

# TECHNICAL PAPERS

## Pentavalent Manganese<sup>1</sup>

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In fused alkaline melts, the lower oxides of manganese react with oxygen until an oxygen-to-manganese ratio of about 2.5 is established (5). For aqueous media, reliable evidence pointing to the existence of pentavalent manganese has only recently been reported (4). The present paper will show that such a valence state can be detected polarographically in strongly alkaline solutions.

A solution containing  $1.00 \times 10^{-3}$  M potassium permanganate and 0.10 M sodium hydroxide was deaerated with nitrogen and then polarographed, using a stationary platinum electrode (6) and an outside saturated calomel electrode (S.C.E.). The resulting curve is shown in Fig. 1.

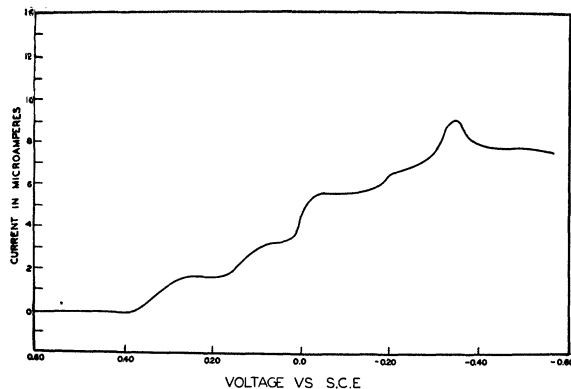


FIG. 1.

The first step of the reduction ( $E_1 = +0.33$ ) has a diffusion current corresponding to a one-electron change (for the particular electrode which was employed) and a formal oxidation potential of  $-0.58$  v, versus the normal hydrogen electrode. Since the permanganate reaction has a normal potential of  $-0.54$  v (2), the first wave can definitely be assigned to this reaction. The second ( $E_2 = +0.13$  v) and third steps ( $E_3 = +0.01$  v) also have diffusion currents corresponding to one-electron changes. Hence the reactions taking place must be  $Mn^{VI} \rightarrow V$  and  $Mn^{V} \rightarrow IV$ . The fourth (and last) step beginning close to  $-0.2$  v must be due to the reduction of  $Mn^{IV}$ . The irregularity of the step can easily be explained by the fact that the electrode is covered with a visible layer of precipitated manganese dioxide.

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There is indirect evidence that the lifetime of pentavalent manganese in 0.1 M hydroxide is not more than a few minutes. The polarographic half-wave potentials and diffusion currents appeared to be independent of the rate at which the motor-driven slide-wire changed the voltage. On the other hand, a current-voltage curve obtained by a manual method (1) resulted in a single broad wave. It was not surprising, therefore, that an attempt to produce pentavalent manganese by electrolysis of manganate at a suitable potential (3) produced a large amount of manganese dioxide. The solution had a bluish color (similar to chromous sulfate) which agrees with the work of Lux (4).

Preliminary studies have also been made in other concentrations of sodium hydroxide. In a 1.0 M solution, the polarogram is very similar to the one described for a 0.10 M solution; but in a 0.010 M solution, the manganate is reduced directly to manganese dioxide in a single two-electron step. A more complete study of changes in half-wave potentials with the concentration of hydroxide will be necessary before the reactions of the  $Mn^{V}$  ion can be described accurately. The results of such a study will help in predicting the behavior of technetium ions.

### References

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## Note on the Genetics of Hypercholesterolemia

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An important aspect of the expanding interest in human genetics is the detection of carriers of hereditary diseases, both in the sense of normal heterozygotes of recessive defects, as in some forms of epilepsy (4), and in the sense of those individuals who exhibit some predisposing condition without showing the characteristic symptoms of the disease, e.g. hyperuricemia in gout (7). It is elementary in all cases to determine on the basis of numerical tests the mode of inheritance, the gene frequency, penetrates, and so on. Boas, *et al.* (1) have