

*Structural Properties and the Relative Electrode Potentials of Synthetic Manganese Dioxides. Part II.\* The Characterisation and the Relative Electrode Potentials of the  $\alpha$ -,  $\gamma$ -, and  $\delta$ -Oxides.*

By K. H. MAXWELL and H. R. THIRSK.

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Analytical data and structural information obtained by electron microscopy and *X*-ray and electron diffraction, relevant to the synthetic  $\alpha$ -,  $\gamma$ -, and  $\delta$ -manganese dioxides used in the e.m.f. experiments are set out in detail; the nomenclature adopted is defined. Reasons are advanced for the particular structural form of some of the oxides and for the changes in structure on sintering and, with certain preparations, on sintering after leaching in order to remove a proportion of the foreign ions present from the material.

The relative electrode potentials of the preparations have been determined with respect to a preparation of  $\beta$ - $\text{MnO}_2$  selected as a standard. Chemically prepared  $\gamma$ - $\text{MnO}_2$  in presence of  $\text{NH}_4^+$  and  $\text{K}^+$  had similar e.m.f.'s, 30—35 mv greater than the value of  $\beta$ - $\text{MnO}_2$ ; commercial  $\gamma$ -oxides had similar values. Whilst the e.m.f.'s of the electrolytically prepared  $\gamma$ -oxides were similar, the fluctuations in value were greater than with the chemical preparations; there was no correlation between electrode potential and available oxygen for the  $\gamma$ -preparations. The e.m.f.'s of the  $\alpha$ -oxides were of the same order as those of the  $\gamma$ -oxides but well crystallised samples all had a standard electrode potential very near to 1.252 v independent of the nature of the foreign ion. There was a regular change in potential as the  $\gamma$ -phase was converted into the  $\alpha$ -phase. The e.m.f.'s of the  $\delta$ -oxides in presence of sodium and potassium were about 50 mv greater, and with calcium and barium 60—70 mv greater than the  $\beta$ - $\text{MnO}_2$  value; the potentials were somewhat unsteady. The e.m.f. rose with the temperature on annealing to a maximum value for preparations heated at 275—300° c, reaching a value of 65—75 mv for sodium and potassium, and 80 mv for calcium and barium preparations. At this stage  $\alpha$ - $\text{MnO}_2$  was detectable in the phase by *X*-ray analysis. There is evidence for the reaction of the  $\delta$ -oxides with the electrolyte at low acid concentrations. An explanation is given for the results of the e.m.f. measurements.

THE industrial importance of the manganese dioxides has recently stimulated interest in synthetic materials prepared under controlled conditions. Certain properties of the oxides have been measured in an attempt to correlate them with their structure. *E.g.*, Moore, Ellis, and Selwood (*J. Amer. Chem. Soc.*, 1950, **72**, 856) examined the magnetic and

• Part I, preceding paper.

crystallographic properties of certain preparations but few results have been published concerning the e.m.f.'s of cells containing synthetic forms of  $\text{MnO}_2$ . It has been observed that the open-circuit voltages of dry cells made with these oxides are higher than those with  $\beta\text{-MnO}_2$  (Skewes, Wadsley, and Walkley, *Austral. J. Appl. Sci.*, 1952, 3, 368); a few measurements on the  $\gamma$ -oxides were also reported by Wadsley and Walkley (*J. Electrochem. Soc.*, 1949, 95, 11).

These workers measured the e.m.f. of the cell  $\text{Ag-AgCl}|\text{MnCl}_2, \text{HCl}|\gamma\text{-MnO}_2\text{-Pt}$  and found a rough correlation between e.m.f. and the active oxygen of the  $\gamma\text{-MnO}_2$  sample. The e.m.f. was some 40 mv higher than that of the cell containing  $\beta\text{-MnO}_2$ .

We now describe the results of observations of electrode potentials for some controlled preparations of oxides of known structural type; this is preceded by a summary of the structural nature of our preparations. In Part I an account was given of the design of a cell and of a generally suitable method for the determination of the potentials of the oxide, and of the establishment of a thermodynamically suitable standard of reference using  $\beta\text{-MnO}_2$ .

Our attention is confined to a description of four groups of oxides:  $\alpha\text{-MnO}_2$ ,  $\beta\text{-MnO}_2$ ,  $\gamma\text{-MnO}_2$ , and  $\delta\text{-MnO}_2$ , and as confusion exists in the general nomenclature applied to the manganese dioxide we define the terms as follows:

$\alpha\text{-MnO}_2$  refers to oxides having tetragonal or pseudo-tetragonal unit cells with a large axial ratio, approximate dimensions being  $a_o \approx b_o \approx 9.8 \text{ \AA}$ ;  $c_o \approx 2.85 \text{ \AA}$ , and  $\beta \approx 90^\circ$  (Byström and Byström, *Acta Cryst.*, 1950, 3, 1946). A foreign-metal ion, A, such as potassium or barium and perhaps ammonium (Butler and Thirsk, *ibid.*, p. 146), seems to be an essential constituent of the structure and an approximate general formula is  $\text{A}_x\text{Mn}_8\text{O}_{16}$ , where  $x$  is usually less than unity.

$\beta\text{-MnO}_2$  (pyrolusite), the selected reference oxide, can be prepared by the thermal decomposition of manganese nitrate. It is the best-known oxide and its structure has been investigated several times and found to be of the rutile type; the electrochemical behaviour has been discussed in Part I (*loc. cit.*).

$\gamma\text{-MnO}_2$ , often produced by precipitation from solution and apparently always formed by electrolytic deposition at the anode (Cole, Wadsley, and Walkley, *J. Electrochem. Soc.*, 1947, 92, 133), is poorly crystalline, the X-ray pattern showing several diffuse lines which can be indexed on the basis of an orthorhombic unit cell with the approximate dimensions  $a_o \approx 4.4 \text{ \AA}$ ;  $b_o \approx 9.3 \text{ \AA}$ ;  $c_o \approx 2.83 \text{ \AA}$  (Byström, *Acta Chem. Scand.*, 1949, 3, 163).

$\delta\text{-MnO}_2$  (manganous manganite) is an extremely finely divided material giving prominent diffractions near  $d_{hkl} = 1.42, 2.44, 3.63, \text{ and } 7.3 \text{ \AA}$ . It is formed either by the alkaline oxidation of manganous hydroxide (Feitknecht and Marti, *Helv. Chim. Acta*, 1945, 28, 129, 149) or by the decomposition of permanganates by hydrochloric acid (McMurdie, *J. Electrochem. Soc.*, 1944, 86, 313).

