nese between colloid and solution, Tests B-1 and B-2 were made. These were identical in all respects with A-1 and A-2, except that radioactive manganese was used throughout. The results are reported in Table II.

TABLE II

| | A-1 | A-2 | B-1 | B-2 |
|---|---|---|---|---|
| Rad. Mn in colloid | 0.0235 | 0.0244 | 0.122 | 0.126 |
| Rad. Mn in filtrate | .0174 | .0167 | .097 | .097 |
| Total Rad. Mn (anal.) | .0409 | .0411 | .219 | .223 |
| Total Rad. Mn added | .0465 | .0465 | .212 | .212 |
| Total Mn added | .212 | .212 | .212 | .212 |

The material balances on radioactive manganese close well for the B series, but less satisfactorily (15% difference) for the A series. It is thought that this might be due to nonlinearity of the counter. In spite of this, however, the results are unambiguous.

Since the A runs are chemically identical with the B runs, it can be assumed that the distribution of total manganese between colloid and filtrate is the same in both. Averaging the results, the ratio of radioactive to total manganese is 0.194 in the colloid and 0.176 in the filtrate. The radioactive manganese, originally present only as colloid, has become almost homogeneously distributed with the total manganese.

The figures indicate that the colloid still holds a little excess radioactive manganese, but the accuracy does not warrant a definite statement.

**Acknowledgment.**—The authors wish to express their indebtedness to the Naval Bureau of Ordnance for support and release of this work and to Dr. John W. Irvine of the M. I. T. Radioactivity Center for aid in planning the radioactivity studies.

## Summary

A study has been made of the catalytic decomposition of hydrogen peroxide with oxides of manganese, formed *in situ* from permanganate or manganous salts and alkali. The use of radioactive tracers indicates that catalysis takes place by alternate reduction and oxidation of manganese. Determination of the conditions under which catalysis occurs shows that the oxidation step of the cycle does not take place unless the solution is saturated with manganous hydroxide. A probable mechanism is

$$\begin{aligned} MnO_2 + H_2O_2 + 2H^+ &\longrightarrow Mn^{++} + 2H_2O + O_2 \\ Mn^{++} + 2H_2O_2 &\rightleftarrows Mn(OH)_2 + 2H^+ \\ Mn(OH)_2 + H_2O_2 &\longrightarrow MnO_2 + 2H_2O \\ \hline 2H_2O_2 &\longrightarrow 2H_2O + O_2 \end{aligned}$$

CAMBRIDGE, MASS. RECEIVED JUNE 3, 1946

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[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL COOPERATION, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

# Mechanism of Decomposition of Hydrogen Peroxide Solutions with Manganese Dioxide. II

BY D. B. BROUGHTON, R. L. WENTWORTH AND M. E. LAING

## Introduction

The results presented in the first article of this series indicated that catalysis of hydrogen peroxide decomposition took place by successive oxidation and reduction of manganese and that no catalysis occurred until the solution was saturated with manganous hydroxide.

Because macroscopic manganese dioxide surfaces cause decomposition even when the bulk of the peroxide solution contains no manganese, and because accumulation of manganous ions in such a solution is quite slow, it appeared advisable to investigate further the decomposition at such surfaces to determine whether the same type of mechanism was operating.

This work was carried out to obtain information on conditions existing at manganese dioxide–hydrogen peroxide interfaces—in particular, to determine whether the solution was saturated with manganous hydroxide.

## Electrode Potential Measurements

**Experimental.**—A stick of porous electrolytic manganese (99.9%) was coated with manganese dioxide by allowing it to stand in 30 weight per cent. hydrogen peroxide for twenty-four hours. Its electrode potential in peroxide solutions was then measured against a saturated calomel electrode, using a conventional circuit. In each test, readings were taken for thirty to sixty minutes, in which time the potentials approached constant values. Errors caused by decomposition of peroxide during the test were small, as renewal of the solution induced only slight additional change in potential. The concentrations of peroxide, of manganous ion and of hydrogen ion were varied systematically, by adjustment with manganous nitrate, nitric acid, and sodium hydroxide.

For comparison, similar measurements were made on electrodes of bright platinum.

**Results and Discussion.**—The potentials of the platinum and manganese dioxide electrodes are plotted in Figs. 1–3 *vs.* concentrations of hydrogen ion, peroxide and manganous ion.

