[CONTRIBUTION FROM THE STEEL CHEMISTRY LABORATORY AT DARTMOUTH COLLEGE]

A Polarographic Study of the Perborate Complex

BY DAVID M. KERN

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Potential measurements of the O_2–H_2O_2 couple in 0–0.5 M borate and millimolar H_2O_2 solutions support the formula $H_2O_2{\cdot}B(OH)_4^-$ for the perborate species, with a dissociation constant $K = 0.03$ mole/l., in agreement with the results of previous workers. At low borate ion concentrations, however, the apparent value of K increases to *ca.* 0.05. The half wave potentials and diffusion currents of the H_2O_2 reduction wave have been determined as a function of the borate ion concentration. The potential data indicate that perborate reduction occurs by way of the H_2O_2 molecule.

In a recent study[1] of the O_2–H_2O_2 couple at the dropping mercury electrode, the diffusion current of H_2O_2 was observed to be much depressed in the presence of borate ion. This effect was attributed to the formation of a perborate complex.[2] The present paper deals in detail with the influence of borate on the O_2–H_2O_2 potential, the diffusion coefficient of H_2O_2 and the half-wave potential of its reduction wave.

The complexation of hydrogen peroxide and borate ion was studied initially by Menzel,[3] using a solvent distribution technique, and recently by Edwards,[4] who observed the effect of hydrogen peroxide on the pH of boric acid and borax solutions. It appears from these investigations that H_2O_2 and borate ion form a whole series of complexes of the type $B_m(H_2O_2)_n$, where B represents the borate ion $B(OH)^-_4$; however, both authors found that their results could be explained fairly well assuming that the only important species was $B{\cdot}H_2O_2$, at least when the initial concentrations of the two substances were in the range 0.05–0.5 M. There is no evidence for a complex with boric acid.

The O_2–H_2O_2 Couple in Borate Buffers.—The potential of the O_2–H_2O_2 couple is conveniently measured at the dropping mercury electrode by observing the potential at which the composite wave crosses the residual current. At that point the mercury drop is functioning as a null point electrode, there being no net conversion of one compound to the other.

The crossing potential is related to the standard potential at 25° by the equation

$$E_c = E^\circ + 0.0296 \log P_{O_2}/C_{H_2O_2} - 0.0592pH \quad (1)$$

This equation represents a linear relation between E_c and pH in solutions of constant O_2 and H_2O_2 concentrations. On addition of borate to the solution, complexation will reduce the H_2O_2 concentration and cause the observed crossing potential E_c' to diverge from the straight line in the positive direction. If it be assumed that the borate complex has the simplest formula, then

$$K = \frac{(H_2O_2)(B)}{(H_2O_2{\cdot}B)} \text{ and } (H_2O_2) = C_{H_2O_2}\left(1 + \frac{(B)}{K}\right)^{-1} \quad (2)$$

where $C_{H_2O_2}$ is the original H_2O_2 concentration.[5] Substituting the reduced H_2O_2 concentration into equation 1, we find for the new crossing potential

$$E_c' = E^\circ + 0.0296 \log P_{O_2}/C_{H_2O_2} + 0.0296 \log (1 + (B)/K) - 0.0592pH \quad (3)$$

The e.m.f. shift occasioned by the presence of borate in a solution of fixed H^+, O_2 and total peroxide concentrations is then given by

$$E_c' - E_c = \Delta E_c = 0.0296 \log (1 + (B)/K) \quad (4)$$

A complication arises for solutions of pH greater than 10.6 because of the acid dissociation of H_2O_2. At these acidities the crossing potential even in borate-free solution diverges from the value calculated from equation 1 by an amount

$$\Delta E_h = 0.0296 \log (1 + K_a/(H^+))$$

Addition of borate increases this divergence to the total value ΔE_b, which is thus due to the combined effect of acid dissociation and perborate complexation. It is easily shown that the quantity ΔE_c defined by equation 4 is related to the experimentally observed shifts ΔE_h and ΔE_b as

$$\exp(\Delta E_c/a) = 1 + \exp(\Delta E_b/a) - \exp(\Delta E_h/a) \quad (5)$$

where $a = RT/2F$, provided that all shifts refer to solutions with identical H^+, O_2 and total peroxide concentrations. At pH <10.6 this equation reduces to $\Delta E_c = \Delta E_b$.

