Standard Potential of the β-Manganese Dioxide Electrode

BY A. K. COVINGTON, T. CRESSEY, B. G. LEVER AND H. R. THIRSK
Chemistry Dept., King's College, University of Durham, Newcastle-upon-Tyne

Received 2nd April, 1962

Difficulties in obtaining steady potentials with the β-MnO_2 electrode in cells containing equimolal concentrations of hydrogen and manganous ions have been shown to be due to an ion exchange between the oxide and the electrolyte. β-MnO_2 prepared by thermal decomposition of manganous nitrate and normally considered stoichiometric was found to take up ~0·1 mmole H^+/g but less if the oxide had been heated in oxygen at 400°. Lengthy pre-treatment of the oxide with the cell electrolyte is necessary to bring the exchange to equilibrium before commencing cell measurements. Dilution of the electrolyte in order to evaluate the standard potential by the customary extrapolation procedures may disturb the equilibrium and again lead to drifting potentials.

Cells containing acetate buffers have been shown to be more suitable and gave standard potentials between 1·233 and 1·241 V depending on the oxide sample. For cells in which pMn as well as pH was kept approximately constant, the application of the Guggenheim theory of mixtures of electrolytes permitted the evaluation of the standard potential which agreed with that from cells with the pH only constant. The technique has application to other oxide systems.

Various forms of manganese dioxide have been characterized mainly by X-ray diffraction, e.g., β-MnO_2 with the same crystal structure as the mineral pyrolusite and the only stoichiometric form, γ-MnO_2 a form with a more open structure and usually less crystalline, and various other disperse forms (α, δ and others) containing foreign cations.[1]

The importance of manganese dioxide as the depolarizer in the Leclanché dry cell has resulted in many electrochemical investigations [2] of the properties of the γ form prepared by electrolytic deposition, one of the first of these being by Tower [3] who proposed the electrode reaction

$$MnO_2 + 4H^+ + 2e \rightarrow Mn^{2+} + 2H_2O \qquad (1)$$

in acid solution. In common with most later investigators he found the e.m.f. of his cells drifted with time. Although less efficient as a depolarizer than the γ-form, the β-form has been studied by several workers [4-8] who have attempted to determine its standard potential. The system is described as largely unsatisfactory [9] and Latimer comments [10] that the difficulty is not the irreversibility of the electrode but the variation in the properties of the oxide even when prepared under very similar conditions.

Points of interest from previous investigations on cells without liquid junction with the β-MnO_2 electrode in acid solution are summarized in table 1. These investigations were carried out either with the cell

$$\mathrm{Pt,H_2 \mid HClO_4,Mn(ClO_4)_2 \mid \beta\text{-}MnO_2,Pt,} \qquad \mathrm{(I)}$$

or

$$\mathrm{Ag \mid AgCl \mid HCl,MnCl_2 \mid \beta\text{-}MnO_2,Pt.} \qquad \mathrm{(II)}$$

It is uncertain whether the hydrogen electrode is reliable in perchloric acid solutions [11] so results from cell I may be suspect and Brown and Liebhafsky [4] found themselves limited to solutions $<0{\cdot}05$ m as below this the e.m.f. fluctuated and a dark deposit appeared on the platinized platinum electrode. All investigators used oxide prepared by the thermal decomposition of the nitrate according to the method of Bhatnagar,[12] except where otherwise stated. Any additional treatment of the oxide is summarized in table 1. All electrodes consisted of a platinum contact to an oxide slurry except for the dip-type electrodes of Wadsley and Walkley.[7]

TABLE 1

workers	cell	E°(V)	oxide	notes
Brown and Liebhafsky [4]	I	1·235-1·237	99 % pure	essential to pretreat oxide with electrolyte for 3 h. E.m.f. constant to 2 mV with no great fluctuations; final reading taken after a few days.
Popoff, Riddick and Becker [5]	I	—	stoichiometric 0·41 % water	e.m.f. not stable even after 9 days.
			97·8 % pure	e.m.f. steady after 2 days. no pretreatment of oxide, platinum contacts only partly covered. Oxides from same preparation but stoichiometric form obtained by successive grinding with nitric acid, water and heating.
Hutchison [6]	I	1·230	$MnO_{1\cdot997}$, 0·25 % water	oxide pretreated 8-10 h in electrolyte. E.m.f. stable only if platinum contacts completely immersed in slurry.
Wadsley and Walkley [7]	II	1·240	$MnO_{2\cdot00}$, 0·1 % water heated in oxygen	e.m.f. in 0·1 equimolal HCl+ $MnCl_2$ constant to 2-3 mV for several days but on dilution became unsteady, impossible to derive E° by extrapolation, estimated from activity coefficients of solution.
		1·20-1·24	pyrolusites, $MnO_{1\cdot98\text{-}2\cdot00}$	E° decreases with increasing non-stoichiometry.
		1·253-1·256	formed by dipping Pt spiral in $Mn(NO_3)_2$ and heating in oxygen at 500°C	two electrodes from a number gave e.m.f. stable to 1-2 mV after a few minutes.
Maxwell and Thirsk [8]	II	1·220-1·231	stoichiometric, nitric acid treatment, heated in oxygen at 400°	oxide pretreated 2-3 days in 0·1 equimolal HCl-$MnCl_2$. E.m.f. steady to 0·1 mV for 24 h after renewal of electrolyte. Solutions successively diluted (to 0·001). Oxide ground 3 times with each new concentration before making up cell. E° varied with starting material of preparation.

The spread in the values of the standard potential is outside that expected from differences in the extrapolation techniques employed. Although the standard potentials quoted by Brown and Liebhafsky [4] and Hutchison [6] differ by only 6 mV, there are discrepancies of up to 20 mV between these workers for e.m.f. measurements in solutions of the same concentration. The pretreatment of the oxide with electrolyte appears to be essential for obtaining steady potentials but no attempt has been made to explain its function. Other important factors appear to be heating the oxide in oxygen and complete immersion of the platinum contact in the oxide slurry.

EXPERIMENTAL

The method of preparing manganese dioxide was that found by previous workers [12, 13] to give stoichiometric samples. Manganese metal was supplied by Blackwells Metallurgical Works, New Metals and Chemicals Ltd., and Johnson Matthey & Co. Ltd. (Specpure grade) (these materials will be referred to as 1 to 3, different preparations from the same starting material will be referred to as, e.g., 1.1, 1.2, etc.).