It was hoped that the relative degrees of polarization of the several electronic reactions probably occurring at the electrode surface would be such that the measured potentials would correspond to one particular reaction, and thus furnish information on conditions existing at the electrode surface.

The following electronic reactions were considered as possibly controlling the potential

$$MnO_2 \longrightarrow Mn^{++} + O_2 + 2e^- \quad (1)$$
$$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O \quad (2)$$
$$H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^- \quad (3)$$
$$2H^+ + {}^1/_2O_2 + 2e^- \longrightarrow H_2O \quad (4)$$
$$Mn \longrightarrow Mn^{++} + 2e^- \quad (5)$$
$$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{++} + 2H_2O \quad (6)$$

Several investigators[1,2] have shown that, in the absence of peroxide, the potential of a manganese dioxide electrode is controlled by (6).

In Figs. 1–3, the theoretical potentials for these reactions at concentrations in the bulk of the solution are indicated by the dashed lines 1–6. Reaction 5 has a potential of about −1000 mv. and is not shown. Evidently, the measured potential does not vary with concentration according to any of the proposed reactions.

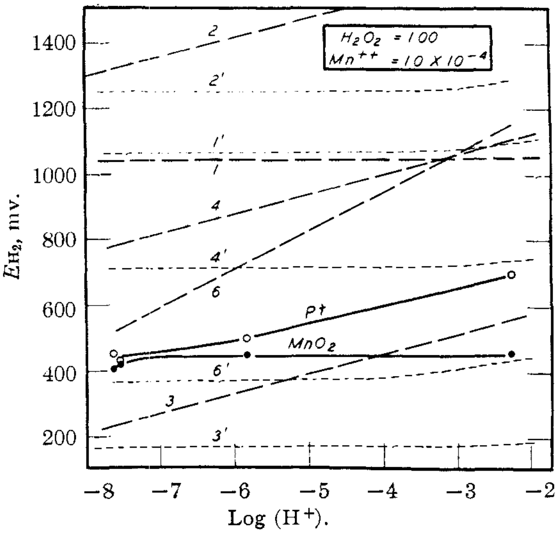

Fig. 1.—Actual and theoretical potentials *vs.* *p*H.

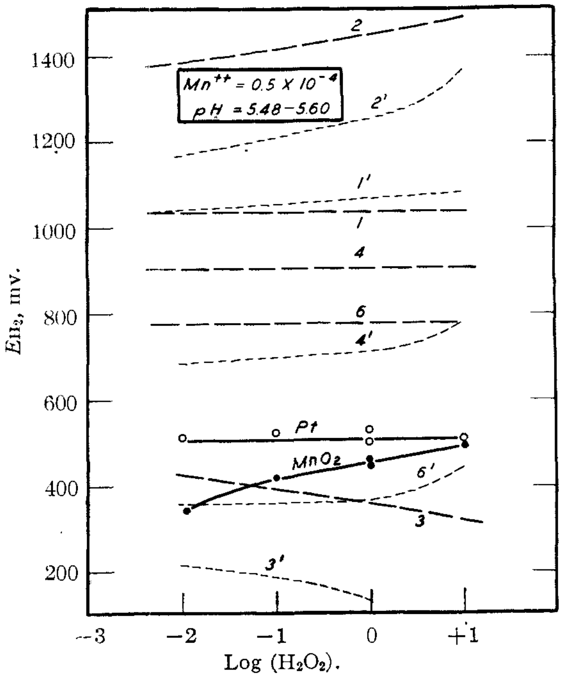

Fig. 2.—Actual and theoretical potentials *vs.* hydrogen peroxide concentration.

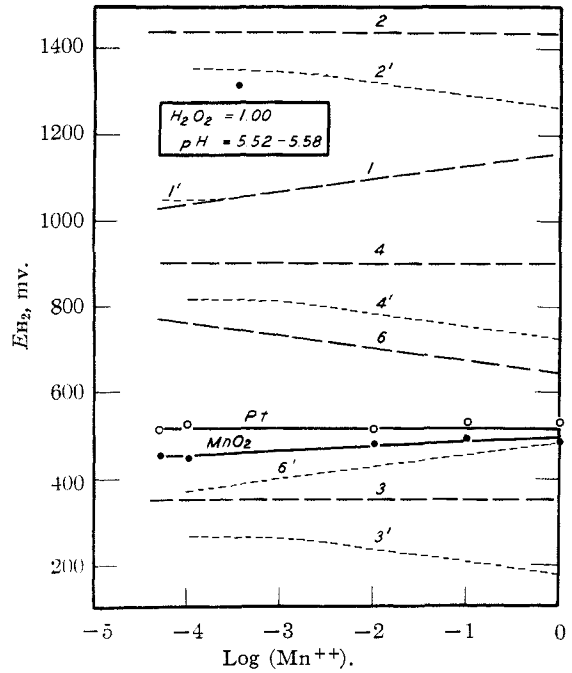

Fig. 3.—Actual and theoretical potentials *vs.* manganous ion concentration.

