Mechanism of Peroxide Reactions: The Reduction of Peroxomonophosphoric Acid at a Platinum Electrode

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The electrochemical behaviour of peroxomonophosphoric acid has been studied on platinized platinum. The process of electroreduction is irreversible and involves one electron in the rate-determining step. From the dependence of the half-wave potential on the acidity it is concluded that the species H_3PO_5, $[H_2PO_5]^-$, and $[HPO_5]^{2-}$ are simultaneously reduced. The electrode reaction is interpreted in terms of a mechanism involving nucleophilic attack by the electrode on the outer peroxidic oxygen of the depolarizer, and mechanistic analogies with the reduction of H_3PO_5 by iodide ion are discussed.

PEROXIDES are easily electrochemically reduced by a process which involves the irreversible breakdown of the oxygen–oxygen bond. Although this class of substances is well known as a source of free radicals, reactions of peroxides occurring through polar paths are quite common not only in the homogeneous [1] but also in the heterogeneous phase.[2] In order to elucidate the kinetic behaviour of peroxo-compounds and find possible analogies between their reduction in solution and at the electrode, we have made a voltammetric study of peroxomonophosphoric acid on platinized platinum and compared the results with those relating to the reduction of the same compound by iodide ion in aqueous solution.[3]

EXPERIMENTAL

Peroxomonophosphoric acid was obtained as a product of the hydrolysis of $Na_4[P_2O_8]$ in an acidic medium.[4] The absence of hydrogen peroxide and of the parent disubstituted peroxide was checked by polarography.[5] Stock solutions of H_3PO_5 were standardized by iodimetry.[6] The remaining chemicals were of analytical grade. Conductivity water was used to prepare the solutions and as a reaction medium.

The voltammetric curves were recorded toward decreasing potentials at 25 ± 0.1 °C with a Polarecord Metrohm E 261 instrument connected to an I.R. Metrohm E 446 compensator. Since at the relatively positive potentials at which peroxo-acids are reduced it is impossible to use mercury due to its dissolution, a platinized-platinum microelectrode was used with periodic renewal of the diffusion layer.[7] The ionic strength was maintained at 0.2 mol dm^{-3} with sodium perchlorate, and the solutions were deaerated with purified nitrogen. The desired acidities, obtained with phosphate and perchloric acid,

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[1] R. Curci and J. O. Edwards, in ' Organic Peroxides,' ed. D. Swern, Wiley–Interscience, New York, 1970, vol. 1, p. 212.

[2] L. S. Silbert, in ' Organic Peroxides,' ed. D. Swern, Wiley–Interscience, New York, 1971, vol. **2**, p. 637.

[3] F. Secco and M. Venturini, *J.C.S. Dalton*, 1976, 1410.

[4] M. M. Crutchfield and J. O. Edwards, ' Peroxide Reaction Mechanisms,' Interscience, New York, 1962, p. 41.

[5] M. Venturini, A. Indelli, and G. Raspi, *J. Electroanalyt. Chem.*, 1971, **33**, 99.

[6] F. Secco and S. Celsi, *J. Chem. Soc. (B)*, 1971, 1792.

[7] D. Cozzi, G. Raspi, and L. Nucci, *J. Electroanalyt. Chem.*, 1966, **12**, 36.

were measured by a Metrohm E 388 potentiometer. All the potentials were referred to the saturated calomel electrode (s.c.e.).

RESULTS

Figure 1 shows a voltammetric curve of H_3PO_5 recorded at pH 9. Two waves (*a*) and (*b*) are exhibited, the first corresponding to an oxidation process and the second to a reduction. By coulometry, the overall number of electrons involved in each process was determined as two. Logarithmic analyses on the ascending part of the voltammetric curves yielded straight lines with gradients ranging between 0.120 and 0.140 V instead of 0.03 V as expected for reversible processes. Moreover, since phosphate ion is not oxidized at the potentials of the anodic wave, the oxidation current cannot be attributed to the phosphate ion which is present in solutions of H_3PO_5 as a product of the hydrolysis of $Na_4[P_2O_8]$. Wave (*a*) is therefore ascribed to the overall process (1), whereas wave (*b*) is due to process (2), both