The metal was dissolved in the minimum quantity of A.R. conc. HNO_3, the solution was filtered hot and the manganous nitrate was recrystallized twice from triple-distilled water. The crystals were decomposed by heating at 145-160° in a stream of air or oxygen to remove oxides of nitrogen and water vapour. When decomposition was almost complete the mass was poured into excess hot water, stirred and filtered off. The oxide was dried at 110°, ground in an agate mortar, boiled with 1 : 1 nitric acid and then water and finally re-dried at 110-120°. Some samples (hereafter indicated by a dash, e.g., 1.6′) were heated in a slow stream of oxygen in an electric furnace at 400° for various periods of time. This procedure was introduced by Kelley and Moore [14] to remove water, the role of oxygen being, they considered, to prevent loss of oxygen.

β-MnO_2 was analyzed for manganese by potentiometric titration of the trivalent pyrophosphate complex in neutral solution,[15] and for available oxygen (oxygen in excess of MnO) by decomposition with conc. HCl and estimation of the liberated chlorine by the iodide-thiosulphate method. The stoichiometry was calculated from the total manganese and the available oxygen, the residue being assumed to be water (table 2). In order to determine small deviations of the oxide from stoichiometry, high accuracy and reliability is required in the analysis. Considerable effort was devoted to trying to improve the accuracy of the available oxygen determination.[16, 17] An all-glass apparatus with the minimum of ground joints was used, incorporating a water-cooled reflux condenser to prevent the acid from distilling over with the risk of the liberation of I_2 from KI by atmospheric oxidation during subsequent titration. The chlorine was swept over in a stream of nitrogen. The oxide was contained in a small glass capsule which floated on the HCl while the apparatus was being assembled. Redistilled HCl was used as a precaution following the findings of Butler and Copp.[18] The usual tap funnel was dispensed with. The reproducibility obtained (0·2 %), was within the accuracy expected in the titration, indicating no loss of chlorine.

TABLE 2

preparation	x in MnO_x	% water (by difference)	H^+ ion uptake mmole H^+/g	$E°$(V)
1·3	1·994, 1·996	1·0	0·05,[c] 0·1 [a]	—
1·3′	1·999, 2·000	0·7	0·114 [b]	1·241
1·4	1·994, 1·995	1·1	—	—
1·4′	1·997, 1·998, 2·000	0·7	0·09 [b]	1·238
1·5′	1·996, 1·999, 2·001	0·8	0·09 [b]	1·236
1·6′	2·000	0·8	0·08 [b]	1·237
1·7	1·995	1·3	0·05 [d]	—

(*a*) 4 months standing in 0·1 N HNO_3 or H_2SO_4, intermittent shaking; (*b*) 3 months standing in 0·1 M HCl, intermittent shaking; (*c*) 200 h continuous shaking; (*d*) 400 h continuous shaking.

The ferrous sulphate, oxalic acid and arsenious oxide methods were found unsuitable because of high blank determinations and the long times (1-2 h) required to dissolve the oxide.

The form of electrode compartment used for the β-MnO$_2$ electrodes is shown in fig. 1. The oxide was retained on the top of a porosity 4 or 5 sintered-glass disc which permitted flushing of the oxide with electrolyte under suction, while compacting the oxide well around the platinum foil or spiral electrode. The electrode vessel consisted of six limbs to contain the MnO$_2$ electrode compartments separated by a tap from one or two further compartments which contained electrolytic silver + silver chloride electrodes prepared on platinum grids according to the directions of Brown.[19]

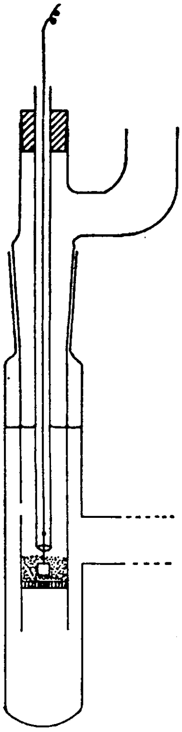


FIG. 1.—Oxide electrode compartment.

E.m.f. measurements were made with a Tinsley type 3126B or Pye vernier potentiometer in an air thermostat controlled at 25·0 ± 0·1° or a water thermostat controlled at 25·00 ± 0·05°. Hydrochloric acid solutions were prepared from constant boiling acid.[20] A.R. manganous chloride was twice recrystallized from triple-distilled water which was used for the preparation of all solutions. Manganous acetate (B.D.H. Ltd.) was twice recrystallized from water acidified with acetic acid. Solutions were analyzed for manganese by the method described above[15] or by E.D.T.A. titration using Erio T indicator,[21] for chloride by Volhard's method, and for hydrogen ion with caustic soda or borax.

RESULTS

CELLS INVOLVING HCl, MnCl$_2$ ELECTROLYTE

Attempts to confirm the work of Maxwell and Thirsk[8] using cell II proved unsuccessful. Oxide samples 1.1 and 2.1, which analyzed MnO$_{1\cdot 99}$-MnO$_{2\cdot 00}$ with up to 3 % water, were ground in an agate mortar with 0·1 m HCl + 0·1 m MnCl$_2$. Each was allowed to stand 24 h in the same electrolyte, which was then renewed several times by decanting before the electrodes were made up (fig. 1). The two preparations differed in potential by 11 mV. Electrodes prepared at the same time from these preparations which had been in addition heated in oxygen for 3 h (1.1′ and 1.2′) were 1-3 mV lower than their counterparts. In this and several other similar experiments, there was no sign of steady potentials being reached in 1200 h.

In Maxwell and Thirsk's technique[8] the oxide was ground further each time it was introduced to a solution of a new concentration. Electrodes were prepared from preparations 1.1 and 2.1 which had been ground and separated into fractions >53 μ, 53-44 μ, <44 μ with phosphor-bronze mesh sieves. Each fraction was pretreated by standing with the electrolyte for 48 h. The coarse fraction gave erratic and the highest potentials, and the fine fraction potentials were a few mV higher than the intermediate fraction. It was concluded that grinding of the oxide between changes of solution concentration should be avoided. All subsequent experiments were performed with the <44 μ fraction, and later nylon sieves were used to avoid risk of contamination.

It seemed that failure to reproduce the steady potentials found by Maxwell and Thirsk[8] might lie in insufficient pretreatment. Increasing the temperature and the time of pretreatment (8 h at 100°, and 48 h at 18°) lowered the potential of each preparation, but the potentials now remained constant to ±2 mV for several days. On replacing the electrolyte the potential although steady, was lower, but on dilution of the electrolyte, the electrodes showed no signs of reaching steady values. Throughout these measurements any slight disturbance of the platinum contact resulted in changes of several mV.