## EXPERIMENTAL

*Preparative and Structural Investigation.*—Many samples of the above oxides were prepared, sintered in oxygen, analysed, and examined by X-ray and electron diffraction and electron microscopy. For details of the experimental techniques see Butler, Maxwell, and Thirsk, *J.*, 1952, 4210; Butler and Thirsk, *J. Electrochem. Soc.*, 1953, 100, 347.

General details relating to the classification of the  $\alpha$ -,  $\gamma$ -, and  $\delta$ -oxides are given in Table 1.

*Electrochemical.*—A cell similar to that used by Wadsley and Walkley (*loc. cit.*) was used and, the same cell reaction being assumed as for  $\beta\text{-MnO}_2$ ,  $E$  is given by

$$E = E^\circ - (RT/2F)[\ln(a_{\pm s}^3/a_{\pm a}^8)] \quad \dots \quad (1)$$

where  $a_{\pm s}$  and  $a_{\pm a}$  are the mean activities of manganous chloride and hydrochloric acid (cf. Part I, p. 4055). In order to reduce the number of measurements and at the same time to obtain as great a variation as possible in the ratio of the activities of manganous chloride and hydrochloric acid, five solutions were employed, being 0.01, 0.03, 0.05, 0.07, and 0.09 m with respect to hydrochloric acid, while the remainder of the ionic strength,  $\mu$ , was kept constant at 0.1 with manganous chloride of molality 0.0300, 0.0233, 0.0167, 0.0100, and 0.0033.

All measurements were made at 25°. As preliminary measurements had shown that a few

of the oxide electrodes were easily polarised even by the small current taken in balancing a potentiometer, an electrometer triode was incorporated in the measuring circuit together with a potentiometer accurate to  $\pm 0.2$  mv. The oxide samples were ground with the first electrolyte and soaked in this solution for several days before the cell was set up. Three electrodes from each oxide sample were used and the e.m.f.'s measured over several days. The electrolyte was then renewed, the oxide reground with the fresh electrolyte and readings were taken for a further few days. The e.m.f. was usually found to stay constant within 1—2 mv over the latter period and this value was recorded. The electrolyte was then changed by decantation and washing with the next electrolyte and the whole procedure repeated.

In order to evaluate the activity factor in equation (1) the value of  $E^\circ$  obtained from the experiments in Part I of this series was employed. Thus the e.m.f.'s of the cells containing the disperse forms of manganese dioxide were put on to the hydrogen scale by measuring them relative to Preparation A (Part I, *loc. cit.*) of  $\beta$ - $\text{MnO}_2$ . Three electrodes were made up from each oxide sample and their e.m.f.'s were measured in five solutions. The mean values of  $E^\circ$  are given in Table 1, together with an estimate of the probable error derived from the standard deviation.

TABLE 1.

| Preparation   | Formula                                 | Phase *              | $E^\circ$ (v)       |
|---|---|----------------------|---------------------|
| 1. Oxidation of acid manganous sulphate solution by ammonium persulphate.   |   |                      |                     |
| (a) Dried at 60°  | $\text{MnO}_{1.95}$                     | $\gamma$             | $1.253 \pm 0.001_4$ |
| (b) Identical with (a) dried at room temp.  | $(\text{NH}_4)_{0.02}\text{MnO}_{1.95}$ | $\alpha, \gamma$ (e) | $1.265 \pm 0.001_0$ |
| (c) Identical with (a) dried at 60°   | $(\text{NH}_4)_{0.03}\text{MnO}_{1.89}$ | $\alpha, \gamma$ (e) | $1.261 \pm 0.001_0$ |
| (d) Identical with (a) dried at 60°   | $(\text{NH}_4)_{0.02}\text{MnO}_{1.89}$ | $\alpha, \gamma$ (e) | $1.261 \pm 0.001_0$ |
| (e) Prep. (a) heated to 200° in $\text{O}_2$  | $\text{MnO}_{1.97}$                     | $\text{MnO}_2$       | $1.248 \pm 0.001_0$ |
| (f) Prep. (b) heated to 200° in $\text{O}_2$  | $(\text{NH}_4)_{0.02}\text{MnO}_{1.98}$ | $\alpha, \gamma$ (e) | $1.257 \pm 0.001_3$ |
| (g) Prep. (b) heated to 400° in $\text{O}_2$  | —                                       | $\alpha$             | $1.252 \pm 0.001_8$ |