Experimental

The potassium borate stock solution was prepared by mixing equivalent amounts of boric acid and potassium hydroxide (rendered carbonate free by treatment with $Ca(OH)_2$). The sodium borate solution was prepared by mixing appropriate amounts of borax and carbonate free (and calcium-free) sodium hydroxide. All chemicals were reagent quality. The H_2O_2 stock solution was standardized potentiometrically against $KMnO_4$ at frequent intervals.

Polarographic measurements were made at 25°. Crossing potentials were determined in solutions of previously measured residual current with the aid of a manual apparatus. The cell solutions were thoroughly air-saturated before H_2O_2 was added and the crossing potential determined. Because of the instability of H_2O_2 in basic solutions, the crossing point drifted in a regular fashion with time, at a rate which increased with decreasing borate concentration. This drift was corrected for by extrapolating successive measurements back to the time when H_2O_2 was added to the solution. The error from this source was certainly less than 1 mv.

In order to avoid errors arising from changes in the H_2O_2 concentration of the stock solution, a series of runs in borate solutions was always accompanied by a run in borate-free solution containing the same volume of H_2O_2. ΔE_c could then be determined directly (after correcting for differences in pH according to equation (1)). In the borate-free reference runs, small amounts of phosphate buffer were added to stabilize the pH.

The pH was measured with a Beckman Type "E" glass electrode with negligible sodium error at the pH of the experiments. The electrode was standardized in commercial buffers. The results would not be affected by errors in the standard, since only changes in pH were significant.

(1) D. Kern, THIS JOURNAL, **76**, 4208 (1954).

(2) A similar phenomenon in the polarography of glyoxal in borate buffers was observed by P. Elving and C. Bennett, *ibid.*, **76**, 1412 (1954).

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

(4) J. Edwards, THIS JOURNAL, **75**, 6154 (1953).

(5) The experiments described here were carried out at constant ionic strength, so it was considered admissible to use concentrations rather than activities in these equations. The O_2 activity was automatically maintained constant throughout because the solutions were in equilibrium with the air.

The ionic strength in all experiments was maintained at 0.5 by addition of alkali nitrate.

Results.—A series of E_c measurements for the O_2–H_2O_2 couple in the *p*H range 6.5–10.5 in 0.5 *M* KNO_3 (containing a small amount of phosphate buffer) established the correctness of equation 1, yielding an excellent linear relationship between *p*H and E_c with the theoretical slope, and a value for $E° = +0.457$ v. *vs.* S.C.E. compared with +0.460 v. obtained previously[6] in a solution of somewhat different composition. Above *p*H 10.5 the potentials diverged very gradually from the extrapolated straight line. The observed shift at a given *p*H was introduced as ΔE_h in equation 5.

Potential measurements were repeated in solutions containing potassium borate, in which the *p*H was varied by adding boric acid up to a concentration of 0.05 *M*. The observed potentials were subtracted from those calculated from equation 1 to obtain the shift ΔE_b. Substitution in equation 5 yielded ΔE_c and *K* was calculated by means of equation 4. Values of *K* at various *p*H in 0.13 and 0.4 *M* potassium borate solutions are given in Table I. These data clearly establish that *K* is independent of *p*H. Since the boric acid concentration varied from 0 to 0.05 *M* in these runs, the constancy of *K* also proves that complexation with boric acid is negligible. The single run at *p*H 8.40 was obtained by making the solution 0.3 *M* in boric acid. The apparent increase in the extent of dissociation is probably due to polymerization to $B_4O_7^{--}$ and the consequent decrease of the true borate ion concentration.

TABLE I

EFFECT OF *p*H ON THE EQUILIBRIUM CONSTANT OF THE PERBORATE COMPLEX

0.13 *M* KBO_2		0.42 *M* KBO_2	
*p*H	*K*	*p*H	*K*
11.02	0.045	11.48	0.028
10.47	.039	11.47	.034
10.21	.040	11.02	.032
9.52	.040	10.81	.028
(8.40	.063)	10.62	.032
		10.43	.030

Additional measurements were made in $NaNO_3$–$NaBO_2$ solutions in which the borate ion concentration was varied from 0 to 0.45 *M*. For the most part the acidity in these runs was maintained greater than *p*H 10.6 by addition of small amounts of boric acid, when necessary.