However, if the liquid adjacent to the manganese dioxide surface is saturated with manganous hydroxide, the ionic concentrations at the surface would be quite different from the bulk concentrations. Surface concentrations, assuming saturation with manganous hydroxide, were calculated as follows.

If the liquid is initially unsaturated with manganous hydroxide, manganese dioxide will be reduced at the surface

$$2H^+ + MnO_2 + H_2O_2 \longrightarrow Mn^{++} + 2H_2O + O_2$$

At steady state, the rate of reduction of manganese dioxide must equal the rate of diffusion of manganous ion through the liquid film. Likewise, since the reaction consumes two hydrogen ions for every molecule of manganese dioxide reduced, the diffusion of manganous ion must be balanced by diffusion of hydrogen ion to the surface or of hydroxyl ion away. Mathematically, in terms of diffusion coefficients and concentration gradients, where subscripts refer to concentrations at the surface or in the liquid bulk

$$2k_{Mn^{++}}(Mn_s^{++} - Mn_b^{++}) = k_{H^+}(H_b^+ - H_s^+) + k_{OH^-}(OH_s^- - OH_b^-) \quad (a)$$

The following equilibria also exist

$$(H_s^+)(OH_s^-) = (H_b^+)(OH_b^-) = K_w \quad (b)$$
$$(Mn_s^{++})(OH_s^-)^2 = K_m \quad (c)$$

The diffusion coefficients were assumed to be in the same ratio as the corresponding ion mobilities

$$k_{Mn^{++}} : k_{H^+} : k_{OH^-} :: 60 : 315 : 174 \quad (d)$$

Values of $K_m$, as a function of peroxide concentration, were given in the first article of this series. In determining $K_m$, it was assumed that the concentration of hydrogen

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(1) J. K. H. Inglis, *Z. Elektrochem.*, **9**, 226 (1903).

(2) D. F. Tower, *J. Chem. Soc.*, **18**, 35 (1895).

peroxide at the surface was the same as in the bulk of the liquid. This assumption does not introduce appreciable error, as $K_m$ changes little with hydrogen peroxide concentration up to one-molal.

From equations (a)–(d), the surface conditions corresponding to given bulk conditions were calculated. As illustration, the effect of changes in bulk *p*H on ion concentrations at the surface are shown in Table I.

Table I

Calculated Ion Concentration at $MnO_2$ Surface

$(H_2O_2)_b = 1.00$; $(Mn^{++})_b = 1.00 \times 10^{-4}$

| $(H^+)_b$ | $(H^+)_s$ | $(Mn^{++})_s$ |
|---|---|---|
| $1.00 \times 10^{-7}$ | $1.31 \times 10^{-9}$ | $1.11 \times 10^{-4}$ |
| $1.00 \times 10^{-5}$ | $1.45 \times 10^{-9}$ | $1.36 \times 10^{-4}$ |
| $1.00 \times 10^{-3}$ | $6.26 \times 10^{-9}$ | $2.52 \times 10^{-3}$ |
| $1.00 \times 10^{-2}$ | $2.02 \times 10^{-8}$ | $2.62 \times 10^{-2}$ |

The potentials corresponding to the surface concentrations are plotted in Figs. 1–3 as lines 1′–6′. In all three plots, the direction of change of the manganese dioxide potential agrees with that of curve 6′. The numerical values also fall closer to this curve than to any other. The discrepancies may be due to the fact that the oxide on the electrode has an oxygen content somewhat below that of manganese dioxide. (An average formula quoted in the literature for oxides formed in this manner is $MnO_{1.88}$.)

