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

Moving Boundaries Formed by Strong Electrolyte Systems

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Moving boundary studies have been made on systems in which the fastest ion of the charge type that produces the new phases is present on both sides of the initial boundary. This feature leads to a moving boundary across which no ion disappears, and this boundary is faster than any other moving boundary in the system. Volume displacements by such boundaries have been measured and compared with those calculated using the Dole theory. The gravitational stability of moving boundary systems is discussed.

A number of studies of both theoretical and experimental nature have treated the behavior of concentration gradients which move away from an initial sharp boundary between two electrolyte solutions during the passage of a current. Dole[1] has developed a theory which can be used to provide a complete description of such a strong electrolyte system. The solution of this problem depends upon a knowledge of the compositions of the two initial solutions and upon a knowledge of the relative mobilities of all of the ion species involved. It is assumed that the relative mobilities of the ions do not vary with concentration.

Let the strong electrolyte solutions which are separated by an initial sharp boundary be designated as α and η such that the α solution is adjacent to the positive electrode and the η solution is adjacent to the negative electrode. The relative mobilities of the ion species are termed r_1, r_2, . . ., r_n; these designations are such that the order is from the most highly negative mobility, r_1, to the most highly positive mobility, r_n. The corresponding concentrations are given in equivalents per liter as c_1^α, c_2^α, . . ., c_n^α and c_1^η, c_2^η, . . ., c_n^η, respectively, for the separate phases. These values of the concentrations and relative mobilities then enter into two equations (equation 33 in ref. 1), one for each initial solution, and the $2(n - 2)$ roots of these equations are shown to be the values of the products of volumes swept out by the boundaries (V liters per faraday) and the relative conductances ($\sigma = \sum_i^n c_i r_i$) of solutions enclosed by these boundaries. There are two solutions contiguous to each boundary; hence, for each boundary there are two $V\sigma$ products, and it may be concluded that $n - 2$ moving boundaries are to be permitted. The Dole theory indicates that the $V\sigma$ products which are obtained from the equation involving the concentrations of the η solution are the values for $V^{\alpha\beta}\sigma^\alpha$, $V^{\beta\gamma}\sigma^\beta$, etc., and the roots from the equation involving the concentrations of the α solution are the values for $V^{\alpha\beta}\sigma^\beta$, $V^{\beta\gamma}\sigma^\gamma$, $V^{\gamma\delta}\sigma^\delta$, etc. In other words, at a particular boundary the $V\sigma$ product applying to the phase nearer a given electrode is a root of the polynomial associated with the original solution which is adjacent to the other electrode. Furthermore, the values of the $V\sigma$ products at the $\alpha\beta$ boundary are restricted to the interval between r_1 and r_2, at the $\beta\gamma$ boundary to the interval between r_2 and r_3, etc. When an ion is absent from one initial solution, however, one of the $V\sigma$ products does not lie within the interval, but it is equal to the relative mobility of the absent ion. When the proper assignment of $V\sigma$ products to the phases has been made, the compositions of the intermediate phases can be determined. The manner in which this is done is described in a later paragraph.

The predictions of the Dole theory have been tested experimentally by Longsworth.[2] However, studies of certain additional types of systems which have not been reported would appear to be of interest. A system (a) should form the moving boundary system (b) during electrolysis, if the mobilities have the relative magnitudes $|r_A| > |r_B| > |r_C|$[3]

(a) A, C, R (α) – A, B, R (δ)

(b) A, C, R (α) :: A, C, R (β) $\longrightarrow$ A, B, R (γ) $\longrightarrow$ A, B, R (δ)

A total of four ion species permits the two moving boundaries, and the proper assignment of the $V\sigma$ products leads to the formulation above. It is particularly important to observe that the fastest moving boundary is not the type which is useful for mobility measurements for the reason that no ion disappears across the boundary. In a similar manner if $|r_R| > |r_S| > |r_T|$, system (c) must develop into system (d).

(c) A, R, S (α) – A, R, T (δ)

(d) A, R, S (α) $\longleftarrow$ A, R, S (β) $\longleftarrow$ A, R, T (γ) :: A, R, T (δ)

The fastest anion, R^-, appears on both sides of the initial boundary; hence, a boundary must move ahead of the boundary across which ions that are absent in the initial phases disappear. The generalizations for these two particular types of systems follow directly from the Dole development.[1]

Experimental

Reagents.—Stock solutions of individual salts, which were prepared from the reagent grade chemicals, were diluted by known factors to obtain the solutions for the experiments. Concentrations of stock solutions were known with sufficient accuracy from direct weighing or analysis that final volume concentrations for 25° were known within 1%.