The results for a number of runs are plotted in Fig. 1. The solid lines are the calculated shifts (by equation 4) for *K* = 0.03, 0.04 and 0.05 mole/l. It is seen that for concentrations greater than 0.2 *M* borate the value of *K* remains constant at 0.030 mole/l. This value is identical with that found by Edwards[4] at 25° and by Menzel[3] at 18°.

At smaller concentrations the complex appears to become less stable, its *K* approaching a value of about 0.05 at the lowest borate concentrations. This effect was observed with both sodium and potassium salts, which were of entirely different chemical origin. Although the relative precision of the experiment was low at small e.m.f. shifts, it is unlikely that the change in *K* can be ascribed to an error in potential measurements. It might be accounted for if the borate ion concentration in dilute solution were less than the stoichiometric value. However, the removal of borate by formation of both $B_4O_7^{--}$ or perborate must have been negligible. Polymerization with boric acid would affect the concentrated borate solutions more than the dilute ones, to which no boric acid was added since their *p*H was naturally below 10.6; and the total peroxide concentration in the experiments was around 0.5 millimolar only. The possibility of adsorption of borate on the glass cell-walls and the frit connecting with the KCl solution of the reference electrode was excluded by acidimetric titration of a dilute borate mixture after contact with the vessel. The changing environment as borate ion is replaced by nitrate may be responsible; on the other hand no effect was observed on replacing sodium ion by potassium.

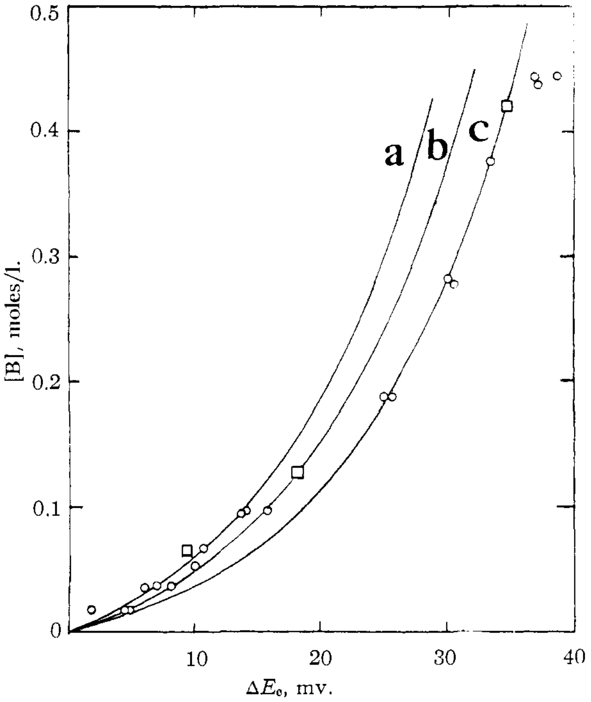

Fig. 1.—The shift in crossing potential of the O_2–H_2O_2 composite wave as a function of the borate ion concentration at μ = 0.5: ○, $NaNO_3$–$NaBO_2$ soln.; □, KNO_3–KBO_2 soln.—each square is the average of at least four runs at the same [B]. The solid lines are calculated by eq. 4, assuming *K* = 0.05, 0.04, 0.03 for a, b, c, respectively.

A slow attainment of equilibrium between borate and perborate, as might be suggested by the above mentioned drift in the null point potential, would account for the phenomenon. The objections to this interpretation of the drifts are (a) they persisted for many minutes (b) similar drifts occurred in borate free solution and (c) the rate was related inversely, rather than directly, to the borate concentration. Certainly the successful prediction of the $E_{1/2}$ shift of H_2O_2 in borate media (see Fig. 4) is a strong argument in favor of rapid equilibrium.

The inconstancy of *K* at low borate concentra-

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[6] See ref. 1. A very similar value for the reversible potential of the O_2-H_2O_2 couple was determined independently by J. Koryta, *Collection Czechoslov. Chem. Commun.*, **18**, 21 (1953).

tions must probably be ascribed to complications in the perborate equilibrium that are not indicated in equation 2. However, the behavior of K does not represent a very serious departure from that expected from the species $H_2O_2{\cdot}B$, and the data at low concentrations are not sufficiently accurate in any event to justify further analysis.