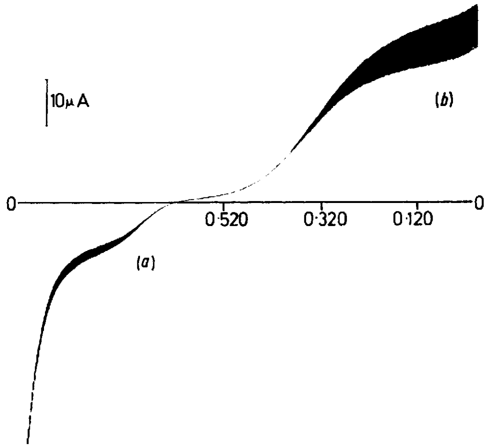

FIGURE 1 Voltammetric curve showing the oxidation (*a*) and reduction (*b*) of H_3PO_5 in aqueous solution. $[H_3PO_5] = 1.5 \times 10^{-3}$ mol dm^{-3}, pH 9, $I = 0.2$ mol dm^{-3}, 25 °C

$$[HPO_5]^{2-} + H_2O \longrightarrow [HPO_4]^{2-} + O_2 + 2H^+ + 2e^- \quad (1)$$

$$[HPO_5]^{2-} + 2H^+ + 2e^- \longrightarrow [HPO_4]^{2-} + H_2O \quad (2)$$

occurring in solution buffered at pH 9.

The limiting current of wave (*a*) was smaller than that of (*b*), its temperature coefficient being 4.0%, and oscillographic analysis of single oscillations showed that the current did not obey the Cottrell equation corrected for sphericity.[8] The limiting current of (*a*) did not increase linearly with increasing concentration of H_3PO_5 and tended to a constant value at peroxide concentrations $> 1.5 \times 10^{-3}$ mol dm^{-3}. Moreover, measurements with different concentrations of phosphate at constant acidity showed that the height of the wave decreased on increasing the amount of phosphate until it disappeared when the phosphate concentration was *ca.* 100-fold higher than the peroxide concentration. These facts suggest that a kinetic process is operative. It should be noticed also that, in the range pH 5—14, the quantity $\Delta E_{\frac{1}{2}}/\Delta pH$ was *ca.* -0.06 V. At acidities $< 10^{-5}$ mol dm^{-3} the wave was masked by water oxidation.

For the reduction process the temperature coefficient of the limiting current was 1.5% per degree and the Cottrell equation was fully obeyed. It is concluded that the limiting current is diffusion controlled. The height of wave (*b*) was proportional to the concentration of H_3PO_5 over the entire range of concentration (10^{-4}—10^{-2} mol dm^{-3}). From the gradients of plots of E against log $[(i_d - i)/i]$ at different acidities values of $n\alpha$ between 0.5 and 0.4 were obtained. Since it is often true that the electron-transfer coefficient, α, is equal to 0.5, it is reasonable to assume that $n = 1$, *i.e.* only one electron is involved in the rate-determining step of the reduction of H_3PO_5.

The dependence of the half-wave potential on the acidity was investigated with particular care. Figure 2 shows a plot of $E_{\frac{1}{2}}$ against $-\log[H^+]$ (calculated from the measured pH by using the Davies equation).[9] At the highest hydrogen-ion concentrations the half-wave potential was nearly independent of acidity, whereas at pH > 1 it decreased as shown in the Figure. The experimental value of $\Delta E_{\frac{1}{2}}/\Delta pH$ was 0.067 V between pH 1 and 10 and decreased to 0.027 V at pH > 10. Since $n\alpha$ is *ca.* 0.5 over the entire range of acidity, it follows [10] that the apparent order of reaction with respect to $[H^+]$ increases from 0 to 0.6 and decreases to 0.2 as the hydrogen-ion concentration is decreased. This means that, together with paths first order in $[H^+]$, paths independent of the acidity are also operative. If one H^+ ion was involved in each of the electroreduction paths a value of 0.120 V would be obtained for $\Delta E_{\frac{1}{2}}/\Delta pH$. The form of the curve of $E_{\frac{1}{2}}$ against $-\log[H^+]$ is reminiscent of that of $k_{obs.}$ against $-\log[H^+]$ in the reaction of H_3PO_5 with iodide ion [3] in which a number of peroxide species, differing in their degree of protonation,