Boundary Velocity Measurements.—The moving boundary experiments were performed in a 2° thermostat by use of a standard Tiselius cell of 3 × 25 mm. cross section. Photographs of 20 sec. exposure on Eastman Kodak Co. Tri-X panchromatic film were taken with the aid of a diagonal knife edge schlieren optical system. Knife edge angles of 7.5 to 40 degrees were used. A current was maintained constant to ±0.02% by means of a galvanometer

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[1] V. P. Dole This Journal, **67**, 1119 (1945).

[2] L. G. Longsworth, *ibid.*, **67**, 1109 (1945).

[3] The notation is that suggested by L. G. Longsworth (ref. 2).

phototube–d.c. amplifier arrangement[4]; currents of 5 to 10 ma. were used in the separate experiments.

The negatives were enlarged and traced by hand, and these tracings were used to determine velocities. To evaluate the displacements on the tracing in terms of displacements in the cell, it was required that the cross sectional area of the Tiselius cell, the vertical camera magnification factor, and the tracing enlargement factor be known. A single factor combining the first two of these was determined by measuring the transference numbers for 0.2 *N* KCl; Longsworth's values[2] for transference numbers were then used to calculate this combined cell and camera factor from observed displacements on the photograph. The accuracy of this calibration is thought to approximate one part per thousand.

Experimental Results.—The systems which have been studied may be described before and after the passage of the current as follows:

(e) K, Li, Cl (α) – K, Na, Cl (δ)
K, Li, Cl (α) :: K, Li, Cl (β) ⟶
K, Na, Cl (γ) ⟶ K, Na, Cl (δ)

(f) K, Cl, BrO_3 (α) – K, Cl, IO_3 (δ)
K, Cl, BrO_3 (α) ⟵ K, Cl, BrO_3 (β) ⟵
K, Cl, IO_3 (γ) :: K, Cl, IO_3 (δ)

It should be mentioned that system (e) was run as a descending boundary system, but (f) was run as an ascending system. This was necessary in order to achieve gravitational stability. (This point will be discussed later in this paper.) The moving boundary patterns must have the characteristics which are indicated inasmuch as $r_{\mathrm{K}} > r_{\mathrm{Na}} > r_{\mathrm{Li}}$ and $|r_{\mathrm{Cl}}| > |r_{\mathrm{BrO_3}}| > |r_{\mathrm{IO_3}}|$; that is to say, according to the nomenclature previouly used, A = K, B = Na, C = Li, R = Cl, S = BrO_3 and T = IO_3. Using the Dole theory it is possible to calculate the values of the quantities $V^{\gamma\delta}$ and $V^{\beta\gamma}$ for system (e) and the values of $V^{\alpha\beta}$ and $V^{\beta\gamma}$ for system (f). The limiting ionic conductance values at 0° listed by Lange[5] have been used to obtain values for the relative mobilities, which are $r_{\mathrm{K}} = 0.973$, $r_{\mathrm{Na}} = 0.621$, $r_{\mathrm{Li}} = 0.467$, $r_{\mathrm{IO_3}} = -0.48_3$, $r_{\mathrm{BrO_3}} = -0.741$ and $r_{\mathrm{Cl}} = -1.000$.

The values of boundary displacements have been calculated from theory, and they have been measured experimentally. The results for systems of the type (e) are listed in Table I and those for systems of the type (f) in Table II. It is necessary to point out that KCl is omitted from the α solution of experiment 3 and from the δ solution of experiment 6. This means that the electrolyte contributing the fastest ion of the charge type which produces the moving boundaries is absent from one of the initial solutions, and in each experiment both moving boundaries are of the type across which ions disappear. The moving boundary patterns in these two special cases are illustrated in the following manner