| 2. Oxidation of a solution of $(\text{MnSO}_4 + \text{H}_2\text{SO}_4 + \text{KNO}_3)$ by $\text{KMnO}_4$   |   |                      |                     |
| (a) Dried at room temp.   | $\text{K}_{0.08}\text{MnO}_{1.93}$      | $\alpha, \gamma$ (e) | $1.266 \pm 0.001_3$ |
| (b) Dried at 60°  | $\text{K}_{0.08}\text{MnO}_{1.91}$      | $\gamma, \alpha$ (e) | $1.263 \pm 0.001_3$ |
| (c) Prep. (a) heated to 200° in $\text{O}_2$  | $\text{K}_{0.08}\text{MnO}_{1.94}$      | $\alpha, \gamma$ (e) | $1.256 \pm 0.001_3$ |
| (d) Prep. (b) heated to 200° in $\text{O}_2$  | $\text{K}_{0.08}\text{MnO}_{1.94}$      | $\alpha, \gamma$ (e) | $1.256 \pm 0.001_3$ |
| 3. $\text{KMnO}_4$ added to an acid solution of $\text{MnSO}_4$ in three portions. After each addition the $\text{MnO}_2$ was filtered off and dried. |   |                      |                     |
| (a) First ppt.  | $\text{K}_{0.02}\text{MnO}_{1.97}$      | $\gamma, \alpha$ (t) | $1.254 \pm 0.001_0$ |
| (b) Second ppt.   | $\text{K}_{0.08}\text{MnO}_{1.94}$      | $\gamma, \alpha$ (e) | $1.261 \pm 0.001_0$ |
| (c) Third ppt.  | $\text{K}_{0.09}\text{MnO}_{1.92}$      | $\alpha, \gamma$ (t) | $1.282 \pm 0.001_4$ |
| 4. Hydrochloric acid added dropwise to a boiling $\text{KMnO}_4$ soln.  |   |                      |                     |
| (a) Dried at room temp.   | $\text{K}_{0.27}\text{MnO}_{2.00}$      | $\delta$             | $1.266 \pm 0.001_4$ |
| (b) Heated to 120° in $\text{O}_2$  | $\text{K}_{0.27}\text{MnO}_{1.96}$      | $\delta$             | $1.275 \pm 0.001_0$ |
| (c) " 200 "   | $\text{K}_{0.27}\text{MnO}_{1.93}$      | $\delta$             | $1.280 \pm 0.001_0$ |
| (d) " 260 "   | $\text{K}_{0.27}\text{MnO}_{1.91}$      | $\delta$             | $1.284 \pm 0.001_0$ |
| (e) " 275 "   | $\text{K}_{0.27}\text{MnO}_{1.91}$      | $\delta, \alpha$ (t) | $1.292 \pm 0.001_0$ |
| (f) " 300 "   | $\text{K}_{0.27}\text{MnO}_{1.90}$      | $\delta, \alpha$ (t) | $1.290 \pm 0.001_3$ |
| (g) " 400 "   | $\text{K}_{0.27}\text{MnO}_{1.89}$      | $\alpha$             | $1.277 \pm 0.001_3$ |
| (h) " 500 "   | $\text{K}_{0.27}\text{MnO}_{1.88}$      | $\alpha$             | $1.252 \pm 0.001_8$ |
| 5. Hydrochloric acid added dropwise to a boiling $\text{NaMnO}_4$ soln.   |   |                      |                     |
| (a) Dried at room temp.   | $\text{Na}_{0.22}\text{MnO}_{1.99}$     | $\delta$             | $1.270 \pm 0.001_0$ |
| (b) Heated to 120° in $\text{O}_2$  | $\text{Na}_{0.22}\text{MnO}_{1.97}$     | $\delta$             | $1.273 \pm 0.001_6$ |
| (c) " 200 "   | $\text{Na}_{0.22}\text{MnO}_{1.93}$     | $\delta$             | $1.278 \pm 0.001_0$ |
| (d) " 250 "   | $\text{Na}_{0.22}\text{MnO}_{1.92}$     | $\delta$             | $1.281 \pm 0.001_1$ |
| (e) " 275 "   | $\text{Na}_{0.22}\text{MnO}_{1.91}$     | $\delta$             | $1.285 \pm 0.001_3$ |
| (f) " 300 "   | $\text{Na}_{0.22}\text{MnO}_{1.91}$     | $\delta, \alpha$ (t) | $1.282 \pm 0.001_0$ |
| (g) " 400 "   | $\text{Na}_{0.22}\text{MnO}_{1.90}$     | $\alpha$             | $1.272 \pm 0.001_0$ |
| (h) " 500 "   | $\text{Na}_{0.22}\text{MnO}_{1.89}$     | $\alpha$             | $1.250 \pm 0.001_3$ |
| 6. Hydrochloric acid added dropwise to a boiling $\text{Ba}(\text{MnO}_4)_2$ soln.  |   |                      |                     |
| (a) Dried at room temp.   | $\text{Ba}_{0.13}\text{MnO}_{2.00}$     | $\delta$             | $1.276 \pm 0.002_3$ |
| (b) Heated at 120° in $\text{O}_2$  | $\text{Ba}_{0.13}\text{MnO}_{1.98}$     | $\delta$             | $1.285 \pm 0.001_3$ |
| (c) " 200 "   | $\text{Ba}_{0.13}\text{MnO}_{1.95}$     | $\delta$             | $1.297 \pm 0.002_3$ |
| (d) " 400 "   | $\text{Ba}_{0.13}\text{MnO}_{1.94}$     | $\delta$             |                     |
| (e) " 500 "   | $\text{Ba}_{0.13}\text{MnO}_{1.91}$     | $\alpha$             |                     |
| (f) " 580 "   | $\text{Ba}_{0.13}\text{MnO}_{1.88}$     | P                    |                     |