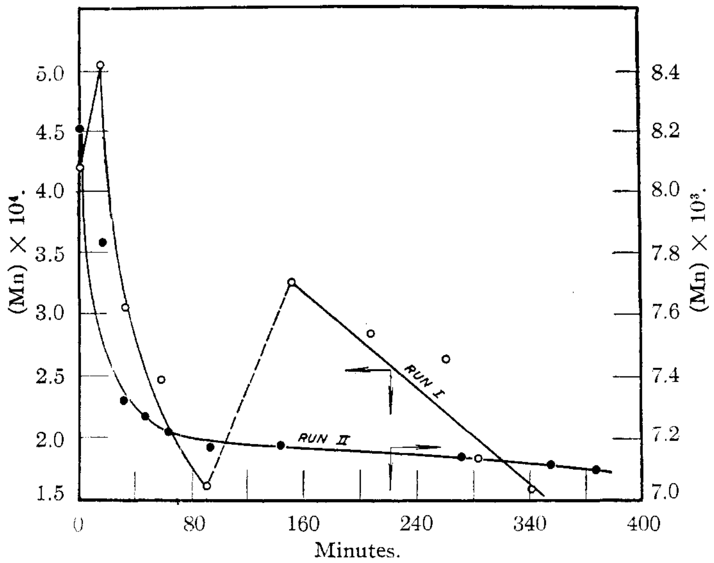

Fig. 4.—Change of manganese concentration with time in decomposing hydrogen peroxide solutions.

If this interpretation is accepted, the solution adjacent to the surface can be assumed saturated with manganous hydroxide. There is then no conflict between the conclusion drawn in the first paper of this series—*i.e.*, that catalysis will not occur unless the solution is saturated with manganous hydroxide—and the fact that macroscopic manganese dioxide surfaces act catalytically in solutions having bulk concentrations below saturation.

The potential of bright platinum is independent of all factors varied except *p*H. This confirms results on platinum black published by Wolff.[3] The numerical values found here are in excellent agreement with Wolff's, except at high *p*H, where his values are about 30 mv. lower.

**Manganese Concentration in Decomposing Hydrogen Peroxide Solutions.**—If the hypothesis of a saturated solution of manganous hydroxide at the manganese dioxide surface is correct, it would be expected that manganous ions would migrate between the surface and solution bulk. To test this, peroxide solutions were brought to a point just below saturation by addition of manganous sulfate and sodium hydroxide, surfaces coated with manganese dioxide were introduced, and the concentrations of manganese in the solution were determined at intervals.

Analyses were performed by oxidation of the manganese to permanganate by addition of potassium periodate and by colorimetric determination of the permanganate. The analyses determine soluble manganese and any present as colloid together.

On Fig. 4, the results of two tests made with initial solutions containing, respectively, 53 and 10% weight peroxide are given.

In Run 2, a decrease in manganese concentration with time is evident. In Run 1, the curve was similar, but showed a sudden increase between one hundred and one hundred and fifty minutes, again followed by a decrease. Because of the violence of the catalysis with 54% hydrogen peroxide, it is thought that this increase may have been caused by a mechanical disruption of the manganese dioxide surface, throwing some finely divided particles out into the liquid, these being determined analytically along with the dissolved manganese.

These apparently anomalous results are understandable in the light of the effect of concentration of hydrogen peroxide on the solubility of manganous hydroxide. In Fig. 5, the solubility of manganous hydroxide is plotted, as calculated from the results of the first paper of this series. The solubility decreases rapidly with decreasing peroxide concentration.

At the manganese dioxide surface, where decomposition is occurring, the peroxide concentration would be lower than in the solution bulk, and the solubility of manganous hydroxide would be correspondingly lower. This would be expected to lead to migration of manganous ions from the solution to the surface and to their deposition there as manganese dioxide.

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(3) Wolff, *Compt. rend.*, **196**, 1113 (1933).

The deposition of manganese on the surface is corroborated visually by the fact that no colloidal manganese dioxide formed in the solutions during the tests, whereas similar tests in which no manganese dioxide surfaces were introduced showed increasing quantities of colloid in the solutions as the peroxide decomposed.

These results are interpreted as confirming the conclusion drawn from the electrode potential measurements that the solution adjacent to the manganese dioxide surface is saturated with manganous hydroxide.

**Acknowledgment.**—The authors are indebted to Dr. T. K. Sherwood and Dr. E. R. Gilliland for many helpful suggestions, and to the Naval Bureau of Ordnance for support and release of this work.