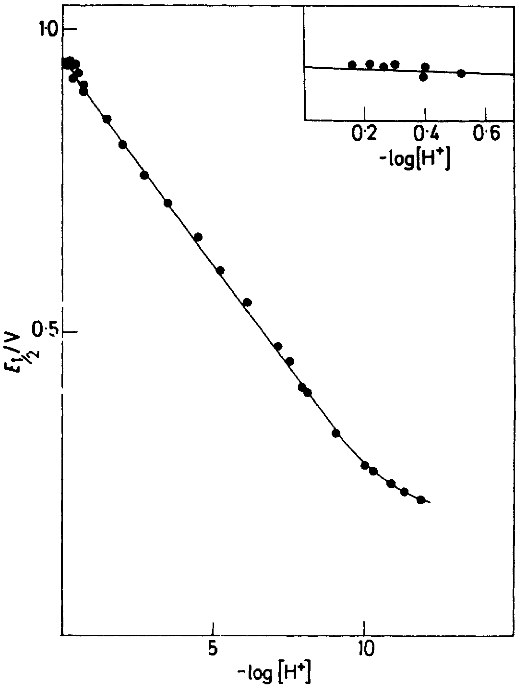

FIGURE 2 Dependence of the half-wave potential of H_3PO_5 (reduction wave) on $-\log[H^+]$ at $I = 0.2$ mol dm^{-3} and 25 °C

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[8] K. J. Vetter, 'Electrochemical Kinetics,' Academic Press, New York, 1967, p. 157.

[9] C. W. Davies, *J. Chem. Soc.*, 1938, 2092.

[10] C. L. Perrin, *Progr. Phys. Org. Chem.*, 1965, 165.

are simultaneously reduced. A reaction scheme which can satisfactorily account for the results is (3)—(5) in which

$$[H_2PO_5]^- + H^+ + e^- \xrightarrow{k_1'} [H_2PO_4]^- + OH \quad (3)$$

$$[HPO_5]^{2-} + H^+ + e^- \xrightarrow{k_2'} [HPO_4]^{2-} + OH \quad (4)$$

$$[HPO_5]^{2-} + e^- \xrightarrow{k_3} [PO_4]^{3-} + OH \quad (5)$$

k_1', k_2', and k_3 are the rate constants of the reduction paths. Reactions (3)—(5) are followed by the fast reaction (6). It

$$OH + e^- \longrightarrow [OH]^- \quad (6)$$

should be noted that reactions (3)—(5) are intended to represent the transfer of an OH group from the peroxide to the electrode and not the formation of free radicals. From this scheme the relation (7) between the half-wave potential and the hydrogen-ion concentration may be derived (see Appendix and Discussion) where K_{A1} and K_{A2} are the first two dissociation constants of H_3PO_5.

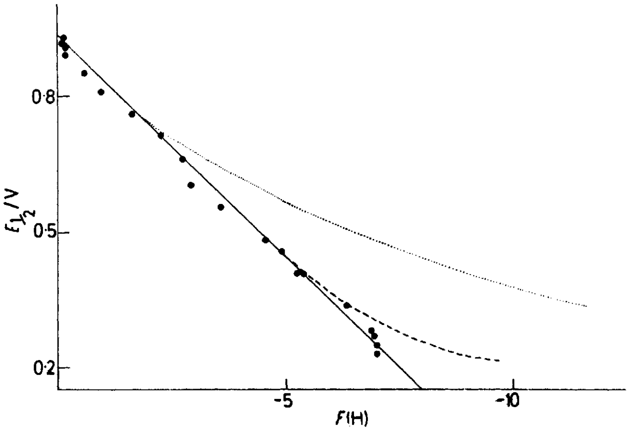


FIGURE 3 Plots of $E_{\frac{1}{2}}$ for the reduction of H_3PO_5 against F(H) where:

$$F(H) = \log \frac{[H^+]^2 + (k_2^0/k_1^0)K_{A1}[H^+] + (k_3^0/k_1^0)K_{A1}K_{A2}}{[H^+]^2 + K_{A1}[H^+] + K_{A1}K_{A2}} \quad (\text{——})$$

$$F(H) = \log \frac{[H^+]^2 + (k_2^0/k_1^0)K_{A1}[H^+]}{[H^+]^2 + K_{A1}[H^+] + K_{A1}K_{A2}} \quad (\text{— — —})$$

$$F(H) = \log \frac{[H^+]^2}{[H^+]^2 + K_{A1}[H^+] + K_{A1}K_{A2}} \quad (\cdot\cdot\cdot\cdot)$$