TABLE I

Experiment		1	2	3
$\overset{\delta}{c}_{\mathrm{KCl}}$		0.0407	0.0152	0.0198
$\overset{\delta}{c}_{\mathrm{NaCl}}$		.0149	.0277	.0185
$\overset{\alpha}{c}_{\mathrm{KCl}}$		.00092	.00092	0
$\overset{\alpha}{c}_{\mathrm{LiCl}}$		.00964	.00964	.00964
$V^{\gamma\delta}$	theory	8.77	12.23	14.09
	exptl.	8.75	12.23	14.18
$V^{\beta\gamma}$	theory	7.75	9.12	11.31
	exptl.	7.65	9.01	11.19
$V^{\gamma\delta}/v^{\beta\gamma}$	theory	1.131	1.341	1.246
$\sigma^{\delta}/\sigma^{\gamma}$		1.304	1.100	1.257

(3) Li, Cl (α) : : Li, Cl (β) ⟶
Na, Cl (γ) ⟶ K, Na, Cl (δ)

(6) K, Cl, BrO_3 (α) ⟵ K, BrO_3 (β) ⟵
K, IO_3 (γ) : : K, IO_3 (δ)

A survey of the data listed in Tables I and II reveals discrepancies between calculated and observed volume displacements that amount to as much as 2.3% in some cases; the average difference is 0.9%. It is felt that this lack of agreement is not serious in view of certain limitations which must be considered. Primarily, there is the theoretical assumption that relative ion mobilities do not vary with concentration; this is only approximately valid. Secondly, the accuracy of the calculated $V\sigma$ products is limited by the uncertainty in the values of the concentrations and mobilities which are substituted in the Dole polynomials.

TABLE II

Experiment		4	5	6
$\overset{\alpha}{c}_{\mathrm{KCl}}$		0.0527	0.0109	0.0200
$\overset{\alpha}{c}_{\mathrm{KBrO_3}}$		.0299	.0300	.0200
$\overset{\delta}{c}_{\mathrm{KCl}}$		.0126	.0031	0
$\overset{\delta}{c}_{\mathrm{KIO_3}}$		.1200	.0800	.0600
$V^{\alpha\beta}$	theory	6.03	13.36	13.56
	exptl.	6.04	13.42	13.56
$V^{\beta\gamma}$	theory	5.40	10.72	11.66
	exptl.	5.29	10.56	11.40
$V^{\alpha\beta}/v^{\beta\gamma}$	theory	1.111	1.246	1.162
$\sigma^{\alpha}/\sigma^{\beta}$		1.131	1.054	1.160

The analysis of system (e) obtained by the use of the Dole theory leads to the conclusion that $V^{\beta\gamma}\sigma^{\gamma} = r_{\mathrm{Na}}$ and $V^{\beta\gamma}\sigma^{\beta} = r_{\mathrm{Li}}$; furthermore, the values of $V^{\gamma\delta}\sigma^{\delta}$ and $V^{\gamma\delta}\sigma^{\gamma}$ must lie in the interval between r_{K} and r_{Na}. With these limits in mind, certain facts of practical interest may be deduced. It would obviously be a happy circumstance to have the moving boundaries resolve rapidly and move at the same time as sharp boundaries. Another way of stating these conditions would be that $V^{\gamma\delta}/V^{\beta\gamma}$, $\sigma^{\delta}/\sigma^{\gamma}$ and $\sigma^{\gamma}/\sigma^{\beta}$ are all considerably larger than unity; the conductance ratios determine the boundary sharpening characteristics. Of these ratios, $\sigma^{\gamma}/\sigma^{\beta}$ is equal to a constant, $r_{\mathrm{Na}}/r_{\mathrm{Li}}$, but $V^{\gamma\delta}/V^{\beta\gamma}$ and $\sigma^{\delta}/\sigma^{\gamma}$ are determined by the concentrations of the two initial solutions. However, the limits which are imposed upon the products $V^{\gamma\delta}\sigma^{\delta}$ and $V^{\gamma\delta}\sigma^{\gamma}$ mean that $V^{\gamma\delta}/V^{\beta\gamma}$ and $\sigma^{\delta}/\sigma^{\gamma}$ cannot have maximum values independently. If $\sigma^{\delta}/\sigma^{\gamma}$ is greater than unity, it may be seen that $r_{\mathrm{Na}} = V^{\beta\gamma}\sigma^{\gamma} < V^{\gamma\delta}\sigma^{\gamma} < V^{\gamma\delta}\sigma^{\delta} < r_{\mathrm{K}}$. If $V^{\gamma\delta}/V^{\beta\gamma}$ approaches an upper limit of $r_{\mathrm{K}}/r_{\mathrm{Na}}$, $\sigma^{\delta}/\sigma^{\gamma}$ must be diminished toward unity, its smallest favorable value. On the other hand, if $\sigma^{\delta}/\sigma^{\gamma}$ approaches a maximum value of $r_{\mathrm{K}}/r_{\mathrm{Na}}$, $V^{\gamma\delta}/V^{\beta\gamma}$ must be reduced toward unity, its minimum value. In a similar fashion for the chloride–bromate–iodate system the least sharp $\alpha\beta$ boundary is to be expected when the velocities of the boundaries have their greatest difference; conversely, the sharpest $\alpha\beta$ boundary should occur when the rate of resolution of the boundaries is lowest. Photographs of the moving boundary patterns of experiments 1, 2, 4 and 5 exhibit the predicted effects regarding sharpness.