In this connection potential measurements were made in 0.4 M borate solution containing varying amounts of H_2O_2. Three measurements were made with H_2O_2 concentrations in the ratio 12:3:1, the highest concentration being about 1.5 mM. The potential shifts were within 2%, or less than the experimental error, of those that would have occurred in the absence of borate. This result proves that only one H_2O_2 molecule enters into the perborate complex.

Carbonate–bicarbonate solutions were also briefly investigated. No significant change was observed in the crossing potential on increasing the carbonate ion concentration from 0.12 to 0.45 M (after correcting for pH changes), indicating that complexation between H_2O_2 and CO_3^{--} must be very weak if it occurs at all.

The Diffusion Current of H_2O_2 in Borate Media.—The effect of borate ion on the H_2O_2 diffusion current was investigated in KNO_3–KBO_2 and $NaNO_3$–$NaBO_2$ mixtures of ionic strength 0.5.

Experimental.—The currents were measured at −1.4 v. *vs.* S.C.E. in all but the two most concentrated borate solutions. In these the currents were measured at −1.5 v., since borate causes a negative shift in the peroxide reduction potential. Well developed waves were observed in all solutions. Cenco Wetting Agent no. 73860-A at 0.03% concentration was found to improve the horizontality of the diffusion current plateaus without affecting their relative heights. Like other surface active agents,[7] this reagent greatly steepens the rising portion of the wave, giving it a reversible appearance. The currents were determined manually in some cases, from polarograms in others. The pH was kept below 10.6 in all runs.

In Fig. 2 the ratio of the diffusion current in borate solution relative to that in pure 0.5 M alkali nitrate solution is plotted against the borate concentration. The simplest interpretation of these data is that perborate has a smaller diffusion coefficient than H_2O_2 and that consequently the average rate of diffusion decreases as the borate concentration increases. If it be assumed that the ratio reaches the limiting value of *ca.* 0.6 at high borate concentrations in solutions of the same viscosity (the asymptotic value of the dashed line in Fig. 2), the ratio of the diffusion coefficients of perborate complex and H_2O_2 must be about 0.36. However, it will be shown below that the shape of the curves in Fig. 2 is not altogether consistent with this interpretation.

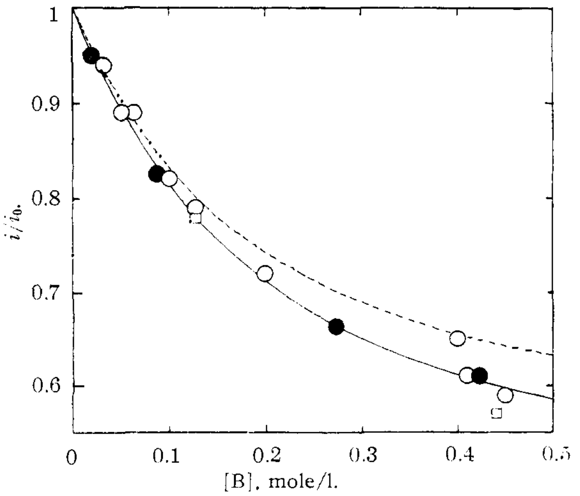

Fig. 2.—The relative diffusion currents of H_2O_2 as a function of the borate ion concentration at $\mu = 0.5$: ○, KNO_3–KBO_2 soln.; □, $NaNO_3$–$NaBO_2$ soln.; ●, $NaNO_3$–$NaBO_2$ soln. containing a surface active agent. The dashed line represents the smoothed data corrected for viscosity changes.

Provided that equilibrium is established very rapidly compared with the rate of diffusion, the effective diffusion coefficient will be the weighted mean

$$D = (K'D_H + D_C)/(K' + 1) \qquad (6)$$

where D_H and D_C are the diffusion coefficients of H_2O_2 and perborate, respectively, and $K' = K/(B)$.

The following simple derivation is offered for the above expression; it refers to a plane electrode only. A lengthy, rigorous proof for the d.m.e. has been given by Koutecky.[8]

Let A and B be two species in extremely rapid equilibrium, of which one or both are reducible at the electrode. The ratio of their concentrations a/b is essentially constant throughout the diffusion layer. The following equations apply

$$\partial a/\partial t = D_a\partial^2 a/\partial x^2 + k_1 b - k_2 a \qquad (7)$$
$$\partial b/\partial t = D_b\partial^2 b/\partial x^2 + k_2 a - k_1 b$$

where k_1 and k_2 are the rates of conversion of b to a and a to b. But $a = Kb$, and therefore

$$\partial a/\partial t = K\partial b/\partial t \text{ and } \partial^2 a/\partial x^2 = K\partial^2 b/\partial x^2 \qquad (8)$$

Combining equations 7 and 8

$$\partial(a + b)/\partial t = D\partial^2(a + b)/\partial x^2$$

where

$$D = (D_aK + D_b)/(K + 1)$$

This equation, with the appropriate boundary conditions, is identical to the one describing the diffusion of a single substance of concentration $a + b$ and diffusion coefficient D. Thus D as defined in the equation above is the effective diffusion coefficient for the two substances in equilibrium.