## Summary

The electrode potential of a manganese dioxide electrode was measured in hydrogen peroxide solutions of various peroxide and ion concentrations. Of a number of possible electrode reactions, the results were in most consistent agreement with the assumption that the potential was controlled by the reaction

$$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{++} + 2H_2O$$

and that the solution immediately adjacent to the manganese dioxide surface was saturated with manganous hydroxide, even though the bulk of the solution was not.

Measurements of the change of manganese concentration in hydrogen peroxide solutions decomposing in contact with macroscopic manganese dioxide surfaces gave results supporting the assumption that the solution adjacent to the surface was saturated with manganous hydroxide.

The inconsistency between the conclusion drawn in the first paper of this series (that catalysis of hydrogen peroxide decomposition by manganese dioxide will not occur unless the solution is saturated with manganese dioxide) and the fact that macroscopic manganese dioxide surfaces act catalytically in solutions having bulk concentrations below saturation is thus removed.

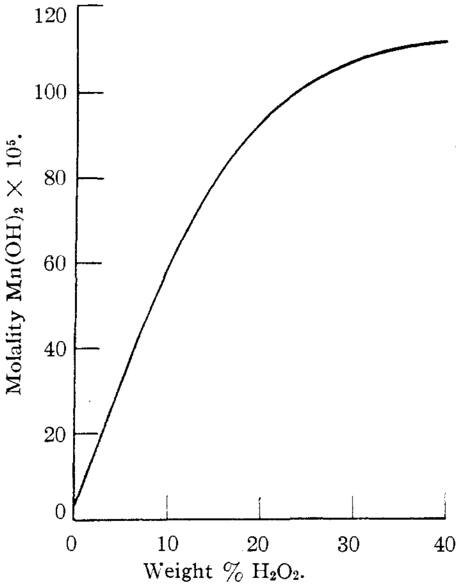

Fig. 5.—Solubility of manganous hydroxide in hydrogen peroxide solutions.

CAMBRIDGE, MASS. RECEIVED JUNE 3, 1946

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF SOUTHERN CALIFORNIA]

# Proton–Deuteron Exchange between Ammonia and Ammoniated Diborane

BY ANTON B. BURG

Earlier publications[1,2,3,4] brought forth several kinds of experimental evidence pointing uniquely to the idea that diborane ($B_2H_6$) behaves toward bases (electron donors) as if it consisted of separable pairs of borine ($BH_3$) radicals, able to share electrons furnished by other molecules. Thus the volatile solid material of the composition $B_2H_6 \cdot 2N(CH_3)_3$ proved to be the borine complex $(CH_3)_3N:BH_3$[1,5] and $B_2H_6 \cdot 2NH_3$ (if prepared carefully by an addition reaction at −120°), behaved as one would expect of the structure $NH_4^+(BH_3)_2NH_2^-$.[2] The latter reacted further with liquid ammonia, evidently drifting toward the equilibrium $NH_4(BH_3)_2NH_2 + 2xNH_3 \rightleftarrows 2BH_3NH_3 \cdot xNH_3$, probably not appreciably complicated by $(NH_4)_2(BH_3)_3NH$ or $(NH_4)_3(BH_3)_4N$. There was no evidence which could reasonably be interpreted to favor the formula $(NH_4)_2B_2H_4$.[6]

Although the borine theory of the base-reactions of diborane appears to be fairly generally accepted, there has recently been a tendency to revive the di-protic acid hypothesis, because of its simple relation to the protonated double bond idea of the structure of diborane.[7] It therefore became necessary to seek new evidence bearing on the subject—evidence preferably simple and yet decisive enough to eliminate all doubt.

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[1] A. B. Burg and H. I. Schlesinger, THIS JOURNAL, **59**, 780 (1937).

[2] H. I. Schlesinger and A. B. Burg, *ibid.*, **60**, 290 (1938).

[3] H. C. Brown, H. I. Schlesinger and A. B. Burg, *ibid.*, **61**, 673 (1939).

[4] H. I. Schlesinger, N. W. Flodin and A. B. Burg, *ibid.*, **61**, 1078 (1939).

[5] S. H. Bauer, *ibid.*, **59**, 1804 (1937).

[6] E. Wiberg, *Z. anorg. allgem. Chem.*, **173**, 210 (1928).

[7] K. S. Pitzer, THIS JOURNAL, **67**, 1126 (1945).