile and styrene, which react very rapidly with hydroxyl radicals, do not affect the exaltation of the oxygen wave it is concluded that reaction (5) is the main terminating step. Thus (1), (3) and (5) account for the oxygen induced electroreduction of hydrogen peroxide to hydroxyl ions at rotated noble metal wire electrodes according to the over-all reaction $H_2O_2 + 2e^- \rightarrow 2OH^-$. From the magnitude of the exaltation an estimate of the length of the chain (eq. 1 and 3) can be obtained.

It is well known in industrial literature[19] that in the preparation of hydrogen peroxide by the electroreduction of oxygen, peroxide is formed until a certain concentration (the value of which depends on the type of electrode and various other factors) is attained. From then on the concentration of the peroxide remains unchanged upon further electrolysis. When this "steady state concentration" has been reached the rate of formation of the peroxide apparently has become equal to its rate of disappearance by its oxygen induced electroreduction. If the concentration of the peroxide were greater than corresponds to the steady state concentration, electrolysis in the presence of oxygen would result in a decrease of the concentration of peroxide. This indeed was observed in our electrolysis experiment at the large platinum electrode.

In the above discussion we have not considered whether O_2 or HO_2 is the reacting species in equation (3). Latimer[20] estimates the free energy of ionization of HO_2 to be 10,000 cal. which yields $10^{-7.3}$ for the ionization constant of HO_2 at 25°, while Weiss[21] gives 10^{-6} at 20°. From Table II it is seen that the exaltation of the oxygen wave is independent of pH in the region between 4 and 9. Making the plausible assumption that HO_2 reacts with a different rate with hydrogen peroxide than O_2^- does, it must be concluded from the above that the O_2^- formed in reaction (1) reacts faster with hydrogen peroxide (reaction 3a) than with hydrogen ions. Under our experimental conditions reaction (3b) apparently cannot occur.

The decrease in the exaltation in strongly alkaline medium (Table II) may be due to a difference between the rates of reaction of H_2O_2 and its anion HO_2^-, the first dissociation constant of hydrogen peroxide being reported equal to 2.4×10^{-12} and the second one to 10^{-25}.[22]

Acknowledgment.—Acknowledgment is made to the Research Corporation for a grant in support of this work.

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