Analysis of the solution after prolonged digestion of oxide with the mixed electrolyte at 100°, showed that 2 % of the oxide had apparently dissolved, and considerable dissolution was also found to have taken place in 0·1 m HCl + 0·1 m MnCl$_2$ mixture at 25° and in 0·1 m HCl. Wadsley and Walkley[7] detected by electron diffraction a change in the surface structure of the oxide after treatment in the mixed electrolyte. The pattern was similar to α-FeOOH which suggested that it was due to MnOOH, and they proposed the reaction

$$MnO_2 + Mn^{2+} + 2H_2O \rightarrow 2\,MnOOH + 2H^+. \qquad (2)$$

A much less marked change in surface structure was found in 0·1 m HCl. Their explanation cannot be correct, for, although the mole ratio of hydrogen ion to manganous ion involved was 2 : 1, the reaction consumed hydrogen ions. Also the oxide was stoichiometric before and after the digestion; any lower-valent manganese compound involved in a reaction such as (2), when 2 % of the oxide apparently dissolved, would have been easily detectable. Any chemical reaction occurring prevents attainment of a steady potential with cells I or II. The change in concentration of the electrolyte depends on the relative amounts of oxide and solution in the electrode compartment which would have been different for the various workers and could account for their different results. However, the explanation in terms of a chemical dissolution of the oxide is inconsistent with the fact that prolonged pretreatment does lead to steadier potentials and thus presumably to the establishing of some equilibrium.

It is well known that the non-stoichiometric forms of MnO_2 can also release hydrogen ions [22-24] giving an acid reaction. This fact, with the evidence above, suggests that MnO_2 can act as a cation exchanger, and attention has been re-directed to these ion exchange properties of oxides recently.[25, 26] The ion exchange character of manganites was pointed out by Jordan,[27] and that of γ-MnO_2 by Johnson and Vosburgh [22] and Kozawa.[24] Radioactive-tracer techniques [28, 29] have been used to show there is a small surface exchange between MnO_2 and Mn^{2+} ions in solution. Kozawa [24] found that β-MnO_2 exchanged 10^{-2} m moles Zn^{2+}/g for H^+ at pH 6, about 50 times less than γ-MnO_2, and Buser and Graf [30] found radiochemically $1{\cdot}2 \times 10^{-2}$ m moles Mn^{2+}/g with β-$MnO_{1{\cdot}92}$, prepared by oxidation of manganous nitrate with ammonium persulphate followed by heating at 400°. These amounts are so small in comparison with those of other forms of the oxide and the manganites that the possible cation exchange character of β-MnO_2 appears to have been overlooked, most workers having regarded the release or adsorption of ions as the formation or removal of surface lower oxide.

EXPERIMENTS TO CONFIRM THE CATION EXCHANGE CHARACTER OF β-MnO_2

Samples were treated with solutions (up to 0·1 N) of HCl, HNO_3 and H_2SO_4 with intermittent shaking for various lengths of time, and the supernatant liquid sampled for analysis. The mole ratio of manganous ion released to hydrogen ion adsorbed was always 1 : 2 within the analytical accuracy (which was ~10 % for samples of low exchange where the value for H^+ was obtained from the difference between two nearly equal titres). The uptake of H^+ varied from 0·05 to 0·2 mmole/g MnO_2 (taking this as a measure of the Mn^{II} in the oxide, then these correspond to $MnO_{1{\cdot}992}$-$MnO_{1{\cdot}997}$), depending upon the sample, the particle size, the time of contact, the amount and vigour of the shaking and to a small extent upon the acid used. The reaction was at first rapid followed by a slow uptake of H^+ which was still (except in sulphuric acid) continuing after 400 h. At 100° the uptake increased by about a factor of 4.

The reversibility of the exchange was demonstrated by placing samples from preparation 1.1, which had been treated in 0·1 M HCl (giving 0·12 mmole H^+/g MnO_2 adsorbed after 20 h vigorous mechanical shaking) in an ethanolamine buffer of pH 8·7 (0·2 M ethanolamine, 0·1 M HCl, 0·05 M NaCl) when, after 140 h continuous shaking, the release of H^+ was 4×10^{-2} mmole/g MnO_2.

The effect of heating a sample in oxygen at 400° for 48 h was to lower the H^+ uptake from 0·12 to 0·05 mmole/g MnO_2, increase the available oxygen content, and decrease the water content. Some analysis figures are given in table 2.

Titration curves were determined by the standard method for cation exchangers.[31, 25] 0·5 g samples of oxide were shaken intermittently for periods up to 8 weeks with solutions of HCl (0-0·1 mmole H^+/50 ml) and NaCl to make the solution 0·1 M in chloride. The pH of the solution after centrifuging was measured with a Marconi TF717A pH meter.

Some results are shown in fig. 2. No change in anion concentration was detected analytically. The curves show that β-MnO$_2$ probably has two functional acidic groupings with pK's of about 3·8 and 5·2 but the inflections in the curves are not particularly distinct. Fig. 2 demonstrates the increase of uptake with increased time of contact with the solution. The rate-of-exchange measurements suggest that the initial rapid uptake of protons occurs at the surface and is followed by a much slower uptake by diffusion into the bulk of the oxide. The B.E.T. surface area, using nitrogen, of samples was $<0{\cdot}1$ m^2 g^{-1}. No difference in surface area could be detected between samples heated in oxygen and untreated samples although the latter did tend to show a greater adsorption with CO$_2$.

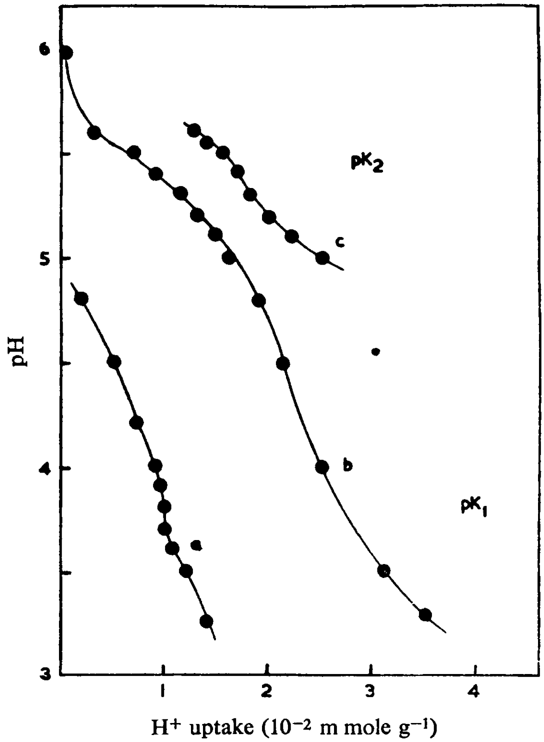


FIG. 2.—Titration curves.

(*a*) preparation 1·7, 8 weeks' shaking; (*b*) preparation 1·3, 2 weeks' shaking; (*c*) as (*b*), but 8 weeks' shaking.

