247. *The Reduction of Permanganate in Buffered Solution: Potentiometric Titration with Hydrogen Peroxide.*

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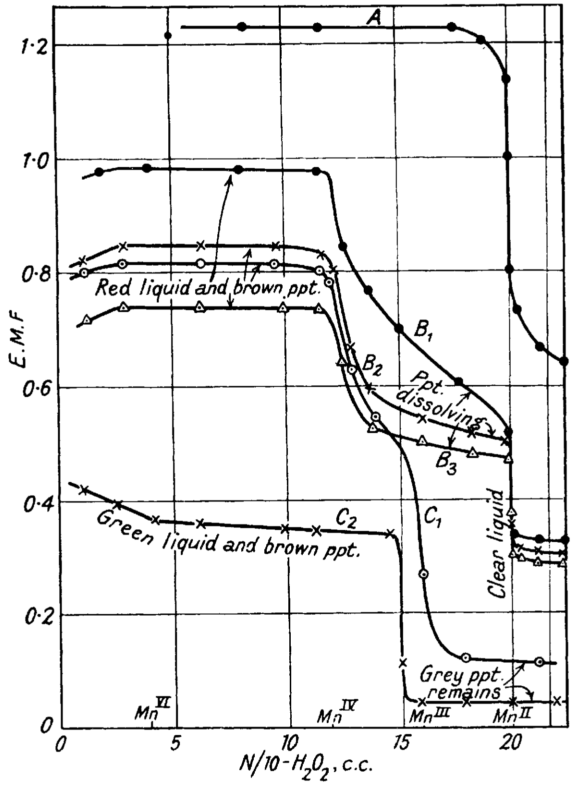
When potassium permanganate is reduced in the presence of hydrofluoric acid there is a tendency for reduction to be arrested at the tervalent manganese stage because complex manganifluorides are formed. The author has shown that under certain conditions reduction may be carried quantitatively to this point when various reducing agents are used (*J. Roy. Soc. S. Africa*, 1931, **20**, 93; 1934, in the press).



In neutral and alkaline solutions, on the other hand, fluorides have no influence at all on the extent of reduction, which is always rather indefinite. The final reduction product is always a mixture of manganese dioxide and sesquioxide, as is shown in curve C_2, which is a typical potentiometric titration curve for a weakly alkaline solution of permanganate with an equivalent solution of hydrogen peroxide.

The presence of even large amounts of fluoride does not alter the form of this curve, but, in the course of a study of this point, one sample of sodium fluoride gave curves such as B_1 and B_2. The difference was traced to sodium silicofluoride as an impurity. Similar curves were subsequently obtained when sodium or magnesium silicofluoride was used instead of fluoride, and a selection of these curves is shown in the figure. Curve A, obtained by reduction in the presence of N-sulphuric acid, has been added for comparison. The actual concentrations in each solution are given in the table.

Titration of 20 *c.c. of* N/10-$KMnO_4$ *by* H_2O_2 (*total vol.,* 180 *c.c.*).

Curve	B_1	B_2	B_3	C_1	C_2
N/2-NaOH, c.c.	0	5	15	5	5
Na_2SiF_6, g.	0·75	0·75	0·75	0·15	0·06

It is evident that in the presence of silicofluoride reduction takes place in definite stages. Manganese dioxide appears as a brown precipitate, and there is a fairly sharp break in the curve when the permanganate has been completely reduced to this stage, the solution losing its reddish colour. As more peroxide is added, the precipitate becomes darker, until the tervalent manganese stage is reached, whereupon it begins to dissolve. Exactly at the bivalent manganese stage the last trace of precipitate dissolves to a clear solution, and the curves show a very sharp break.

This effect of silicofluoride is easily explained as due to buffer action. When permanganate is reduced by hydrogen peroxide the solution becomes alkaline. Silicofluorides react, however, with alkalis as follows: $SiF_6'' + 4OH' \longrightarrow Si(OH)_4 + 6F'$, thereby maintaining the hydroxyl-ion concentration at a value too low for precipitation of manganous hydroxide. According to Britton (J., 1925, **127**, 2110), manganous hydroxide begins to be precipitated from dilute solutions of manganese salts when the p_H value of the solution reaches 8·8. The influence of decreasing amounts of silicofluoride is clearly brought out in curves B_2, C_1, and C_2. Solutions B_2 and C_1 were both acid at the beginning, owing to sodium silicofluoride, but C_1 became alkaline during the reduction, and the precipitated manganese dioxide did not redissolve.

Experimental.—In all cases 20 c.c. of $N/10$-potassium permanganate were titrated with $N/10$-hydrogen peroxide at room temperature. The course of reduction was followed electrometrically on a potentiometer circuit, a bright platinum wire being used as one electrode, and the saturated calomel as a second electrode. The liquid was mechanically stirred. The *E.M.F.* values plotted are those actually read, *i.e.*, they refer to the saturated calomel as zero. The potential showed a continual drift, and the values after an interval of 15 minutes were taken, at which point the rate of change had become very slow.

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