Structural Properties and the Relative Electrode Potentials of Synthetic Manganese Dioxides. Part I. The E.M.F. of the Cell $Pt–H_2|HCl,MnCl_2|\beta\text{-}MnO_2–Pt$.

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In order to compare the relative electrode potentials of the synthetic manganese dioxides the standard electrode potential of the system shown in the Title has been redetermined by use of the cell

$Pt–Ag,AgCl|HCl,MnCl_2|\beta\text{-}MnO_2–Pt$

A figure of 1·220 v has been selected, and is employed to calculate the activity function of the electrolyte solutions used in the determination of the relative electrode potentials of the different oxides.

IN the investigation of an electrode system it is important to ascertain the cell reaction; materials for which thermochemical data are available must be used and the calculated and experimental e.m.f. compared. The only suitable form of manganese dioxide is $\beta\text{-}MnO_2$ (pyrolusite); this oxide has been selected by the Bureau of Standards ("Selected Values of Thermodynamic Properties," New York, 1947). We propose to relate the e.m.f.'s of cells containing the disperse forms of manganese dioxide to that of a similar cell containing $\beta\text{-}MnO_2$. The present paper is concerned with experiments designed to establish a reference value for the standard electrode potential of the electrode $\beta\text{-}MnO_2|Mn^{++},H^+$ and to provide activity data for the calculation of the relative electrode potentials of the α-, δ-, and γ-oxides.

Four attempts have previously been made to determine the standard electrode potential of $\beta\text{-}MnO_2$ in acid solution. Brown and Liebhafsky (*J. Amer. Chem. Soc.*, 1930, **52**, 2545) used the cell system $Pt–H_2|Mn(ClO_4)_2,HClO_4|\beta\text{-}MnO_2–Pt$, and obtained potential differences steady to ±1 mv, and, by estimating the values of the activity coefficients from data for similar salts arrived at a value for $E°$ for the $\beta\text{-}MnO_2$ electrode relative to hydrogen of 1·236 v at 25°. (Unless otherwise stated $E°$ will have this significance in this and the following paper.)

Popoff, Riddick, and Becker (*J. Amer. Chem. Soc.*, 1930, **52**, 2624) employed the same system, but were unable to obtain steady potential differences and concluded that the electrode was irreversible. Hutchinson (*J. Amer. Chem. Soc.*, 1947, **69**, 3051) found the same erratic behaviour when the platinum foil contact was only partly immersed in the oxide. However, when the foil was completely covered by the oxide slurry he observed reasonably steady potential differences and from his results derived $E^\circ = +1{\cdot}230$ v. Wadsley and Walkley (*J. Electrochem. Soc.*, 1949, **95**, 11), using the cell system Pt–Ag,AgCl|$MnCl_2$,HCl|β-MnO_2–Pt, were unable to obtain steady readings in solutions more dilute than 0·1 m, with the conventional type of oxide electrode. With a much smaller electrode with the MnO_2 formed on a platinum spiral, only one electrode out of several behaved satisfactorily.

The differences in the reported values for E° probably arise from two main causes: small differences in the preparative methods and differing methods of estimating the activity coefficients. The first may give rise to small and variable amounts of impurities in the manganese dioxide lattice affecting the e.m.f. of the cells. With regard to the second, if Brown and Liebhafsky's results are combined with the activity coefficients taken by Hutchinson, the derived value of E° is increased to 1·241 v. Thus it would appear that the main cause of the discrepancies is the method of preparation.