Assuming then that the perborate equilibrium is very rapid and is represented correctly by equation 2, the ratio of diffusion currents in borate and borate-free solution is

$$i/i_0 = \sqrt{(K' + D_C/D_H)/(K' + 1)} \qquad (9)$$

Before the data are fitted to this equation, they must be corrected for changes in the diffusion current arising from changes in the viscosity of the medium. This correction factor was determined from measurements of the IO_3^- wave in these solutions at a pH of 10.5. The corrected experimental ratios fall on the dashed line in Fig. 2.

Equation 9 does not represent the experimental facts very well. When the corrected ratios at 0.05, 0.1, 0.2 and 0.4 M borate are substituted in, the corresponding values of D_C/D_H are calculated to be 0.63, 0.53, 0.49 and 0.39, whereas they should of course remain constant. If K is taken as 0.030 mole/l. over the entire range of borate, instead of being obtained from Fig. 1, the D_C/D_H values vary

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(7) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. 11, Interscience Publishers, New York, N. Y., 2nd Edition, 1952, p. 558.

(8) J. Koutecky, *Collection. Czechoslav. Chem. Communs.*, **19**, 857 (1954). See also V. Kařena and L. Matoušek, *Chem. Listy*, **46**, 525 (1952).

even more. The dashed curve is much better represented by the equation

$$i/i_0 = \frac{7.6\sqrt{K'}}{1 + 7.6\sqrt{K'}} \qquad (9a)$$

the agreement everywhere being within 3/2%, or less than the experimental error, as shown in Table II.

TABLE II

$E_{1/2}$ AND i_d OF THE H_2O_2 REDUCTION WAVE IN BORATE SOLUTION RELATIVE TO THEIR VALUES IN BORATE-FREE SOLUTION

(B), moles/l.	$\Delta E_{1/2}$, v.	i/i_0 cor.	K moles/l.	K'	i/i_0 calcd. (eq. 9a)
0.05	−0.055	0.90	0.050	1.0	0.89
.10	− .103	.83	.040	.40	.83
.20	− .174	.74	.030	.15	.75
.40	− .241	.66	.029	.072	.67

Potential data presented in the next section afford direct evidence that in perborate solutions, H_2O_2 alone is reduced, perborate being removed by dissociation to peroxide after the resultant displacement of the equilibrium. There exists considerable evidence that this equilibrium is mobile.[9] Nevertheless it is conceivable that the interconversion might not be rapid enough to achieve equilibrium at the surface during reductions, and that the observed diffusion current is actually partially controlled by the rate of perborate dissociation. The current would then decrease with increasing borate ion concentration as the part contributed by the H_2O_2 present in the solution diminished, even if D_C and D_H were equal. It is interesting that the Koutecky theory of kinetic waves[8,10] leads to a relationship of precisely the same form as equation 9a. However this theory assumes that the electroactive member in the equilibrium is not, as it is here, present in significant concentration in the bulk of the solution.

The following facts argue against this explanation for the decrease in the current ratio: (a) the potential shift of the peroxide wave with increasing borate ion concentration is that to be expected if borate and peroxide are at equilibrium at the surface (see below); (b) the relation between the corrected height of the mercury reservoir and the diffusion current shows no kinetic character.[11] Nevertheless these observations are not exact enough to exclude every trace of kinetic character. The insufficiency of equation 9 may then be attributed to this and/or to the presence of small concentrations of peroxide species other than the two assumed in equation 2.

The Half-wave Potential of H_2O_2 in Borate Media.—Borate shifts the H_2O_2 wave to more negative potentials. The change of $E_{1/2}$ as a function of the borate concentration is shown in Fig. 3. This effect can be ascribed to the lower H_2O_2 concentrations existing at the drop surface in borate solutions. If H_2O_2 is the reducible species, a higher potential will be required to sustain the same rate of H_2O_2 reduction, which may be assumed to be first order with respect to the surface H_2O_2 concentration.