The appropriateness of the reaction scheme (3)—(5) to the experimental behaviour is shown by Figure 3 where $E_{\frac{1}{2}}$ is plotted against the logarithmic term of equation (7).

$$E_{\frac{1}{2}} = \text{constant} + \frac{2.3RT}{\alpha nF} \cdot \log \frac{[H^+]^2 + (k_2^0/k_1^0)K_{A1}[H^+] + (k_3^0/k_1^0)K_{A1}K_{A2}}{[H^+]^2 + K_{A1}[H^+] + K_{A1}K_{A2}} \quad (7)$$

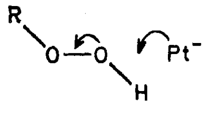
A straight line was obtained of gradient 0.1 V which is in agreement with the value of $2.3RT/\alpha nF$ given by logarithmic analysis. The Figure also shows that strong systematic deviations from linearity occur if a reaction scheme involving only paths k_1' and k_2' is considered. Higher errors are obviously observed when only path k_1' is considered. The best fit was obtained by introducing into equation (7) the values 2×10^{-3} and 10^{-7} for k_2^0/k_1^0 and k_3^0/k_1^0 respectively (correlation coefficient R 0.991). With $k_2^0/k_1^0 = 2 \times 10^{-3}$ and $k_3^0/k_1^0 = 10^{-5}$ a worse fit was obtained (R 0.977), and with $k_3^0/k_1^0 = 10^{-4}$ and $k_3^0/k_2^0 = 10^{-7}$ R is 0.966. The spectrophotometric values[11] of 0.08 and 5.0×10^{-6} mol dm^{-3} were used for K_{A1} and K_{A2}.

DISCUSSION

For the oxidation process, the change of the limiting current with the peroxide concentration and in particular the high temperature coefficient favour the hypothesis that a chemical reaction is responsible for the voltammetric behaviour. We do not possess sufficient data to formulate the precise nature of this reaction. The decrease in current density on addition of phosphate might suggest that this substance can affect the process, for instance by decreasing the concentration of one of the species taking part in the rate-determining reaction.

In the peroxide electrode reduction it is assumed that one hydrogen-ion reaction is included in each of the reaction paths (3) and (4). However, from the kinetic results it is impossible to determine whether the protons are added prior or simultaneously with electron transfer.[10] In both cases the activated complexes are $[H_3PO_5]^-$, $[H_2PO_5]^{2-}$, and $[HPO_5]^{3-}$. The first possibility, which is equivalent to a rapid pre-equilibrium of the substrate with its protonated form, is in our opinion preferred because at lower acidities, where the protonated form of $[H_2PO_5]^-$, *i.e.* H_3PO_5, prevails, the half-wave potentials become independent of $[H^+]$. Moreover it should be noted that reactions occurring by ' concerted ' uptake of protons should be sensitive to general-acid catalysis. Although this test is not a sufficient basis to distinguish between the two possibilities in the field of electrode kinetics,[10] it seems useful to report that we found that, at given acidities, the half-wave potentials were unaffected by changing the nature and the concentration of the buffers.

The results for the reduction process are more interesting for our purpose of finding analogies between reductions in the homogeneous and heterogeneous phase. In particular, the data can be reasonably discussed in terms of a polar mechanism involving nucleophilic attack by the electrode on the outer peroxidic oxygen of the peroxo-acid.[12] We can represent this by (8) where $[RO]^-$ is leaving and the OH group is transferred to the electrode. According to (8) the more acidic the leaving group the more is the reduction facilitated. This is supported by the plot in Figure 4 which shows that $E_{\frac{1}{2}}$ changes linearly with the leaving-group basicity (pK_{ROH}). The values of $E_{\frac{1}{2}}$ used correspond to pH values at which each of the species predominates. In particular, at pH 0, $\alpha = 0.92$ for H_3PO_5, at pH 5 $\alpha = 0.95$ for $[H_2PO_5]^-$,



(8)

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[11] C. J. Battaglia and J. O. Edwards, *Inorg. Chem.*, 1965, **4**, 552.