Our procedure, which the foregoing results suggested, was to prepare β-MnO_2 by a standardised method and to try to obtain steady potential differences down to a concentration as small as possible in order to make a graphical extrapolation. The cell system employed was that used by Wadsley and Walkley (*loc. cit.*) and the solutions were made equimolal in manganese chloride and hydrochloric acid. By assuming the cell reaction

$$2Ag + MnO_2 + 4HCl = MnCl_2 + 2H_2O + 2AgCl \quad . \quad . \quad . \quad . \quad (1)$$

and neglecting the very small contributions due to the activity of water, the reversible e.m.f. is given by

$$\begin{aligned} E &= E^\circ_c - (\boldsymbol{R}T/2\boldsymbol{F})[\ln (a_s/a_a{}^4)] \\ &= E^\circ_c - (\boldsymbol{R}T/2\boldsymbol{F})[\ln (m_{\pm s}{}^3/m_{\pm a})] \end{aligned}$$

For equimolal solutions $\quad m_{\pm s}{}^3 = 9m^3;\ m_{\pm a}{}^8 = 81m^8$

By substitution and rearrangement

$$E - 2{\cdot}303\boldsymbol{R}T/2\boldsymbol{F}(\log 9m^5) = E^\circ_c - 2{\cdot}303\boldsymbol{R}T/2\boldsymbol{F}[\log (\gamma_{\pm s}{}^3/\gamma_{\pm a}{}^8)]$$

where the subscripts a and s refer respectively to HCl and $MnCl_2$, and E°_c is the standard potential of β-MnO_2 with respect to the silver–silver chloride electrode.

A plot of the left-hand side against a suitable function of the ionic strength will yield E°_c when extrapolated to zero molality. E° can then be readily calculated from the value of the standard electrode potential of the silver–silver chloride electrode, —0·2225 v at 25° (Harned and Ehlers, *J. Amer. Chem. Soc.*, 1932, **54**, 1350).

EXPERIMENTAL

Preparation of β-MnO_2.—Electrolytic manganese (100 g.) (Prep. of samples A, B, and C) or the equivalent amount of manganese carbonate (Prep. of samples D and E) were dissolved in the minimum amount of concentrated nitric acid. The solution was filtered while hot and allowed to cool. The resulting crystals of manganese nitrate were recrystallised three times from a small amount of water. The purified solid was decomposed at 130—140°, in a stream of air to remove oxides of nitrogen and water vapour. When decomposition was nearly complete, the whole was poured into water and stirred, and the solution filtered. The dioxide was dried in air at 120°, ground in an agate mortar, and boiled with 1 : 1 nitric acid and then with water. It was next dried in air at 160°, ground again, and finally heated to 400° in a slow stream of oxygen. The product was a dense, dark grey powder. Analysis showed it to be stoicheiometric MnO_2 and the *X*-ray diffraction pattern agreed in detail with that published in the A.S.T.M. index.

Silver–silver chloride electrodes were prepared by Brown's method (*J. Amer. Chem. Soc.*, 1934, **56**, 646). The cell was of the convential H type, one limb of which contained the silver–silver chloride electrode, and the other the MnO_2 powder completely covering a small piece of foil sealed into a soft glass tube, which gave electrical contact.

Manganese chloride ("AnalaR" grade) was twice recrystallised from water. A stock solution in distilled water was prepared and analysed and all solutions were made by dilution. Constant-boiling hydrochloric acid was prepared by Foulk and Hollingsworth's method (*J. Amer.*

Chem. Soc., 1923, **45**, 122) and from this a stock 0·2m-solution was made up and used for the preparation of the electrolyte.

All measurements were made at 25° with a potentiometer accurate to 0·1 mv. Altogether, seven solutions were employed, the molalities of each component being 0·1, 0·05, 0·02, 0·01, 0·005, 0·002, 0·001, and all solutions were equimolal in manganous chloride and hydrochloric acid.

The oxide was ground well with the electrolyte and soaked for several days. The cell was set up with fresh electrolyte and measurements were made for two days; the electrolyte was then renewed and readings taken for a further two days. The potential differences remained steady over the final 24 hr. and are the values recorded in the Table. When changing to a fresh electrolyte concentration the previous solution was decanted and the oxide ground with the new solution, allowed to settle, and decanted again. This was repeated three times for each change of electrolyte. The final values for the e.m.f. were those recorded after the second sample of electrolyte had been introduced. In all cases the final equilibrium value remained constant to 0·1 mv during 24 hr. except for the two most dilute solutions where fluctuations of the order ±0·3 mv were observed.