The ion-exchange between β-MnO$_2$ and the cell electrolyte must be brought to equilibrium to obtain steady potentials from the electrode. The pretreatment of oxide with cell electrolyte is thus an attempt to reach ion-exchange equilibrium. However, this equilibrium will be disturbed when the cell electrolyte is diluted to obtain a series of e.m.f. values for extrapolation to the standard potential. It would be feasible to proceed in this way bringing the exchange to equilibrium each time in each solution as Maxwell and Thirsk [8] attempted to do, provided the potential of the electrode is not a function of the position of the exchange equilibrium, i.e., of the ratio of Mn^{2+} to H$^+$ ions on its surface.

CELLS INVOLVING BUFFERED ELECTROLYTES

The buffered cell of Harned and Ehlers,[32] gives the pK of a weak acid from the known standard e.m.f.; however, the procedure may be reversed.[33, 34] The use of a buffer solution as cell electrolyte offers advantages. Any small amount of ion exchange taking place after the pretreatment of the oxide in the solution will not affect the hydrogen ion concentration and the change in the manganous ion concentration will, from eqn. (1), have an effect on the e.m.f. four times smaller than a change in hydrogen ion concentration. On dilution of the electrolyte, the pH change should be small and ion exchange equilibrium on the oxide surface should be maintained.

The cell chosen which contains the cations Mn^{2+} and H^+ only was

$$\text{Ag} \mid \text{AgCl} \mid \text{HAc}(m_1),\text{MnAc}_2(m_2),\text{MnCl}_2(m_3) \mid \beta\text{-MnO}_2,\text{Pt} \qquad \text{(III)}$$

where Ac = acetate.

The results for a solution with $m_1 = m_2 = 0{\cdot}1$ m, $m_3 = 0{\cdot}001$ m (pH = 4·84) in which various oxide samples had been pretreated for 24 h are shown in fig. 3. A preparation which had been heated in oxygen for 3 h (1.1′), gave duplicate electrodes agreeing closely and remaining constant to 0·5 mV even on renewing the electrolyte. The potential of preparation 1.1 before heat treatment was 20 mV higher but less steady. A sample of preparation 1.1 converted to the acid form by treatment in HCl, $MnCl_2$ mixture showed a fall in potential of ~ 14 mV in 100 h. Its fall was uninterrupted by changing the cell electrolyte, indicating that the fall was due to surface changes in the oxide rather than concentration potentials in the solution.

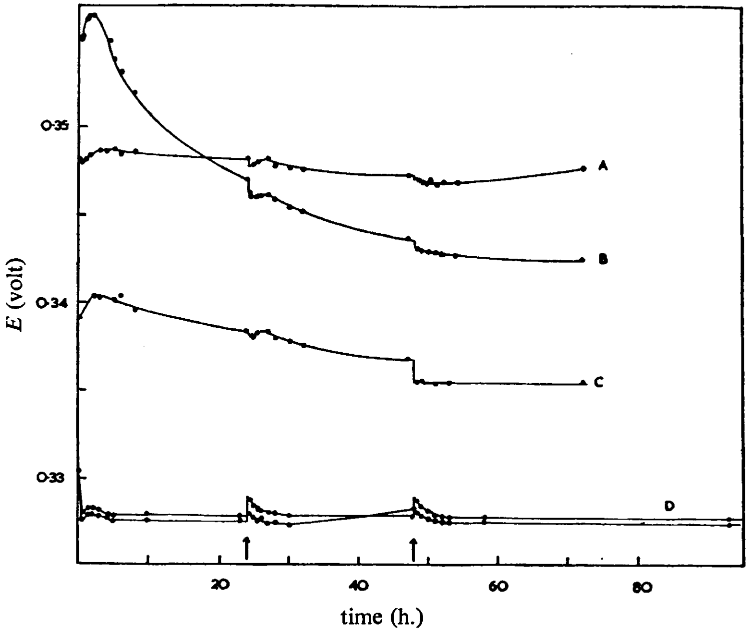


FIG. 3.—↑ indicates electrolyte renewed.

A, preparation 1.2; B, preparation 1.2 converted to acid form; C, preparation 3.1; D, preparation 1.2′.

Since oxygen heat-treated samples gave steadier potentials, probably due to their lower exchange capacities, these were used in all further studies. Solutions with $m_2 = 0{\cdot}04$ to 0·005 were prepared by dilution of a stock solution in which $\frac{1}{2}m_1 = m_2 = m_3$. Each oxide sample was pretreated with the most concentrated solution. Two electrodes were prepared from each sample, and measurements were taken in successively diluted solutions. In the concentrated solutions, electrodes reached 1 mV of their final values within a few hours but in the dilute solutions slow changes of potential continued for several days. Potentials of duplicate electrodes usually agreed to ±0·2 mV. Some oxide samples after

24 h pretreatment in a dilute solution were taken through an increasing range of concentration but values in the same solution obtained from the decreasing and increasing series sometimes differed by 2-3 mV.

These findings were confirmed in a second series of measurements in which a slightly different ratio of electrolyte concentrations (0·348 $m_1 = m_2 =$ 0·690 m_3) was employed to give a lower pH (the measured pH varied 0·3 unit on tenfold dilution). The oxide samples were treated for a week in the most concentrated electrolyte for the decreasing series or most dilute electrolyte for the increasing series. Some results are shown in table 3.

TABLE 3

preparation m_2	decreasing m_2				increasing m_2				
	1·3′	1·4′	1·5′	1·6′	1·3′	1·4′	1·5′	1·6′	pH
0·0309$_1$	480·0	477·1	475·4	477·2	478·1	475·1	474·3	475·1	4·32
0·0309$_1$ [a]	477·4	475·3	474·2	475·5					
0·0246$_9$	473·5	471·0	469·1	470·7	472·6	469·8	468·6	469·1	—
0·0219$_2$	469·5	467·0	465·4	467·0	469·8	467·1	465·6	466·5	4·40
0·0141$_8$	458·9	456·1	454·9	456·0	460·1	457·3	455·4	456·1	4·45
0·00665	441·4	439·1	437·1	438·5	443·3	439·7	437·9	439·0	4·51
0·00393$_9$	430·2	427·9	425·5	427·7	432·7	430·0	425·3	427·9	4·57
0·00393$_9$ [b]					429·3	425·8	424·5	425·5	

(*a*) following decreasing series; (*b*) following increasing series.