Discussion

Gravitational Stability; Concentration Changes across Moving Boundaries.—Gravitational stability at phase boundaries is a matter of practical interest which the theory does not treat. In order to run experiments successfully, it is obviously important that convection from unfavorable density gradients should not disturb the boundaries. If one wishes to investigate a certain type of system, the choice of ion components depends not only upon relative mobilities which would produce the desired type of pattern during the passage of current but upon relative contributions to solution density which would permit a gravitationally stable system. For example, some other ion with the same mobility as BrO_3^- could not be used successfully in place of BrO_3^- if it gave a contribution to density so much smaller than that of BrO_3^- that the β solution of (f) should become less dense than the α solution.

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[4] To be described in a forthcoming publication by N. E. Bonn H. L. Marvin and R. A. Alberty.

[5] J. Lange, *Z. physik. Chem.*, **A188**, 284 (1941).

The equation which defines the apparent molal volume of a solute may be rearranged to the form $\Delta d = c(M_2 - d_0\phi_V)/1000$, where ϕ_V is the apparent molal volume of the solute, M_2 is the molecular weight of the solute, c is the concentration of the solute in moles per liter, d_0 is the density of pure solvent, and Δd is the increment in density of the solution over that of the pure solvent. For water as the solvent, the equation becomes $\Delta d = c(M_2 - \phi_V)/1000$ as an approximation. Furthermore, for a dilute solution which contains more than one solute, the approximation $\Delta d = \sum_i c_i[M_i - (\phi_V)_i]/1000$ is assumed to be valid. This equation is useful in predicting the densities of the various phases in a moving boundary experiment. The authors found it more convenient to estimate in advance by this calculation rather than by the tediousness of trial and error experimentation whether or not a certain system would have the required density characteristics. The concentrations of the intermediate phases, which are necessary in making the calculations of the densities, were calculated using equation 32 of the paper by Dole.[1]

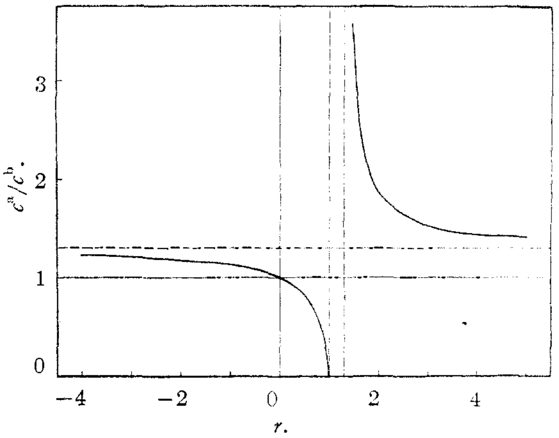

Fig. 1.—The value of c^a/c^b for an ion of relative mobility r as a function of relative mobility. (c^a and c^b are the ion concentrations ahead of and behind the moving boundary.) The graph has been constructed for the case in which $\sigma^a/\sigma^b = 1.25$. The dashed horizontal line is at $c^a/c^b = 1.25$. The dashed vertical lines are at $r = 1.00$ and 1.25.