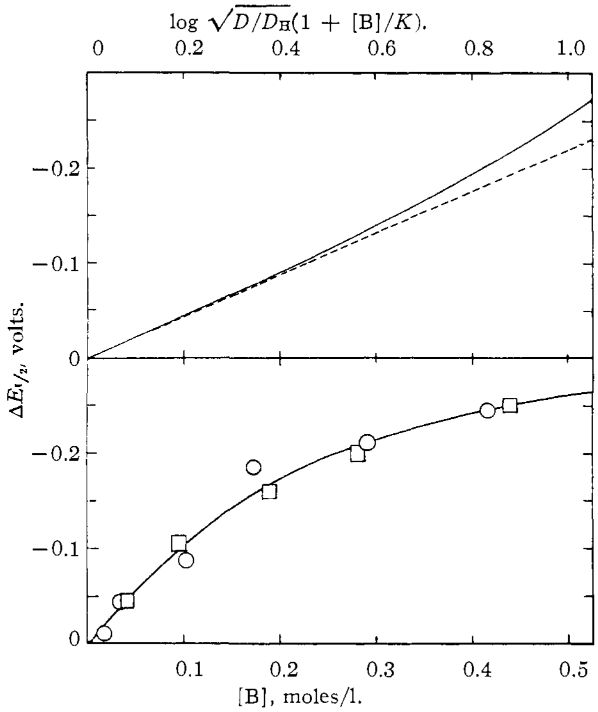

Fig. 3.—Below: the $E_{1/2}$ shift of the H_2O_2 reduction wave as a function of the borate ion concentration at $\mu = 0.5$: ○, KNO_3–KBO_2 soln.; □, $NaNO_3$–$NaBO_2$ soln. Above: plot of eq. 12 using the smoothed data from the plot beneath. The dashed straight line is for comparison.

If absolute rate theory is applied to the irreversible H_2O_2 wave in the usual manner,[12] the expression obtained for the current at any point in the wave is

$$i = \text{const.} \times (H_2O_2)_0 \exp(-\alpha nFE/RT) = k_e(H_2O_2)_0 \quad (10)$$

where α is a constant between 1 and 0, and $(H_2O_2)_0$ is the surface concentration. The following equation may be used to relate the current to the flux of H_2O_2 and perborate to the surface, assuming that rapid equilibrium exists between the two species

$$i = \text{const.} \times \sqrt{D}(C_{\text{bulk}} - C_0) = i_d - \text{const.} \times \sqrt{D}C_0 \quad (11)$$

where C is the sum of the perborate and H_2O_2 concentrations, and D is defined by equation 6. Combining these with equation 2, we find that for corresponding points in the wave (*i.e.*, same i/i_d) in borate and borate-free solution

$$E_b - E = \Delta E = -\frac{2.3RT}{\alpha nF} \log\left(\sqrt{D/D_H}\,(1 + (B)/K)\right) \quad (12)$$

A more exact analysis using the method of Koutecky[10] leads to a result that is identical except for a factor of the square root of the ratio of the droptimes at the two potentials. Since the maximum potential difference was only 0.25 v., this factor could be safely neglected.

A plot of ΔE's from Fig. 3 against the log term in equation 12 is found to exhibit a slight curvature.

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(9) J. Edwards, THIS JOURNAL, **75**, 6151 (1953).

(10) J. Koutecky, *Collection Czechoslav. Chem. Communs.*, **18**, 607 (1953).

(11) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, p. 91.

(12) See ref. 11, p. 35.

This is to be expected, since the log $(i_d - i)/i$ *vs.* E plot for the H_2O_2 wave is not a straight line either, indicating an α which is potential dependent. The α's obtained from both plots are *ca.* 0.2 (assuming $n = 1$).