TABLE 1. (Continued.)

| Preparation  | Formula                                | Phase *  | $E^\circ$ (v)              |
|--|--|----------|----------------------------|
| 7. Prep. 6 boiled with 4N-HNO <sub>3</sub> for 4 hr.   |  |          |                            |
| (a) Dried at 120°  | Ba <sub>0.02</sub> MnO <sub>1.97</sub> | α        | 1.264 ± 0.001 <sub>2</sub> |
| (b) Heated at 400° in O <sub>2</sub>   | Ba <sub>0.02</sub> MnO <sub>1.98</sub> | α        | 1.253 ± 0.001 <sub>0</sub> |
| 8. Hydrochloric acid added dropwise to a boiling Ca(MnO <sub>4</sub> ) <sub>2</sub> soln.    |  |          |                            |
| (a) Dried at room temp.  | Ca <sub>0.12</sub> MnO <sub>1.99</sub> | δ        | 1.288 ± 0.001 <sub>7</sub> |
| (b) Heated at 200° in O <sub>2</sub>   | Ca <sub>0.12</sub> MnO <sub>1.97</sub> | δ        | 1.304 ± 0.002 <sub>0</sub> |
| (c) " 400 "  | Ca <sub>0.12</sub> MnO <sub>1.93</sub> | δ        |                            |
| (d) " 500 "  | Ca <sub>0.12</sub> MnO <sub>1.86</sub> | α        |                            |
| (e) " 580 "  | Ca <sub>0.12</sub> MnO <sub>1.94</sub> | q        |                            |
| 9. Prep. 8 boiled with 4N-HNO <sub>3</sub> for 4 hr.   |  |          |                            |
| (a) Dried at 120°  | Ca <sub>0.01</sub> MnO <sub>1.98</sub> | α        | 1.261 ± 0.001 <sub>0</sub> |
| (b) Heated at 400 in O <sub>2</sub>  | Ca <sub>0.01</sub> MnO <sub>1.98</sub> | α        | 1.258 ± 0.001 <sub>1</sub> |
| 10. B.D.H. sample.   |  |          |                            |
| (a) As obtained  | K <sub>0.21</sub> MnO <sub>1.96</sub>  | δ        | 1.276 ± 0.001 <sub>0</sub> |
| (b) Heated at 120° in O <sub>2</sub>   | K <sub>0.21</sub> MnO <sub>1.94</sub>  | δ        | 1.279 ± 0.001 <sub>0</sub> |
| (c) " 200 "  | K <sub>0.21</sub> MnO <sub>1.93</sub>  | δ        | 1.281 ± 0.001 <sub>3</sub> |
| (d) " 250 "  | K <sub>0.21</sub> MnO <sub>1.92</sub>  | δ        | 1.292 ± 0.001 <sub>3</sub> |
| (e) " 275 "  | K <sub>0.21</sub> MnO <sub>1.92</sub>  | δ, α (t) | 1.296 ± 0.001 <sub>6</sub> |
| (f) " 300 "  | K <sub>0.21</sub> MnO <sub>1.91</sub>  | δ, α (t) | 1.294 ± 0.001 <sub>2</sub> |
| (g) " 400 "  | K <sub>0.21</sub> MnO <sub>1.90</sub>  | α        | 1.284 ± 0.001 <sub>0</sub> |
| (h) " 500 "  | K <sub>0.21</sub> MnO <sub>1.90</sub>  | α        | 1.252 ± 0.001 <sub>6</sub> |
| 11. Electrolytic deposition at a Pt anode from an acid solution of MnSO <sub>4</sub> at 75°. |  |          |                            |
| (a) Dried at room temp.  | MnO <sub>1.96</sub>                    | γ        | 1.258 ± 0.001 <sub>0</sub> |
| (b) Identical with (a)   | MnO <sub>1.95</sub>                    | γ        | 1.254 ± 0.001 <sub>0</sub> |
| (c) Identical with (a)   | MnO <sub>1.98</sub>                    | γ        | 1.258 ± 0.001 <sub>0</sub> |
| 12. Prep. 11 boiled with 2N-HNO <sub>3</sub> for 4 hr. Dried at room temp.                   |  |          |                            |
| (a)  | MnO <sub>1.98</sub>                    | γ        | 1.255 ± 0.001 <sub>2</sub> |
| (b)  | MnO <sub>1.98</sub>                    | γ        | 1.255 ± 0.001 <sub>0</sub> |
| (c)  | MnO <sub>1.97</sub>                    | γ        | 1.255 ± 0.001 <sub>0</sub> |
| 13. Commercial electrolytic preparations from various sources.                               |  |          |                            |
| (a)  | MnO <sub>1.92</sub>                    | γ        | 1.255 ± 0.001 <sub>8</sub> |
| (b)  | MnO <sub>1.93</sub>                    | γ        | 1.252 ± 0.001 <sub>3</sub> |
| (c)  | MnO <sub>1.92</sub>                    | γ        | 1.251 ± 0.001 <sub>1</sub> |
| (d)  | MnO <sub>1.96</sub>                    | γ        | 1.253 ± 0.001 <sub>7</sub> |
| (e)  | MnO <sub>1.93</sub>                    | γ        | 1.255 ± 0.001 <sub>4</sub> |
| (f)  | MnO <sub>1.91</sub>                    | γ        | 1.251 ± 0.001 <sub>2</sub> |
| (g)  | MnO <sub>1.97</sub>                    | γ        | 1.250 ± 0.001 <sub>1</sub> |
| (h)  | MnO <sub>1.91</sub>                    | γ        | 1.235 ± 0.002 <sub>6</sub> |
| 14. Samples 13 boiled with 2N-HNO <sub>3</sub> for 4 hr. Dried at room temp.                 |  |          |                            |
| (a)  | MnO <sub>1.98</sub>                    | γ        | 1.238 ± 0.001 <sub>0</sub> |
| (b)  | —                                      | γ        | 1.242 ± 0.001 <sub>2</sub> |
| (c)  | —                                      | γ        | 1.250 ± 0.001 <sub>0</sub> |
| (d)  | MnO <sub>1.97</sub>                    | γ        | 1.251 ± 0.001 <sub>0</sub> |
| (e)  | MnO <sub>1.97</sub>                    | γ        | 1.242 ± 0.001 <sub>0</sub> |
| (f)  | —                                      | γ        | 1.246 ± 0.001 <sub>0</sub> |
| (g)  | —                                      | γ        | 1.242 ± 0.001 <sub>0</sub> |
| (h)  | MnO <sub>1.98</sub>                    | γ        | 1.247 ± 0.001 <sub>0</sub> |

\* t = trace; e = equal amounts; p = very poorly crystallised α-MnO<sub>2</sub> + α-Mn<sub>2</sub>O<sub>3</sub>; q = poorly crystallised α-MnO<sub>2</sub>; decomp.

## DISCUSSION

*Structural Properties.*—Initially the reason for the production of α- and γ-forms of the oxides from Preparation 1 (see Table 1) was not clear; in certain cases γ-MnO<sub>2</sub> was obtained with strong diffractions at 4.03, 2.42, 2.12, and 1.63 Å whilst with other preparations, an apparently identical procedure being used, a mixture of α- and γ-forms in approximately equal amounts was precipitated. With Preparation 2 (a), potassium permanganate being

used as oxidising agent, a mixed phase invariably resulted; other workers have reported either  $\gamma$ -MnO<sub>2</sub> (Moore, Ellis, and Selwood, *loc. cit.*) or  $\alpha$ -MnO<sub>2</sub> (Cole, Wadsley, and Walkley, *loc. cit.*).

Preparation 3 was carried out to investigate this matter further. To an acid solution of manganous sulphate without potassium nitrate the required quantity of potassium permanganate for complete precipitation was added in three equal portions. After each addition the precipitate was filtered off. The precipitate first collected was found to be  $\gamma$ -MnO<sub>2</sub> with a trace of  $\alpha$ -MnO<sub>2</sub>, very weak reflections being observed at interplanar spacings corresponding to the strongest lines of the  $\alpha$ -MnO<sub>2</sub> pattern. The second precipitate contained both the  $\alpha$ - and the  $\gamma$ -phase in about equal amounts, the strong lines of the two phases having approximately equal intensities. The last-formed portion of the precipitate was found to be almost  $\alpha$ -MnO<sub>2</sub>, with only a faint reflection at  $d_{hkl} = 4.03 \text{ \AA}$  indicating the presence of a trace of the  $\gamma$ -oxide.

The best substantiated idea of the structure of the  $\gamma$ -MnO<sub>2</sub> is due to Byström (*loc. cit.*) who pointed out that the lines of the  $\gamma$ -MnO<sub>2</sub> pattern are those which are common to ramsdellite and pyrolusite, if the pyrolusite lines are indexed on the basis of a unit cell having twice the value of the normal  $b_0$  axis. It was therefore suggested that  $\gamma$ -MnO<sub>2</sub> was intermediate in structure between ramsdellite and pyrolusite. In a later paper Byström and Byström (*loc. cit.*) stated that the arrangement of manganese ions probably changes from that of ramsdellite to pyrolusite at random since the network of oxygen ions is essentially the same in both structures. In order to explain the fact that with many synthetic preparations involving the precipitation of the dioxide from solution either the  $\alpha$ - or the  $\gamma$ -form resulted. Byström and Byström suggested that the primary product is the formation of double strings of octahedra common to both  $\alpha$ -MnO<sub>2</sub> and ramsdellite. If a sufficient concentration of large metal ions is present these double strings cluster round then in the  $\alpha$ -MnO<sub>2</sub> manner. If there are too few or no large ions in solution the double strings can join in a disordered ramsdellite arrangement and by rearrangement in the boiling solution are converted into the structure known as  $\gamma$ -MnO<sub>2</sub>.