	E.M.F. in volts				
Molality (m)	A	B	C	D	E
0·1	0·8792	0·8799	0·8812	0·8906	0·8871
0·05	0·8343	0·8348	0·8361	0·8458	0·8419
0·02	0·7757	0·7762	0·7777	0·7876	0·7838
0·01	0·7311	0·7310	0·7325	0·7425	0·7372
0·005	0·6850	0·6849	0·6860	0·6962	0·6902
0·002	0·6254	0·6257	0·5274	0·6369	0·6314
0·001	0·5812	0·5815	0·5832	0·5928	0·5861

The e.m.f.'s were extrapolated by Hitchcock's method (*J. Amer. Chem. Soc.*, 1928, **50**, 2076, according to eqn. 2). The extrapolations yielded the following values for the standard electrode potential when converted from the silver–silver chloride scale to the hydrogen scale: A, $1{\cdot}220_2$; B, $1{\cdot}220_7$; C, $1{\cdot}222_2$; D, $1{\cdot}231_6$; E, $1{\cdot}226_0$.

DISCUSSION

Striking features of the results are the widely differing values found for the five samples and the constancy with which the differences are maintained in all the solutions. Preparations A and B gave an e.m.f. within 1 mv of one another at all concentrations, although the magnitude of the difference varies somewhat. The e.m.f. of the cell containing oxide C was about 2 mv greater than the cell with oxide A, while preparations D and E were about 12 and 6 mv respectively greater. In view of the close agreement between samples A and B and because these are also the lowest values we have tentatively taken the value E° to be ±1·220 v as the standard electrode potential of β-MnO_2 in acid solution. According to Wadsley and Walkley (*loc. cit.*) a calculation of the e.m.f. of the cell used led to a figure of 1·229 v. This calculation assumed the values for the entropy and heat of formation of manganese dioxide determined by Kelley and Moore (*J. Amer. Chem. Soc.*, 1943, **65**, 782) and Shomate (*ibid.*, p. 785) and the free energy of formation of the manganous ion from the heat of dilution of hydrochloric acid and the free energies of the chloride ion and water from the National Bureau of Standards "Tables of Selected Values of Thermodynamic Properties" (Nat. Bur. Stand., Washington, 1947).

It is considered that our value of 1·220 v, together with the reproducibility of the individual measurements, is sufficient justification for assuming the reversible reaction for the behaviour of the MnO_2 electrode in the cell we have selected for the comparison of the e.m.f.'s of the various oxides to be that written in eqn. 1. In Part II (following paper) we have related the relative electrode potentials of the disperse forms of manganese dioxide to this value and used it to calculate the activity function of the electrolyte solutions employed. This is a somewhat arbitrary procedure as it assumes that the samples A and B represent the oxide in its most stable form. Any absolute error for the derived values of E° for the disperse oxides can be ascribed to this choice; the relative values will be unaffected.

The differing results for β-MnO_2 have not been explained. Analysis showed them all to be stoicheiometric MnO_2 within the accuracy of the analytical method and all the *X*-ray diffraction patterns were identical. The differences might be due to very small traces of other elements incorporated in the lattice during preparation and thus modifying the free energy of formation. Spectrographic analysis detected very small traces of iron in all the oxides. Since the limit of the sensitivity of this method can be about 5 p.p.m., we estimate that the amount of iron in these oxides cannot be much greater than *ca.* 10 p.p.m. and is certainly less than 100 p.p.m. No estimate of the relative amounts of the impurity in each oxide could be made, although the lines of the iron spectrum seemed to be weaker in samples A, B, and C than in the others. The widely differing results obtained by other workers may be caused by the presence of varying traces of impurity undetected by ordinary analytical methods and, to a greater or less degree, of strain in the oxide according to the method of preparation.

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