In this second series, the electrodes which had been prepared from oxides showed a lower uptake of hydrogen ions than most of those used in the first series, and were not susceptible to potential variation on moving the platinum contact as were those in the first series. Some of the variation between electrodes could result from the platinum contacts used, as with the PbO$_2$ system.[35] In one cell the platinum contacts were removed, cleaned in boiling aqua regia and replaced in a different slurry. The electrolyte was renewed in the oxide compartment to recompact the oxide around the contact and potential measurements were continued. It was concluded that the effect of the platinum contact was small as the potential changes were the same (0·5 mV) as produced by flushing the oxide with fresh electrolyte. Electrodes in which the oxide slurry completely covered the platinum contact gave more stable potentials than those where some platinum was exposed, in confirmation of previous findings.[6]

Assuming the electrode reaction is that given in eqn. (1) then the e.m.f. of cell III is given by

$$E = E^\circ - \frac{1}{2}k \log \frac{a_{\mathrm{Mn}^{2+}} a^2_{\mathrm{H_2O}}}{a^4_{\mathrm{H}^+} a^2_{\mathrm{Cl}^-}}$$

where $k = (RT/F) \ln 10$.

Introducing $K = a_{\mathrm{H}^+} a_{\mathrm{Ac}^-}/a_{\mathrm{HAc}}$ then

$$E = E^\circ - \frac{1}{2}k \log \frac{a_{\mathrm{Mn}^{2+}} a^4_{\mathrm{Ac}^-} a^2_{\mathrm{H_2O}}}{a^4_{\mathrm{HAc}} a^2_{\mathrm{Cl}^-}} + 2\,k \log k.$$

Assuming that the salts are completely dissociated, then

$$E = E^\circ - \frac{1}{2}k \log \frac{(m_2+m_3)(2m_2+m_{\mathrm{H}^+})^4 a^2_{\mathrm{H_2O}}}{(m_1-m_{\mathrm{H}^+})^4(2m_3)^2} - \frac{1}{2}k \log \frac{\gamma_{\mathrm{Mn}^{2+}}\gamma^4_{\mathrm{Ac}^-}}{\gamma^4_{\mathrm{HAc}}\gamma^2_{\mathrm{Cl}^-}} + 2k \log K. \qquad (3)$$

Neglecting $m_{\mathrm{H}^+}(\simeq 10^{-5})$, putting γ_{HAc} and $a_{\mathrm{H_2O}}$ equal to unity and $\frac{1}{2}m_1 = m_2 = m_3$, then simplifying gives

$$E = E^\circ + 2k \log 2m_2 - \frac{1}{2}k \log \frac{\gamma^6_{\mathrm{MnAc_2}}}{\gamma^3_{\mathrm{MnCl_2}}} + 2k \log K.$$

If the activity coefficients are expressed by the equation

$$\log \gamma_{\pm} = -\frac{2AI^{\frac{1}{2}}}{1+1{\cdot}56I^{\frac{1}{2}}}+BI,$$

where the numerical value in the denominator corresponds to a distance of closest approach of the ions of 4·7 Å which has been shown to be appropriate for 2 : 1 electrolytes,[36] then a plot of $E^{\circ\prime}$, where

$$E^{\circ\prime} \equiv E - \tfrac{1}{2}\,k \log 2m_2 - 3k\frac{AI^{\frac{1}{2}}}{1+1{\cdot}56I^{\frac{1}{2}}} - 2k \log K$$

against m_2 (since $I = 6m_2$) should give a straight line from which the standard e.m.f. of the cell can be evaluated. A plot of $E^{\circ\prime} + E^{\circ}(\text{Cl}^- \mid \text{AgCl} \mid \text{Ag})$ is shown for preparation 1.2′ in fig. 4 where the values $K = 1{\cdot}753 \times 10^{-5}$ mole kg^{-1},[37] $E^{\circ}(\text{Cl}^- \mid \text{AgCl} \mid \text{Ag}) = 222{\cdot}4$ mV,[38] $A = 0{\cdot}5084$ mole$^{-\frac{1}{2}}$ kg$^{\frac{1}{2}}$ and $k = 59{\cdot}16$ mV have been used. For this sample the standard potential was 1·233 V; other samples gave 1·239 V (1.1′) and 1·233 V (2·1′), but less reliance is placed in these as the potentials were less stable.

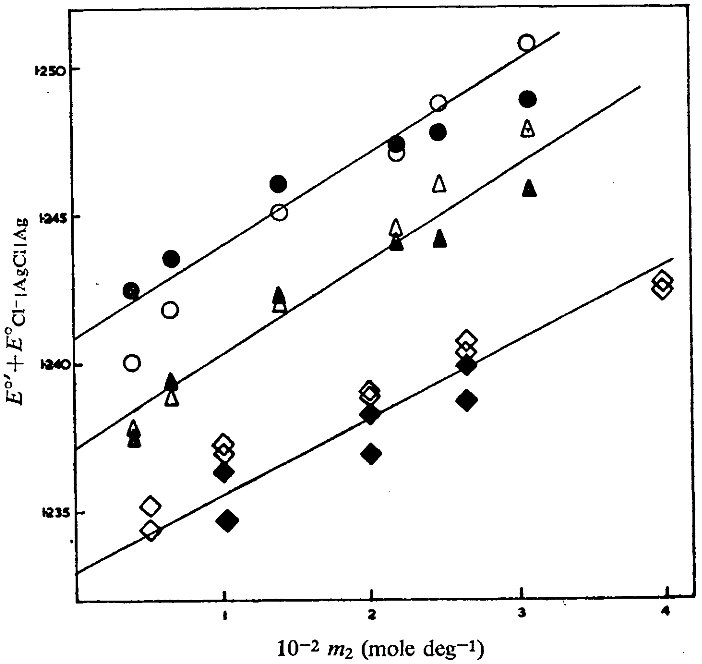


FIG. 4.—Filled symbols, increasing m_2 series; open symbols, decreasing m_2 series; circles, triangles, second series, preparations 1.3′, 1.6′; diamonds, first series, preparation 1.2′.

E° values from the second series are shown in table 2, and lie in about the same range as the first series. The results for two of the series 2 preparations are also shown in fig. 4. The same slope was drawn through the points for each oxide sample but the slopes differ for the two series because of the different molality ratios used. It will be noted that the standard potential of preparation 1.3′ (1·241 V) is higher than those of the other three preparations of the same series which have slightly lower exchange capacities; thus a relation may exist between the standard potential and the exchange capacity or stoichiometry of the sample. This increase in standard potential with decreasing stoichiometry is in the opposite direction to the relation found by Wadsley and Walkley,[7] but it is confirmed by the fact that samples gave potentials 20 mV higher before heat treatment in oxygen, than after, and this treatment improves the stoichiometry of the oxide.

EXPERIMENTS WITH CELLS CONTAINING BUFFERED ELECTROLYTE AND CONSTANT Mn^{2+} CONCENTRATION

Although the ion exchange equilibrium will be maintained on tenfold dilution better for cell III than for cell II in that the pH is almost constant, pMn changed by one unit. To overcome this a series of cells was studied in which additional manganous chloride was added to the buffer to maintain pMn approximately constant.