These ideas are supported by the results from Preparation 3. The first precipitate, formed when the concentration of potassium ions in solution was small is very largely the  $\gamma$ -phase. As the concentration of potassium ions increased the amount of  $\gamma$ -MnO<sub>2</sub> decreased and the final precipitate was almost entirely  $\alpha$ -MnO<sub>2</sub>. As a mixed phase also resulted from Preparation 1, it is probable that the ammonium ion, which has approximately the same ionic radius as the potassium ion, is also acting similarly as a necessary component of the oxide.

Electron microscopy showed that the  $\alpha$ -phase in both Preparations 1 and 2 existed as needles of maximum length  $1\mu$  in Preparation 1 and much smaller in 2, and the general details are discussed at some length by Butler and Thirsk (*loc. cit.*). The  $c_0$  axis of the unit cell is parallel to the long axis of the crystals even on this microscopic scale and the orientation is the same as that reported from X-ray studies on the rare macroscopic single crystals of cryptomelane and hollandite (Byström and Byström, *loc. cit.*; Ramsdell, *Amer. Mineralogist*, 1943, 28, 497).

Preparation 4 and the commercial sample Preparation 10 show the four diffuse lines characteristic of the  $\delta$ -MnO<sub>2</sub> X-ray pattern. Heating to 250°C made little difference apart from a slight sharpening of the lines; on heating to 275° extra faint lines appeared at spacings of 2.39, 2.15, and 1.83 Å corresponding to the 121, 301, and 141 reflections of  $\alpha$ -MnO<sub>2</sub>: when heated to 400° the complete  $\alpha$ -MnO<sub>2</sub> pattern was obtained and the crystallinity was slightly improved by heating to 500°. With Preparation 5, the  $\delta$ -MnO<sub>2</sub> produced from the sodium permanganate did not yield  $\alpha$ -MnO<sub>2</sub> diffractions until the oxide had been heated to 300°, whereupon faint reflections were observed.

When examined by electron microscopy  $\delta$ -MnO<sub>2</sub> appeared to consist of irregular plates of very small size. The  $\alpha$ -MnO<sub>2</sub>, formed by heating the  $\delta$ -oxide containing potassium, existed as needles similar to those already described but when sodium was the third element no preferred direction of growth and no apparent orientation of unit cell with the external morphology of the crystallites was detected. However the greater sharpness of the 002 reflection in the X-ray pattern than of the other lines indicated

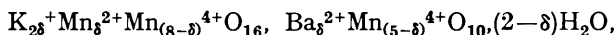
that the crystals were also more ordered parallel to the  $c_o$  axis. The electron micrographs of samples of Preparation 4 (300°) and Preparation 10 (300°) in general appear like  $\delta$ -MnO<sub>2</sub> but by refining the method of dispersion by means of a 1% colloid solution, Mr. E. H. Boulton (of these laboratories) was able to show that whilst the majority of the material was typically  $\delta$ -MnO<sub>2</sub>, 3–4% existed as minute needles characteristic of  $\alpha$ -MnO<sub>2</sub>. Unfortunately, owing to the dispersion necessary to reveal the morphology of the preparation an adequate local concentration for an electron-diffraction pattern was not discovered.

The actual structure of  $\delta$ -MnO<sub>2</sub> is not known although two proposals have been made as to the probable arrangement in the oxide. Feitknecht and Marti (*loc. cit.*) suggested that it had a layer lattice and was derived from the manganous hydroxide structure which is of the cadmium type. This idea draws support from the preparation of the  $\delta$ -oxide by oxidation of manganous hydroxide, and virtually the suggestion is that the structure of the  $\delta$ -MnO<sub>2</sub> can be derived from that of manganous hydroxide by the replacement of manganous and hydroxyl ions by those of the tervalent manganese and oxygen. This idea is unconvincing since the oxide can equally well be made by decomposing permanganates by hydrochloric acid. It appears that the principal evidence in favour of this structure is that the three outer lines of the  $\delta$ -MnO<sub>2</sub> diffraction pattern have spacings which are submultiples of the line at 7.3 Å, which might indicate a prominent basal plane characteristic of a layer lattice.

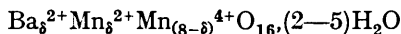
McMurdie (*loc. cit.*) considered the  $\delta$ -oxide to have a poorly crystalline  $\alpha$ -MnO<sub>2</sub> arrangement. The four diffuse lines which constitute the  $\delta$ -MnO<sub>2</sub> X-ray pattern can be indexed as 110, 220, 121, and 002 reflections from a lattice based on a tetragonal unit cell with dimensions  $a_o = 10.3$  Å,  $c_o = 2.83$  Å. We have noted that this phase, like  $\alpha$ -MnO<sub>2</sub>, is only formed when a large excess of a suitable foreign cation is present and we also favour a distorted  $\alpha$ -MnO<sub>2</sub> arrangement as providing the most likely picture of the structure.

The analytical figures of Table 1 are of interest in connection with the transition of  $\delta$ -MnO<sub>2</sub> to  $\alpha$ -MnO<sub>2</sub>. The oxides were analysed for manganese, available oxygen, and the foreign cation. It is common practice, especially in mineralogical papers, to express the percentage of the foreign-metal ion as its oxide; manganese as MnO; to include the oxygen with the determined available oxygen, and to express the whole as total oxygen. In the analyses in Table 1 manganese is assumed to be present as MnO while the extra oxygen is the experimentally found available oxygen. The foreign ion is not expressed as an oxide.