[12] M. Venturini and F. Secco, *J.C.S. Perkin II*, 1973, 491.

and at pH 9.5 $\alpha = 1$ for $[HPO_5]^{2-}$. Moreover, since[13] $(\alpha nF/2.3RT)\Delta E_{\frac{1}{2}}$ is equal to $\Delta\log k^0$ where k^0 is the rate constant of a given electrochemical reaction,[10] from the gradient of the line in Figure 4 one obtains $\Delta\log k^0/\Delta pK_{ROH} = 0.53$, a value very similar to that for the analogous plot for the peroxide reductions by I^- in aqueous solution.[3] Taking into account that the value of the electron-transfer coefficient is also *ca.* 0.5, one can say that bond making and breaking in the transition state are proceeding to the same extent.[14] That the peroxide reduction in the heterogeneous and in the homogeneous phase occurs by the same mechanism is better shown by the straight line in Figure 5 where the logarithms of rate constants of peroxide electroreduction are plotted against log k for the reduction by I^- ion.

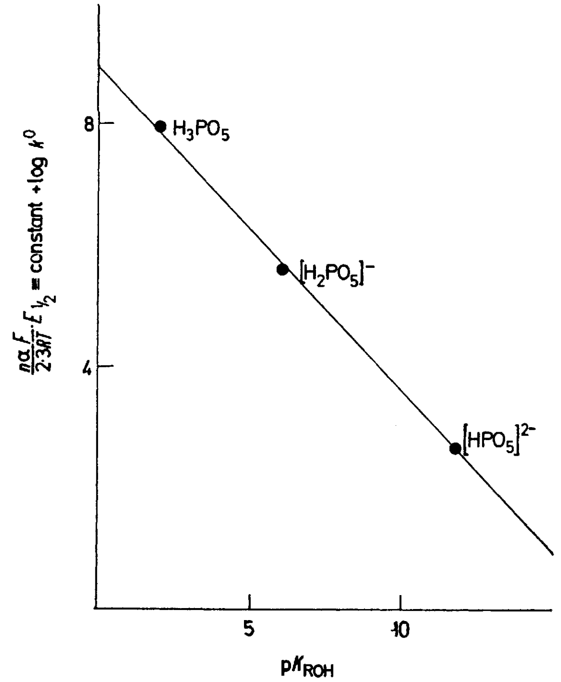

FIGURE 4 Dependence of peroxide half-wave potentials on the leaving-group basicity (pK_{ROH})

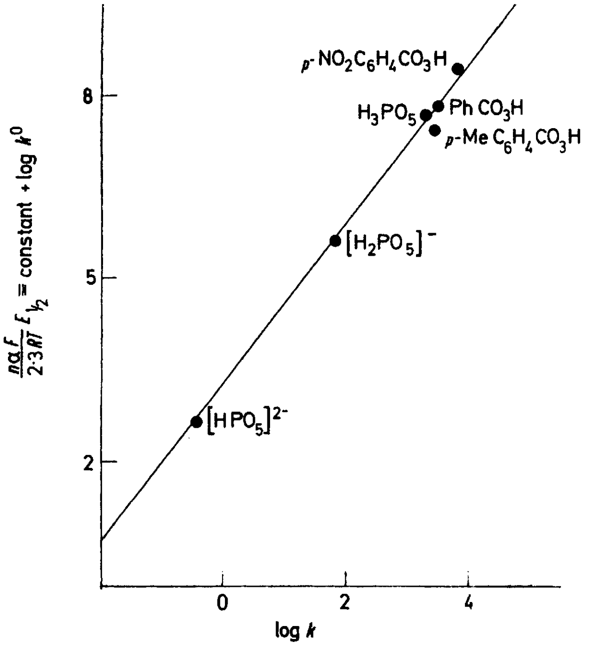

FIGURE 5 Plot of the logarithm of the rate constant for the peroxide electrode reduction against log k for the reduction by iodide ion in aqueous solution at 25 °C and $I = 0.2$ mol dm^{-3} ($Na[ClO_4]$)

Finally it should be noted that analogies between the electrode and I^- reductions have been found for other peroxides such as peroxodisulphate,[15] peroxodiphosphate,[5] and perbenzoic acids[12] and also in oxo-compound reductions such as those of seleninic acids[16] and of periodate ion.[17]