Five solutions were prepared by appropriate mixing of a stock solution containing 0·16 m acetic acid+0·08 m manganous acetate, with a stock solution of 0·08 m manganous chloride to give $m_2 = 0{\cdot}04-0{\cdot}005$ with $m_1 = 2m_2$, $m_2+m_3 = 0{\cdot}08$ and hence constant ionic strength, $I = 0{\cdot}24$.

Electrodes were prepared from an oxide which had been heated in a stream of oxygen for 48 h (3.1′). Both increasing and decreasing concentration series were performed, the oxide having been pretreated with the appropriate solution for 11 days with continuous mechanical shaking. Triplicate electrodes agreed to ±1 mV; mean values are recorded in table 4. Differences increasing to 2·5 mV in the most dilute solution were found between the results from the increasing and decreasing concentration series. All electrodes reached equilibrium in a few hours and remained steady to within 0·2 mV for 24 h. The potentials were unaffected by mechanical disturbance of the platinum contacts.

TABLE 4

m_2	decreasing m_2		increasing m_2		mean $E^{\circ\prime\prime}$
	E(V)	$E^{\circ\prime\prime}$(V)	E(V)	$E^{\circ\prime\prime}$(V)	
0·0400	$0{\cdot}450_8$	$1{\cdot}243_2$	$0{\cdot}450_4$	$1{\cdot}242_8$	$1{\cdot}243_0$
0·0267	$0{\cdot}456_6$	$1{\cdot}241_7$	$0{\cdot}458_1$	$1{\cdot}243_2$	$1{\cdot}242_5$
0·0200	$0{\cdot}459_5$	$1{\cdot}241_5$	$0{\cdot}461_5$	$1{\cdot}243_5$	$1{\cdot}242_5$
0·0100	$0{\cdot}463_7$	$1{\cdot}241_8$	$0{\cdot}465_1$	$1{\cdot}243_2$	$1{\cdot}242_5$
0·0050	$0{\cdot}465_1$	$1{\cdot}241_4$	$0{\cdot}467_5$	$1{\cdot}243_8$	$1{\cdot}242_6$

Guggenheim's theory [37, 39] of mixtures of electrolytes gives for the activity coefficient of a species RX$_2$ in the presence of other 2 : 1 electrolytes:

$$\log \gamma_{R,X} = \log \gamma^{st} + \tfrac{1}{4}\sum_{X'} B_{R,X'} m_{X'} + \tfrac{1}{2}\sum_{R'} B_{R',X} m_R, \tag{4}$$

where the first summation extends over all anions X′, and the second over all cations R′; $\log \gamma^{st}$ is the Debye-Hückel term chosen as a standard and specific interactions are represented by the coefficients $B_{R,X'}$, $B_{R',X}$. Guggenheim chooses $\log \gamma^{st} = -AI^{\frac{1}{2}}/1+I^{\frac{1}{2}}$ for 1 : 1 electrolytes but the exact choice of unity for the numerical coefficient of $I^{\frac{1}{2}}$ in the denominator is arbitrary. For 2 : 1 electrolytes it seems preferable to use a larger factor of 1·56 as before, thus the specific interaction coefficients must not be confused with the values tabulated by Guggenheim and Turgeon.[37]

Using (4),

$$\log \gamma_{MnAc_2} = \log \gamma^{st} + \tfrac{1}{4}B_{Mn,Cl}m_{Cl} + \tfrac{1}{4}B_{Mn,Ac}m_{Ac} + \tfrac{1}{2}B_{Mn,Ac}m_{Mn}, \tag{5}$$

and

$$\log \gamma_{MnCl_2} = \log \gamma^{st} + \tfrac{1}{4}B_{Mn,Cl}m_{Cl} + \tfrac{1}{4}B_{Mn,Ac}m_{Ac} + \tfrac{1}{2}B_{Mn,Cl}m_{Mn}, \tag{6}$$

where

$$\log \gamma^{st} = -2AI^{\frac{1}{2}}/(1+1{\cdot}56I^{\frac{1}{2}}).$$

We assume [41]

$$\log \gamma_{HAc} = B_{HAc}I, \tag{7}$$

where B_{HAc} is a salting coefficient.

The water activity is put equal to the mole fraction of water in the solution and thus

$$\ln a_{\mathrm{H_2O}} = -\ln\{1+0{\cdot}018(m_1+3m_2+3m_3)\} \simeq -0{\cdot}018(m_1-3m_2+3m_3). \qquad (8)$$

Inserting eqn. (5), (6), (7), (8) in (3) and simplifying gives, for the constant ionic strength experiments,

$$E = E^\circ + \left\{\tfrac{1}{2}k\log\frac{(0{\cdot}08-m_2)^2}{0{\cdot}02} + 3k\frac{AI^{\frac{1}{2}}}{1+1{\cdot}56I^{\frac{1}{2}}} + 2k\log K\right\}$$

$$-\tfrac{1}{2}k\,[\tfrac{3}{2}B_{\mathrm{Mn,Ac}} - \tfrac{3}{2}B_{\mathrm{Mn,Cl}} + 0{\cdot}031]\,m_2 - \tfrac{1}{2}k\,0{\cdot}08\,[3B_{\mathrm{Mn,Ac}} - 12B_{\mathrm{HAc}} - 0{\cdot}047].$$

Then, defining $E^{\circ\prime\prime}$ as E minus the terms in braces, a plot of $E^{\circ\prime\prime}$ against m_2 should give a straight line of slope

$$(3k/4)[B_{\mathrm{Mn,Ac}} - B_{\mathrm{Mn,Cl}} + 0{\cdot}021], \qquad (9)$$

and intercept

$$E^\circ - (3k/2)0{\cdot}08[B_{\mathrm{Mn,Ac}} - 4B_{\mathrm{HAc}} - 0{\cdot}016]. \qquad (10)$$

For cell III in which only pH was constant, inserting the above expressions for the activity coefficients, and the relations $\tfrac{1}{2}m_1 = m_2 = m_3$; $I = 6m_2$, gives

$$E = E^\circ + \tfrac{1}{2}k\log 2m_2 + 2k\log K + 3k\frac{\mathrm{A}I^{\frac{1}{2}}}{1+1{\cdot}56I^{\frac{1}{2}}}$$

$$-3k(B^{5}_{4\,\mathrm{Mn,Ac}} - \tfrac{1}{4}B_{\mathrm{Mn,Cl}} - 4B_{\mathrm{HAc}} - 0{\cdot}021)m_2$$

and defining $E^{\circ\prime}$ as before, the slope of the plot of $E^{\circ\prime}$ against m_2 (fig. 4) is

$$-\tfrac{3}{4}k(5B_{\mathrm{Mn,Ac}} - B_{\mathrm{Mn,Cl}} - 16B_{\mathrm{HAc}} - 0{\cdot}084) = 0{\cdot}25\ \mathrm{V\ mole^{-1}\ kg}. \qquad (11)$$

Combining (9) with (11) gives $B_{\mathrm{Mn,Ac}} - 4B_{\mathrm{HAc}}$ required to evaluate E° from (10).