As precipitated,  $\delta$ -MnO<sub>2</sub> contains almost the stoichiometrically required quantity of available oxygen, but this diminishes steadily as the oxide is heated at increasing temperatures. If we associate this decrease in available oxygen with the entry of the foreign metal into sites in the lattice, the process would seem to occur continuously over the range 100–400° and to be practically complete at the latter temperature. The approximate general formula for  $\alpha$ -MnO<sub>2</sub> being  $A_xMn_8O_{16}$ , the oxides may be considered, as with the similar naturally occurring minerals cryptomelane, psilomelane, and hollandite, to be semiconductors and in the case of these minerals the formulæ may be written respectively as



and



(Rees, "Chemistry of the Defect Solid State," Methuen, 1954, p. 88), the amount of foreign ion entering the lattice directly controlling the relative quantity of Mn<sup>2+</sup> and Mn<sup>4+</sup> ions present. A similar formulation could be employed with the synthetic materials. In the structural analysis of hollandite Byström and Byström found that the large metal (Ba<sup>++</sup>) ions occupied positions in the "tunnels" formed between the strings of MnO<sub>6</sub> octahedra; they came to the conclusion that a maximum of only one large metal ion per unit cell was allowable, corresponding to  $x = 1$  in the general formula. Our analyses, however, show that both potassium and sodium enter the lattice continuously up to  $x = 2$ , when the formula could be written (K<sub>2</sub>O)Mn<sub>8</sub>O<sub>15</sub> and  $n$  in MnO <sub>$n$</sub>  would be 1.88. This suggests that the potassium and sodium atoms occupy sites additional to the one per unit cell suggested by Byström and Byström.

If, as with Preparations 6 and 8, the foreign ions are barium and calcium a somewhat different state of affairs exists. On heating to 400° three diffuse lines were obtained and these could be indexed as the 200, 121, and 002 reflections of a structure based on a unit cell having  $a_0 = 10.5 \text{ \AA}$  and  $c_0 = 2.82 \text{ \AA}$ . The designation  $\delta\text{-MnO}_2$  is retained for these preparations in spite of its not conforming completely to our definition. On heating to 500° a poorly resolved  $\alpha\text{-MnO}_2$  pattern was obtained from the product. Attempts to improve the crystallinity by heating to 580° were unsuccessful for no sharpening of the  $\alpha\text{-MnO}_2$  diffractions took place and, in addition, the oxide started to decompose, a pattern of  $\alpha\text{-Mn}_2\text{O}_3$  (bixbyite) appearing. The analyses show, as in the case of the sodium and potassium compounds, a similar decrease in available oxygen content on heating. In this case the amount of barium and calcium was only one-half that of the sodium or potassium, giving  $x = 1$ ; the formula  $\text{BaMn}_8\text{O}_{16}$  corresponds on a valency basis to  $\text{K}_2\text{Mn}_8\text{O}_{16}$ .

Unpublished work by us has shown that  $\alpha\text{-MnO}_2$  containing potassium does not decompose until heated above 900° and is more readily formed from the  $\delta$ -oxide; these results may be quite reasonably explained if in this case we follow Byström and Byström and associate one foreign ion with each unit cell. If all the available sites are thus occupied, corresponding to  $x = 1$ , the distance between neighbouring barium ions is only 2.85 Å. As the ionic diameter of  $\text{Ba}^{++}$  is 2.76 Å it would follow that strong repulsive forces must occur between the doubly charged ions leading to structural instability and the decomposition of the oxide at temperatures of the order of 580°.

In accepting the Byström picture for the barium compound whilst rejecting the full implication (a maximum of one foreign cation per unit cell) for the sodium and potassium compounds, we may appear inconsistent but the behaviour of the two groups of preparations is strikingly different. It should be remembered that Byström and Byström carried out a full structural analysis on hollandite only ( $A = \text{Ba}^{++}$ ) and since Gruner (*Amer. Mineralogist*, 1943, **28**, 497) had shown the mineral to be isostructural with corondite and cryptomelane they applied their findings to the latter pair of minerals as well. Since the ionic diameters of  $\text{Ba}^{++}$ ,  $\text{Pb}^{++}$ , and  $\text{K}^+$  are very close this seems to be justifiable, although it would be reasonable to expect that a marked difference in chemical behaviour might follow by the interchange of doubly and singly charged ions.

The problem of the conversion of the  $\delta$ - into the  $\alpha$ -phase and the concurrent stability of the latter was examined by the experiments embodied in Preparations 7 and 9. It was considered that if part of the barium or calcium could be removed from the material so that all available sites were no longer occupied, the conversion into  $\alpha\text{-MnO}_2$  might take place readily without decomposition. The precipitates were therefore leached with 4*N*-nitric acid for four hours, washed, and dried at 120°. X-Ray diffraction showed that this treatment was sufficient to convert both preparations into  $\alpha\text{-MnO}_2$  with a crystallinity at least as good as that of the best crystallised potassium-containing preparations. A slight further improvement in crystallinity followed on heating to 400°. The value of  $x$  in the general formula was reduced to about 0.1 and this would render unnecessary any short barium- or calcium-ion distances in the  $\alpha\text{-MnO}_2$ . It is considered that these experiments are strong confirmation of our ideas concerning the difficulty of obtaining  $\alpha\text{-MnO}_2$  from Preparations 6 and 8.

*Electrochemical Properties.*—The values of  $E^\circ$ , relative to the hydrogen electrode, calculated from the e.m.f. of the individual electrodes show, for each preparation, a good agreement among themselves and the general assumption that the cell reaction is the same for these cells as for that containing  $\beta\text{-MnO}_2$ . The results will be discussed in groups according to the structures.

The two samples of  $\gamma\text{-MnO}_2$  prepared by chemical oxidation [1(*a*) and 3(*a*)] had a practically identical e.m.f. in spite of the somewhat different methods of preparation and the presence of potassium in 3(*a*). The value was *ca.* 30–35 mv above the value for the cell containing  $\beta\text{-MnO}_2$  and was decreased by 5 mv when the oxide was heated to 200° to give 1(*e*). The  $\gamma\text{-MnO}_2$  formed by electrolytic deposition at the anode (Preparation 11) had a value very close to this, being nearly 40 mv positive to that of  $\beta\text{-MnO}_2$ . The commercial electrolytic preparations all had values in the range 30–35 mv above

that of  $\beta$ - $\text{MnO}_2$  although the scatter of 5 mv over all the samples shows that different conditions of formation influence the potential to a small extent.

No correlation was observed between e.m.f. and available oxygen although Preparation 11 which had the highest value of  $n$  (in formula  $\text{MnO}_n$ ) also showed the highest e.m.f. Boiling with nitric acid had the effect of bringing their formulæ together but the values for the e.m.f. did not approach one another. The active oxygen content increased to the value  $n = 1.97$  but the values for the e.m.f. all showed a decrease which varied for the different preparations, some being affected considerably [13(a)] whilst with others [13(c)] the e.m.f. was reduced hardly at all.