APPENDIX

If the three reaction paths (3)—(5) are operative at the same potential the overall current density i is the sum of three contributions and, on the basis of the irreversible electrode processes,[13] can be expressed by equation (A1) in

$$i = n'FA(k_1'[H_2PO_5^-]_S[H^+] + k_2'[HPO_5^{2-}]_S[H^+] + k_3[HPO_5^{2-}]_S) \quad (A1)$$

which A is the electrode surface, n' is the faradaic equivalent, k_1', k_2', and k_3 are rate constants dependent on the potential, and the subscript S indicates the concentrations of the electroactive species on the electrode surface. If we assume, for the reasons given in the Discussion section, that fast protonation equilibria precede the potential determining steps, as in equations (A2) and (A3), then

$$[H_2PO_5] + H^+ \xrightleftharpoons{K_{A_1}^{-1}} H_3PO_5 + e^- \xrightarrow{k_1} [H_2PO_4]^- + OH \quad (A2)$$

$$[HPO_5]^{2-} + H^+ \xrightleftharpoons{K_{A_2}^{-1}} [H_2PO_5]^- + e^- \xrightarrow{k_2} [HPO_4]^{2-} + OH \quad (A3)$$

$k_1' = k_1K_{A1}^{-1}$ and $k_2' = k_2K_{A2}^{-1}$ and the half-wave potential is pH-dependent unless the protonation equilibria are fully displaced to the right-hand side. In buffered solutions the hydrogen-ion concentration at the electrode surface can be considered to be equal to the concentration in the bulk of the solution and it is reasonable to assume that $[H_2PO_5^-]_S/[H_3PO_5]_S$ and $[HPO_5^{2-}]_S/[H_2PO_5^-]_S$ are not different from the same quantities in the homogeneous phase, so that K_{A1} and K_{A2} are equal to the concentration quotients at the electrode surface. Under these conditions, using equilibrium relations and the mass balance for the peroxide, equation (A1) becomes (A4), and since the relation[13]

$$i = n'FA \cdot \frac{k_1 + k_2K_{A1}[H^+]^{-1} + k_3K_{A1}K_{A2}[H^+]^{-2}}{1 + K_{A1}[H^+]^{-1} + K_{A1}K_{A2}[H^+]^{-2}} \cdot [PO_5]_{S(T)} \quad (A4)$$

$$k = k^0\exp[-\alpha nF(E - E^0)/RT] \quad (A5)$$

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[13] (*a*) J. Heyrovsky and J. Kuta, 'Principles of Polarography,' Academic Press, New York, 1966, p. 205; (*b*) P. Zuman, *Progr. Phys. Org. Chem.*, 1967, **5**, 81.

[14] W. P. Jencks, 'Catalysis in Chemistry and Enzymology,' McGraw-Hill, New York, 1969, p. 78.

[15] L. Muller, *J. Electroanalyt. Chem.*, 1967, **13**, 275.

[16] M. Venturini, F. Secco, and D. De Filippo, *J. Electroanalyt. Chem.*, 1972, **40**, 339.

[17] F. Secco and M. Venturini, *J. Electroanalyt. Chem.*, 1974, **54**, 351.

between k and the potential E is as in (A5), one obtains (A6) provided that αn has the same value for each of the three electroactive species.

$$i = n'FA\exp[-\alpha nF(E - E^0)/RT] \cdot \frac{k_1^0 + k_2^0K_{A1}[H^+]^{-1} + k_3^0K_{A1}K_{A2}[H^+]^{-2}}{1 + K_{A1}[H^+]^{-1} + K_{A1}K_{A2}[H^+]^{-2}} \cdot [PO_5]_{S(T)} \quad (A6)$$

On the other hand, since in this study it was experimentally found that the height of the waves is independent of the pH, one can reasonably assume that the diffusion coefficients of the three species of the peroxide are identical and can therefore write the relation[18] between i and the concentration gradient in the form (A7) where P is a

$$i = P\{[PO_5]_T - [PO_5]_{S(T)}\} \quad (A7)$$

constant. By introducing into equation (A6) $[PO_4]_{S(T)}$ as obtained from (A7) under the conditions of diffusion-limited current, one obtains (A8) which, for $i = i_d/2$, reduces to (7).

$$E = E^0 + \frac{RT}{\alpha nF} \cdot \ln \frac{n'FAk_1^0}{P} + \frac{RT}{\alpha nF} \cdot \ln \frac{[H^+]^2 + (k_2^0/k_1^0)K_{A1}[H^+] + (k_3^0/k_1^0)K_{A1}K_{A2}}{[H^+]^2 + K_{A1}[H^+] + K_{A1}K_{A2}} - \frac{RT}{\alpha nF} \cdot \ln \frac{i}{i_d - i} \quad (A8)$$

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[18] Ref. 13*a*, p. 73.