A positive slope could be drawn for the decreasing series and a negative slope for the increasing series. The difference of 2·5 mV at the low m_2 end could be due to some effect of the pretreatment of the oxide for the two series, in solutions of different chloride ion concentration. However, taking the mean of the determinations in each solution the slope of the line is effectively zero, thus $B_{\mathrm{Mn,Ac}} - B_{\mathrm{Mn,Cl}} = -0{\cdot}021$ and $E^{\circ\prime\prime} = 1{\cdot}2426$ V. Using (11), $B_{\mathrm{Mn,Ac}} - 4B_{\mathrm{HAc}} = -1{\cdot}386$ mole^{-1} kg, and $E^\circ_{\mathrm{H^+,Mn^{2+}}\,|\,\mathrm{MnO_2,Pt}} = 1{\cdot}233$ V. The value is almost exactly the same if the calculation is made using either the decreasing series with its positive slope, or the increasing series with the negative slope. Different values of B's are involved. The result agrees with the value obtained from the cell with the pH constant only, for a similarly prepared oxide sample.

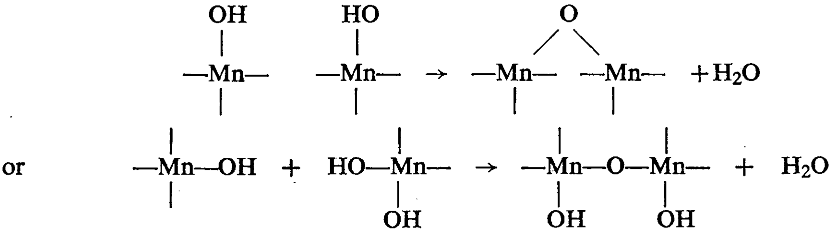
CONCLUSIONS

The standard potential of the electrode $\mathrm{H^+,Mn^{2+}}\,|\,\beta\text{-}\mathrm{MnO_2,Pt}$ varies from 1·233 to 1·241 V for different preparations. These results are in fair agreement with those of Brown and Liebhafsky[4] (1·236 V) and Hutchison[4] (1·230 V) despite the difficulties experienced by some other workers[5, 7] with β-$\mathrm{MnO_2}$ in strong acid solution, which have now been demonstrated to be due to the cation exchange properties of the oxide. The lower potentials (1·220 V) of Maxwell and Thirsk are suspect since their technique of grinding the oxide during a series of e.m.f. measurements is probably detrimental and their results at low dilutions (0·005-0·001 m), heavily weighted in their method of extrapolation, were most likely not equilibrium values. It is noted that the potential estimated by Wadsley and Walkley[7] from thermochemical data[42] was 1·229 V.

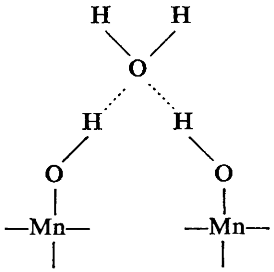
The small amount of exchangeable ions present in oxide normally considered as stoichiometric is sufficient to give rise to drifting potentials. The small deviations from stoichiometry can be calculated from the number of exchangeable manganous ions. A correlation may exist between the hydrogen ion uptake or stoichiometry and the observed standard potential of a given sample in the second series. Further study of this example where there is a large variation of standard potential may throw light on other systems where the effect is small but makes necessary for every new piece of precise work the redetermination of the standard potential.[43]

Although the treatment of β-MnO$_2$ as a cation exchanger may be a semantic device,[26] it does permit the characterization of oxide samples by the ion exchange methods. The surface area of the β-MnO$_2$ o amples is too small for the exchange to be a surface phenomenon and the long tir uired for the exchange to reach equilibrium supports this in indicating diffusion of ions within the oxide structure. Kozawa [24] has found a correlation between exchange capacity of γ-MnO$_2$ samples and (B.E.T.) surface area and it is possible that the more open structure of γ-MnO$_2$ permits exchange equilibrium to be achieved more rapidly than for the denser β-form. If this is so it should be possible to measure the potential of the γ-oxide provided the ion exchange can be kept at equilibrium during a series of e.m.f. measurements.

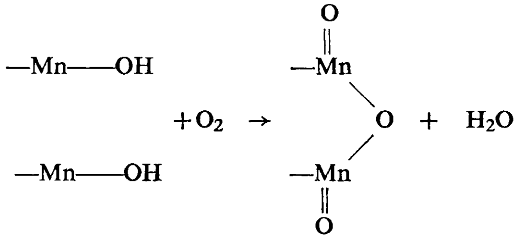
Heating in oxygen reduces the exchange capacity, improves the stoichiometry and removes water. Sasaki and Kozawa [44] have shown that water liberated at 110° may be readsorbed reversibly but water lost at higher temperatures is not. This "combined" water is probably present as surface OH groups on the polymeric oxide and an alternative representation of the formula of an oxide, e.g., 1.4′, $\mathrm{MnO_{1{\cdot}998}}$ 0·7 % H_2O would be $\mathrm{MnO_{1{\cdot}964}(OH)_{0{\cdot}068}}$. At high pH these OH groups can exchange hydrogen ions for other cations, but this formula corresponds to a maximum exchange capacity of 0·8 mmole H$^+$/g; the measured capacity was found to be an order of magnitude lower. Some of the adjacent OH groups combine to lose water on heating



and if the oxygen bridge is strain free this loss may be irreversible. These processes may leave widely separated OH groups so it is unlikely that water can be completely removed. Water lost at 110° is probably hydrogen bonded to these OH groups as with silicaceous materials where its presence can be shown by infra-red spectra.[45]



Different spatial arrangements of the surface OH groups would give rise to the two functional acid groupings observed in the titration curves. The role of the nitric acid treatment introduced by Popoff [5] besides oxidation is probably to leach out manganous ions remaining in the oxide and to replace them by H$^+$ ions; the resultant OH groups can then combine to lose water decreasing the exchange capacity as observed. The role of oxygen is probably to provide an oxidizing atmosphere and not just to prevent loss of oxygen since it has been shown by differential thermal analysis [24] that β-MnO$_2$ does not decompose until 580°. Parallel improvement of stoichiometry with decrease of exchange capacity and water content could be attributed to the reaction



$$\begin{array}{l} \text{—Mn——OH} \\ \text{—Mn——OH} \end{array} + O_2 \rightarrow \begin{array}{c} O \\ \| \\ \text{—Mn} \\ \diagdown \\ O \\ \diagup \\ \text{—Mn} \\ \| \\ O \end{array} + H_2O$$

Lower oxides have apparently been detected [46, 47, 7] on MnO_2 surfaces by electron diffraction but the surface structure of OH groups and Mn^{II} may give rise to lines similar to those found for the lower oxides.