The  $\gamma$ -oxide produced by chemical oxidation has an e.m.f. which fluctuates more than that produced electrolytically. These fluctuations are about  $\pm 1$  mv from the final equilibrium value and appear to be quite random, no definite trend being observed. This was not the case with the electrolytic oxides, which, on attaining their final value, remained extremely constant for as long as measurements were continued, even though individual electrodes from the same sample showed slight differences from one another. When the electrolytic preparations were boiled with nitric acid the cells made up from them showed precisely the same fluctuations as those observed with the chemically prepared  $\gamma$ - $\text{MnO}_2$ . Thus the electrolytic  $\gamma$ - $\text{MnO}_2$  would appear to have some property which is particularly desirable in an electrochemical system.

The well-crystallised samples of  $\alpha$ - $\text{MnO}_2$  [4(h), 5(h), and 10(h)] all had an e.m.f. more than 30 mv greater than the cell containing  $\beta$ - $\text{MnO}_2$ , practically the same value as that containing  $\gamma$ - $\text{MnO}_2$ . This is not surprising since the structures of the  $\alpha$ - $\text{MnO}_2$  minerals and ramsdellite are built up from the double strings of octahedra and differ only in the method of linking, so it would be expected that both structures would have approximately the same free energies of formation. The mixed phases of  $\alpha$ - and  $\gamma$ - $\text{MnO}_2$  produced in Preparations 1 and 2 were all about 40—45 mv above the  $\beta$ - $\text{MnO}_2$  potential; this was reduced by some 10 mv after the oxides were annealed at 200° and by a further 5 mv after heating to 400° when  $\alpha$ - $\text{MnO}_2$  was the only phase present [1(g)]. This last value is the same as that observed for the  $\alpha$ - $\text{MnO}_2$  in 4(h), 5(h), and 10(h) so that the nature of the foreign ion in the structure appears to play no part in determining the e.m.f. when the oxide is well crystallised.

This point may be illustrated by a consideration of Table 2 in which the method of preparation, formulæ, and electrode potential of six different specimens of  $\alpha$ - $\text{MnO}_2$  containing in all five different foreign cations are listed.

TABLE 2.

| Method of prep.   | Nature of oxide   | $E^\circ$ (v) |
|---|---|---------------|
| Oxidation of acidified $\text{MnSO}_4$ by $(\text{NH}_4)_2\text{S}_2\text{O}_8$ | $\gamma \rightarrow \alpha$ by heating at 400° in $\text{O}_2$ . $(\text{NH}_4)_{0.03}\text{MnO}_{1.98}$  | 1.252         |
| HCl added to boiling $\text{NaMnO}_4$   | $\delta \rightarrow \alpha$ by heating at 500° in $\text{O}_2$ . $\text{Na}_{0.22}\text{MnO}_{1.89}$  | 1.250         |
| HCl added to boiling $\text{KMnO}_4$  | $\delta \rightarrow \alpha$ by heating at 500° in $\text{O}_2$ . $\text{K}_{0.27}\text{MnO}_{1.68}$   | 1.252         |
| HCl added to boiling $\text{Ba}(\text{MnO}_4)_2$                                | $\delta \rightarrow \alpha$ by boiling with 4N- $\text{HNO}_3$ drying at 120° and heating at 400° in $\text{O}_2$ . $\text{Ba}_{0.02}\text{MnO}_{1.98}$ | 1.252         |
| HCl added to boiling $\text{Ca}(\text{MnO}_4)_2$                                | $\delta \rightarrow \alpha$ by boiling with 4N- $\text{HNO}_3$ drying at 120° and heating at 400° in $\text{O}_2$ . $\text{Ca}_{0.01}\text{MnO}_{1.98}$ | 1.258         |
| B.D.H. Sample   | $\delta \rightarrow \alpha$ by heating at 400° in $\text{O}_2$ . $\text{K}_{0.21}\text{MnO}_{1.90}$   | 1.252         |

The two oxides, the second and fifth oxide in Table 2, which gave e.m.f.'s differing slightly from 1.252 volts differed also in other properties; the former did not show the usual straw-like shape of  $\alpha$ - $\text{MnO}_2$  but occurred as a fairly uniform material without elongation in any particular direction; the latter was still a rather poorly crystallised material.

The potential of the  $\alpha$ - $\text{MnO}_2$  corresponded to a molar free energy of formation of about 680 cal. less than for  $\beta$ - $\text{MnO}_2$ ; it is important to note that it has a more open structure.

The results of Preparation 3 illustrate the change in the potential of the oxides as the composition changes from nearly pure  $\gamma$ - $\text{MnO}_2$  to the nearly pure  $\alpha$ -phase. As the amount of the  $\alpha$ -oxide increases the potential rises steadily and with the last-formed portion of the precipitate the e.m.f. is 30 mv greater than that from the first precipitated material. Even though 3(c) shows the typical  $\alpha$ - $\text{MnO}_2$  X-ray pattern the e.m.f. of this cell is 30 mv greater than the cells containing 4(h) and 10(h). It follows that this form of the oxide may have



large variations in an estimate of the free energy of formation calculated from differences in the e.m.f.

The e.m.f.'s of the cells containing  $\delta$ -MnO<sub>2</sub> were about 50 mv greater than for  $\beta$ -MnO<sub>2</sub> in the case of the oxides precipitated from potassium and sodium permanganates. Oxides formed from barium and calcium permanganates were approximately 60 and 70 mv respectively above the  $\beta$ -MnO<sub>2</sub> potential. With all these preparations it was extremely difficult to obtain steady potentials. Repeated grinding and prolonged soaking with the electrolyte were necessary before even moderately stable results were obtained and even then readings could not be made in the two solutions where the acid concentration was lowest (p. 4059). After measuring the e.m.f. in the three most acid solutions a further attempt was made to measure these oxides in the two less acid solutions. However, their behaviour was exactly the same as before and satisfactory values were only obtained for the three solutions of highest acid concentration.

The oxides obtained by heating the  $\delta$ -MnO<sub>2</sub> showed an interesting effect; the e.m.f. of the cells made up from them all rose steadily as the temperature of annealing increased. Preparations 4, 5, and 10 all behaved similarly, the potential increasing as the sintering temperature increased and reaching a maximum value for the oxides heated at 275° and 300°. The potentials of the oxides heated in this range were about 65–75 mv above that of  $\beta$ -MnO<sub>2</sub>. These are the oxides in which sufficient  $\alpha$ -MnO<sub>2</sub> had been formed for it to be detectable by X-ray diffraction. Heating at higher temperatures resulted in a marked decline in the e.m.f.; the value for the oxides heated at 400° had dropped to 50–60 mv above that for  $\beta$ -MnO<sub>2</sub> while for those heated to 500° it was about 30 mv positive to the standard. With all these sintered preparations it was again found impossible to obtain readings in the solutions of lowest acid concentration and their behaviour was the same as that of  $\delta$ -MnO<sub>2</sub> as precipitated. With the oxides heated at 400° and 500° it was possible, after prolonged soaking of the oxide, to measure the e.m.f. in cells containing the electrolyte 0.03 m in hydrochloric acid.

