

the reactions between hydrogen peroxide and aldehydes in water.

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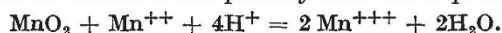
¹Lapworth, *J. Chem. Soc.*, 995 (1903); 120 (1904).

²Ghijzen, Dissertation, Delft (1942). Reiche, "Alkylperoxide und Ozonide" (Leipzig, 1931).

Reaction between Manganous Ion and Manganese Dioxide

THE decrease of manganous ion concentration which occurs when a manganous salt is shaken with manganese dioxide has been known for a long time. Being most marked with freshly precipitated oxides, it is not surprising it should first have been considered an adsorption. For some time this observation has found practical application in the removal of soluble manganese in water supplies¹, while recently it has been shown of significance in the chemistry of the dry cell depolarizer², and also in the oxidation-reduction cycle of manganese in the soil^{3,4}.

In all instances the primary reaction is probably



Except in the presence of concentrated acid, the equilibrium is such that the amount of Mn^{+++} is very small. In the presence of pyrophosphoric acid, which forms a stable complex anion with trivalent manganese⁵, the reaction may proceed far to the right⁴. In the absence of complex-forming substances and in neutral and slightly alkaline solutions, a new solid phase appears, the reaction again proceeding to the right. One solid phase which has been observed at pH values as low as 4.5 has been identified as manganite². Its formation may be shown by rewriting the above equation so as to assume hydrolysis of the manganic ion, thus



Dion and Mann³ state the reaction proceeds only in the reverse direction. This is contrary to the above findings² and to our own. In seeking a cause for potential drift with a manganese dioxide electrode⁶, we have found that some such reaction proceeds even when the dioxide has the dense heat-stable pyrolusite structure; that it leads to the production of a lower oxide even at pH values as low as 1; and that this oxide has a structure not previously described.

Half-gram portions of dioxide obtained by heating pure manganous nitrate were allowed to stand for two days at room temperature with 50 ml. of the solutions shown in the accompanying table. The solid residues after washing and drying at room temperature *in vacuo* were examined by one of us (J. M. C.) by both the X-ray and electron diffraction methods. In each instance the X-ray powder pattern showed only the lines of pyrolusite. However, the electron diffraction pattern from the sample treated with hydrochloric acid and manganous chloride had rings distinctly different from those of pyrolusite. The other treated samples gave a pyrolusite pattern, but in addition showed weakly the stronger rings of

Reactants	X-ray diffraction pattern	Electron diffraction pattern
Original MnO_2	pyrolusite	pyrolusite
$\text{MnO}_2, \text{MnCl}_2, 0.1 M, \text{HCl } 0.1 M$	pyrolusite	pyrolusite and new oxide (strong)
$\text{MnO}_2, \text{HCl } 0.1 M$	pyrolusite	pyrolusite and new oxide (weak)
$\text{MnO}_2, \text{Mn}(\text{ClO}_4)_2, 0.1 M, \text{HClO}_4, 0.1 M$	pyrolusite	pyrolusite and new oxide (weak)

the new pattern. When manganese dioxide is dissolved in concentrated hydrochloric acid and the manganese tetrachloride hydrolysed, this new pattern is not obtained, but rather the pattern of γMnO_2 or of pyrolusite⁶.

The rings of the new pattern given by the sample treated with hydrochloric acid and manganous chloride show arcing when the specimen is tilted, most of the arcs lying along one diameter. This indicates that the substance is in the form of thin flakes, of the order of 100 Å. or less in thickness, lying flat on the supporting film of collodion. It seems probable that these flakes were formed by the breaking-off of an altered surface layer from the particles during the process of grinding the sample under secondary butyl alcohol. Lattice spacings and ring intensities are given below.

D	Int.	D	Int.
5.1	W	1.74	M
4.39	S	1.62	M
4.12	S	1.58	MW
3.34	W	1.50	W
2.46	S	1.30	W
2.35	M	1.27	MW
2.06	MW		

This pattern is similar to that of goethite, αFeOOH , and there is good agreement between the observed spacings and those calculated for an orthorhombic cell with dimensions $a = 4.42, b = 10.4, c = 2.83 \text{ \AA}$., which are close to the dimensions of the goethite cell. However, interpreted on this basis, some reflexions are present which are not permitted by the space group of goethite, and some reflexions given by goethite are absent. Hence the substance cannot be considered as truly isomorphous with goethite. The data are not sufficient to allow a more definite determination of structure. Recently Gruner⁸ has briefly described a new mineral (groutite) found in Minnesota which has the cell dimensions $a = 4.56, b = 10.70, c = 2.85 \text{ \AA}$. It is considered, however, that these dimensions differ significantly from those of the oxide described here. No manganese analogue of goethite is reported by Dana, who lists the groups:

goethite (αFeOOH), diaspore (αAlOOH),
lepidocrocite (γFeOOH), boehmite (γAlOOH),
manganite (γMnOOH).

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