The use of a buffered cell offers several advantages for the study of manganese dioxides, and probably for other oxide systems. The best results were obtained when the manganous ion concentration was also maintained constant on dilution of the cell electrolyte. The standard potential agreed well with that for a similar oxide preparation obtained from the buffered cell. This justifies the use of the Guggenheim theory which is most likely to be a good approximation for mixtures of the same charge type [39] for estimating the activity terms in this system where only moderate accuracy is obtainable (± 2 mV). It may be possible to use cells I and II if the electrolyte is maintained not at equal concentrations of acid and salt during dilution but so that $m_{\text{Mn}^{2+}} \propto m^2_{\text{H}^+}$ to keep the exchange at equilibrium, but the treatment of the activity term would be difficult.

A preliminary account of this work was presented before the Second International Symposium on Batteries organized by the Interdepartmental Committee on Batteries of the Ministry of Aviation held at Bournemouth, Hants, in October, 1960.

We thank Dr. H. Marsh for carrying out the surface area measurements, D.S.I.R. for the award of an Advanced Course Studentship (T. C.) and Durham Chemicals Ltd., for the award of a Memorial Studentship (B. G. L.).

[1] Wadsley and Walkley, *Rev. Pure Appl. Chem. Austral.*, 1951, **1,** 203.
[2] for a review, see Vosburgh, *J. Electrochem. Soc.*, 1959, **106,** 839.
[3] Tower, *Z. physik. Chem.*, 1895, **18,** 17.
[4] Brown and Liebhafsky, *J Amer. Chem. Soc.*, 1930, **52,** 2595.
[5] Popoff, Riddick and Becker, *J. Amer. Chem. Soc.*, 1930, **52,** 2694.
[6] Hutchison, *J. Amer. Chem. Soc.*, 1947, **69,** 3051.
[7] Wadsley and Walkley, *J. Electrochem. Soc.*, 1949, **95,** 11.
[8] Maxwell and Thirsk, *J. Chem. Soc.*, 1955, 4054.
[9] Ives in *Reference Electrodes*, ed. Ives and Janz (Academic Press, New York, 1961).
[10] Latimer, *Oxidation Potentials* (Prentice Hall, 1938).
[11] Boksay, Csakvari and Lengyel, *Z. physik. Chem.*, 1957, **207,** 223.
[12] Bhatnagar *et al.*, *J. Chem. Soc.*, 1939, 1433.
[13] Moore, Ellis and Selwood, *J. Amer. Chem. Soc.*, 1950, **72,** 856.
[14] Kelley and Moore, *J. Amer. Chem. Soc.*, 1943, **65,** 782.
[15] Lingane and Karplus, *Ind. Eng. Chem. Anal.*, 1946, **18,** 191.
[16] Eberius and LeBlanc, *Z. anal. Chem.*, 1932, **89,** 81.
[17] Braddock-Roger and Kringer, *Anal. Chem.*, 1933, **5,** 342.
[18] Butler and Copp, *J. Chem. Soc.*, 1956, 725.
[19] Brown, *J. Amer. Chem. Soc.*, 1934, **56,** 646.
[20] Foulk and Hollingsworth, *J. Amer. Chem. Soc.*, 1923, **45,** 1220.
[21] Flaschka, *E.D.T.A. Titrations* (Pergamon Press, 1959).
[22] Johnson and Vosburgh, *J. Electrochem. Soc.*, 1952, **99,** 317.
[23] Sasaki, *Memoirs Faculty Eng., Nagoya Univ.*, 1951, **3,** 81.

[24] Kozawa, *J. Electrochem. Soc.*, 1959, **106,** 552.
[25] Amphlett, McDonald and Redman, *J. Inorg. Nucl. Chem.*, 1958, **6,** 236.
[26] Kraus *et al*, *Proc. 2nd Conf. Peaceful Uses Atomic Energy* (U.N., Geneva), 1957, **28,** 3.
[27] Jordan, *Helv. chim. Acta*, 1951, **34,** 699.
[28] Polissar, *J. Amer. Chem. Soc.*, 1936, **58,** 1372.
[29] Bone, *Thesis* (University of Durham, 1957).
[30] Buser and Graf, *Helv. chim. Acta*, 1955, **38,** 810.
[31] Kunin, *Ion Exchange Resins* (Wiley, New York, 2nd ed., 1958), p. 337.
[32] Harned and Ehlers, *J. Amer. Chem. Soc.*, 1932, **54,** 1350.
[33] Owen, *J. Amer. Chem. Soc.*, 1935, **57,** 1526.
[34] Bates and Vosburgh, *J. Amer. Chem. Soc.*, 1937, **59,** 1188.
[35] Vaughen and Lietske, *J. Amer. Chem. Soc.*, 1957, **79,** 4266.
[36] Guggenheim and Stokes, *Trans. Faraday Soc.*, 1958, **54,** 1646.
[37] Guggenheim and Turgeon, *Trans. Faraday Soc.*, 1955, **51,** 747.
[38] Guggenheim and Prue, *Trans. Faraday Soc.*, 1954, **50,** 231.
[39] Guggenheim, *Kgl. Danske. Vid. Selsk. Mat.-fys. Med.*, 1955, **30,** no. 14.
[40] Guggenheim, *Phil. Mag.*, 1935, **19,** 588.
[41] Randall and Fairley, *Chem. Rev.*, 1927, **4,** 291.
[42] Walkley, *J. Electrochem. Soc.*, 1948, **93,** 316; **94,** 41.
[43] Bates *et al.*, *J. Chem. Physics*, 1956, **25,** 361; 1957, **26,** 222.
[44] Sasaki and Kozawa, *J. Electrochem. Soc. Japan*, 1957, **25,** 115, E23.
[45] Kiselev in *The Structure and Properties of Porous Materials* (10th Colston Symposium, ed. Everett and Stone), p. 195.
[46] Butler and Thirsk, *J. Electrochem. Soc.*, 1953, **100,** 297.
[47] Brenet, Forestier and Boisier, *Congrès Microscopic électronique, Paris* (1950 édition). *Revue d'Optique*, 1952.