The preparations of  $\delta$ -MnO<sub>2</sub> containing Ba<sup>++</sup> and Ca<sup>++</sup> (6 and 7) were similar to one another in their behaviour on being heated. As precipitated, they were respectively 60 and 70 mv positive to  $\beta$ -MnO<sub>2</sub> and on heating to 200° the values of the e.m.f. were about 80 mv above that of our standard. The oxides heated to 400° did not give a steady e.m.f. in any of the five electrolytes. However, the mean value seemed to be even higher than those of the oxides heated to 200° although subject to oscillations of about  $\pm 7$ –8 mv.

After most of the Ba<sup>++</sup> and Ca<sup>++</sup> had been removed by boiling with nitric acid [7(a) and 9(a)] the oxides were found to have the  $\alpha$ -MnO<sub>2</sub> structure and the e.m.f. had dropped to 40 mv above that of  $\beta$ -MnO<sub>2</sub>. It was reduced by a further 10 mv after heating at 400° when the value 30 mv positive to our standard was found. To explain the e.m.f. results in the  $\delta$ -MnO<sub>2</sub>  $\rightarrow$   $\alpha$ -MnO<sub>2</sub> transition, the rise to a maximum value and the subsequent decline following the formation of  $\alpha$ -MnO<sub>2</sub> as the temperature of sintering was increased must be accounted for.  $\delta$ -MnO<sub>2</sub>, as precipitated, had almost the theoretically required amount of available oxygen for the formula MnO<sub>2</sub>. On sintering, this available oxygen decreased, owing to the entry of the foreign-metal ions into lattice positions. If  $\delta$ -MnO<sub>2</sub> has a poorly crystalline and distorted  $\alpha$ -MnO<sub>2</sub> arrangement, the process can be pictured as follows. During the heating the large ions pass continuously into positions in the tunnels in the structure. The double strings of octahedra are probably "staggered" and not oriented exactly parallel to one another. This continuous passage of the foreign ions into the oxide leads to a gradual change in the structure up to a point where the disordered arrangement becomes unstable with respect to the more regular  $\alpha$ -MnO<sub>2</sub> system at the temperature of heating and an ordering process takes place. The results from electron microscopy suggest that the formation of  $\alpha$ -MnO<sub>2</sub> takes place at certain nuclei which then grow throughout the bulk of the oxide.

The breadth of the lines of the X-ray diffraction photographs indicates that the crystallite size in the  $\delta$ -MnO<sub>2</sub> preparations is extremely small and surface free energy must play some part in determining the e.m.f. of the cells containing these oxides. The surface free energy is unlikely to increase on sintering so that our explanation of the rise in the e.m.f. on heating is still valid. When the  $\alpha$ -MnO<sub>2</sub> is first formed the needle-shaped

crystallites are poorly developed and even the oxides heated at 400° showed some broadening of the X-ray diffraction lines. The decrease in the e.m.f. observed after the formation of  $\alpha$ -MnO<sub>2</sub> for the oxides heated at 400° and 500° is probably due to the removal of lattice defects and the decrease in surface free energy as the crystallites develop in size and regularity. This decrease is probably taking place continuously over the whole sintering range but in the lower temperature region its effect is masked by the process of the entry of the foreign-metal ions into the structure.

Reference will finally be made to an effect which was noticed with  $\delta$ -MnO<sub>2</sub> and many of the  $\alpha$ -MnO<sub>2</sub> preparations, particularly 4, 5, and 10. After the electrolyte had been introduced and the cell set up, a steady fall in the measured e.m.f. was observed; this continued for as long as readings were taken, in some cases for as long as two weeks. When the electrolyte was renewed, with as little disturbance of the MnO<sub>2</sub> slurry as possible, the e.m.f. returned to within 1 mv of the original value and then started to fall as before; this occurred each time the electrolyte was changed. To obtain an e.m.f. of use as a comparison with other preparations it was necessary to standardise the method of measurement. After renewal of the electrolyte for the second time the cell was left for twelve hours to settle down. Readings were then made during the next six hours and as these were constant to about 1 mv they were taken as the e.m.f. of the cell and are the values used to calculate the values of  $E^\circ$  given in Table 1.

The rate of the decrease in the e.m.f. varied considerably, being 2—3 mv per day in the case of  $\delta$ -MnO<sub>2</sub> heated in the temperature range 200—300° and less than 1 mv per day for the  $\alpha$ -MnO<sub>2</sub> preparations heated to 400° and 500°. It might be argued that disturbing the electrode caused the e.m.f. to rise, as happens with powder electrodes, and we were only observing the subsequent decline. However, this effect was not observed with  $\gamma$ -MnO<sub>2</sub> preparations which were subjected to identical treatment or with the mixed  $\alpha$  and  $\gamma$  phases produced in Preparations 1 and 2. Also, all the cells were left for twelve hours before measurements were taken and it would be expected that the electrode had by then settled down. It is concluded that some spontaneous reaction is occurring between the electrode and the electrolyte. In view of the inability to obtain e.m.f. readings for the same preparations in solutions of low acid concentration it seems likely that this reaction involves the hydrochloric acid.

Reference was made in an earlier paper (Butler and Thirsk, *J. Electrochem. Soc.*, 1953, 100, 297), to the possible existence of lower oxides, particularly MnO, as surface layers in the majority of preparations involving precipitation from solution. With  $\delta$ -MnO<sub>2</sub> electron diffraction revealed only the presence of MnO and Mn<sub>3</sub>O<sub>4</sub> and it is these oxides which show the most rapid fall in e.m.f. with time. An explanation of the decreasing e.m.f. is therefore that it is due to the dissolution of a lower oxide in the acid electrolyte. This would produce an increase in the concentration of manganous chloride and an accompanying decrease in the hydrochloric acid. As the change in e.m.f. with concentration is governed by the ratio of the activities of manganous chloride and hydrochloric acid the relative effect of these interdependent concentration changes would be large. The idea also accounts successfully for the e.m.f.'s returning to its original value on renewal of the electrolyte and provides further evidence for the existence of lower surface oxides, in particular in the cases where they had been observed by electron diffraction.

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