In order to avoid the uncertainty in the value of α, it is preferable to employ the above equations to predict the relative values of i/i_d at the *same* potential in the various borate solutions. At the same potentials, and hence the same k_c, it follows from equations 10 and 11 that over the entire range of borate concentrations

$$(1/i - 1/i_d)\,KC/(K + (B)) = \text{const.} \qquad (13)$$

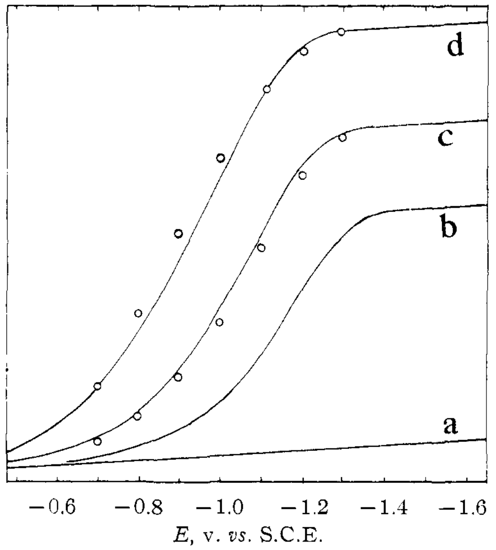

Fig. 4.—Current voltage curves of H_2O_2 of approx. the same concentration in borate solutions of $\mu = 0.5$: a. residual current; b. 0.44 M borate; c, 0.123 M borate; d. no borate. The circles are points calculated on the basis of curve b and eq. 13.

To test this equation polarograms were run in *ca.* 0.5 millimolar H_2O_2 solutions containing 0, 0.123 and 0.44 M sodium borate plus sufficient sodium nitrate to bring the ionic strength up to 0.5. A cell of very low resistance was used. With the wave at 0.44 M borate as a basis, those at the other two concentrations were constructed by the application of equation 13, using K values obtained from Fig. 1. The calculated points in Fig. 4 are seen to agree quite satisfactorily with the tracings of the recorded waves.

This agreement does not imply that equation 2 gives a correct picture of the perborate equilibrium, since the experimental values of K were used, which vary with the borate concentration. When a constant value $K = 0.030$ was used, agreement was poorer. However the agreement does show that the equilibrium observed between H_2O_2 and perborate in the bulk of the solution by means of E_c measurements also exists at the drop surface at the rising portion of the wave, and supports a reduction mechanism which is first order with respect to H_2O_2, as assumed in equation 10.

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HANOVER, N. H.

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

Potentiometric Titrations in Liquid Ammonia. IX. Reduction of Iodides of Zinc, Cadmium and Mercury[1]

BY GEORGE W. WATT AND PHILIP S. GENTILE

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Potentiometric titration of the iodides of zinc(II), cadmium(II) and mercury(II) with potassium in liquid ammonia shows only the reduction to the corresponding elemental metals and provides no evidence for the intermediation of the +1 oxidation states of these metals. From related titrations involving higher ratios of reductant to salt, evidence for the formation of the intermetallic compounds KCd_3, KHg and KHg_2 was obtained. The anticipated KZn_4 was not detected.

Earlier publications from this Laboratory have illustrated the use of potentiometric titration data in the interpretation of the reactions that occur between salts and solutions of alkali metals or alkali metal amides in liquid ammonia. For example, these techniques have been used to establish the identity of the sulfides that are formed when the polysulfides of the alkali metals are titrated with standard solutions of these metals.[2] Similarly, the titration of potassium tetracyanonickelate (II) and potassium hexacyanocobaltate (III) with ammonia solutions of potassium has provided information relative to the mechanism of these reduction reactions as well as evidence for the +1 oxidation state of cobalt.[3]

Recent reports of evidence possibly indicative of the +1 oxidation states of magnesium[4] and calcium[5,6] prompt us to report in this paper our earlier efforts to detect the +1 oxidation states of zinc, cadmium and mercury by the potentiometric titration of the corresponding iodides with solutions of potassium in liquid ammonia.

The literature provides no convincing evidence for the +1 oxidation state of zinc, although there

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(1) This work was supported in part by the Atomic Energy Commission, Contract AT-(40-1)-1639.

(2) G. W. Watt and J. B. Otto, Jr., *J. Electrochem. Soc.*, **98**, 1 (1951).

(3) G. W. Watt, J. L. Hall, G. R. Choppin and P. S. Gentile, THIS JOURNAL, **76**, 373 (1954).

(4) R. L. Petty, A. W. Davidson and J. Kleinberg, *ibid.*, **76**, 363 (1954).

(5) P. Ehrlich and L. Gentsch, *Naturwissenschaften*, **40**, 460 (1953).

(6) G. Wehner, *Z. anorg. allgem. Chem.*, **276**, 72 (1954).