Figure 1 illustrates the manner in which the ratios of ion concentrations across moving boundaries depend upon the ion mobilities. The superscripts a and b denote phases ahead of and behind a moving boundary, respectively. Although the figure has been constructed for a particular case in which $\sigma^a/\sigma^b = 1.25$, the general features of the figures are the same for all cases in which $\sigma^a/\sigma^b > 1$, which is a necessary condition in order that a moving boundary is not rapidly destroyed by diffusion. It is seen that c^a/c^b is greater than unity for each ion having a mobility greater than $V\sigma^a$ and that c^a/c^b is less than unity for each ion of the same sign as V having a mobility less than $V\sigma^b$. In the system, there can be no ion with a mobility lying between $V\sigma^a$ and $V\sigma^b$, but if $r = V\sigma^a$ the corresponding ion is absent behind the boundary, and if $r = V\sigma^b$ the corresponding ion is absent ahead of the boundary. For each and every ion having a mobility opposite in sign to that of V, c^a/c^b is greater than unity, and it approaches the value of σ^a/σ^b as the mobility becomes infinitely large in absolute value. This last statement means that the total concentration of ions in equivalents per unit volume is always greater ahead of a moving boundary than behind it. In this sense, the likelihood of having stable density gradients in ascending boundary patterns is unfavorably prejudiced. Of course, the ultimate prediction about the density of a given phase depends not only upon concentrations but upon the particular density increments.

Inasmuch as the $\gamma\delta$ boundary in (e) is a moving boundary across which no ion disappears, it is interesting to see how the concentrations change in crossing it. The compositions of all the phases for experiment 1 (an experiment of type (e)) are given in Table III. Since r_K is larger than $V^{\gamma\delta}\sigma^\delta$ and $V^{\gamma\delta}\sigma^\gamma$, it must follow that $c_K^\delta/c_K^\gamma > 1$. On the other hand, r_{Na} is less than $V^{\gamma\delta}\sigma^\delta$ and $V^{\gamma\delta}\sigma^\gamma$, and it follows that $c_{Na}^\delta/c_{Na}^\gamma < 1$. For the chloride–bromate–iodate system, chloride is more concentrated in the α solution than in the β solution but, conversely, bromate is less concentrated.

TABLE III

PHASE COMPOSITIONS FOR MOVING BOUNDARY SYSTEM IN EXPERIMENT 1, WHICH ARE PROVIDED BY THE DOLE THEORY

Phase	α	β	γ	δ
$V\sigma$	$V^{\alpha\beta}\sigma^\alpha = 0$	$V^{\alpha\beta}\sigma^\beta = 0$ $V^{\beta\gamma}\sigma^\beta = 0.467$	$V^{\beta\gamma}\sigma^\gamma = 0.621$ $V^{\gamma\delta}\sigma^\gamma = 0.702$	$V^{\gamma\delta}\sigma^\delta = 0.916$
c_{KCl}	0.00092	0.0034_6	0.0066_1	0.0407
c_{NaCl}	0	0	.0415	.0149
c_{LiCl}	.00964	.0364	0	0

General Conclusions.—Fast moving boundaries of the type which has been described impose limitations on certain types of mobility measurements. Suppose that M^{+n} is a metal ion which possesses acidic properties so that the presence of an appreciable concentration of hydrogen ion is needed to repress the formation of hydrolyzed species such as $M(OH)^{+n-1}$. A mobility measurement of M^{+n} must then be carried out by forming an initial boundary in the following way

$$\text{H, A, X } (\alpha) - \text{H, M, X } (\delta)$$

Here HX is a strong acid, and A^+ is a slower cation than M^{+n}. Due to the very high mobility of H^+, the passage of current must produce the type of a system

$$\text{H, A, X } (\alpha) :: \text{H, A, X } (\beta) \longrightarrow \text{H, M, X } (\gamma) \longrightarrow \text{H, M, X } (\delta)$$

The mobility of M^{+n} is given by the equation $\mu_M = v^{\beta\gamma}\kappa^\gamma$, where $v^{\beta\gamma}$ is the volume swept out by the $\beta\gamma$ boundary in ml. per coulomb and κ is the specific conductance of the γ solution. The difficulty here is that a conductance value for a solution not initially present is required. A sampling operation is thus necessary in order that the mobility of M^{+n} can be determined.

Mobility measurements on certain easily hydrolyzed anions would be complicated in a similar manner. For example, $PO_4^{\equiv}$ exists only in the presence of high concentrations of hydroxide ion.

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

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

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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[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

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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).