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THE MANGANOUS-MANGANESE DIOXIDE AND THE MANGANOUS-PERMANGANATE ELECTRODES

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The following investigation was undertaken in order to secure a more accurate "normal potential" for the manganous-manganese dioxide electrode. It constitutes the final step necessary for the calculation of the oxidation potential of the manganous-permanganate electrode.

I. The Manganous-Manganese Dioxide Electrode.—The data in the literature for this electrode are very discordant. The value for the normal potential usually given is based on the consistent results of Tower.[1] Smith[2] in an attempt to use this electrode for the determination of the concentration of the hydrogen ion, failed to duplicate the observations made by Tower. In both cases the manganese dioxide was deposited electrolytically. Brown and Tefft[3] failed to prepare pure manganese dioxide, or manganese dioxide hydrated, or with water only as a contamination, by electrolysis.

Preliminary observations made in this Laboratory indicated that the more consistent results obtained by Tower were due to a very exact duplication of conditions in the depositions of the manganese dioxide. The determinations proved that the manganese dioxide deposited electrolytically was apparently in a more active state than that prepared by the method used by Brown and Tefft.[3] The electrodes prepared by depositing manganese dioxide electrolytically were in a more active form and as a result the data of Tower could not be used to calculate the true equilibrium values.

The electromotive force of the cell $H_2/HClO_4(m_1)$, $Mn(ClO_4)_2(m_2)/MnO_2$, in which m indicates the molality, was studied at 25°. The equation to represent the reaction of the cell is $MnO_2 + 2HClO_4 + H_2 \longrightarrow Mn(ClO_4)_2 + 2H_2O$ and to represent the manganous-manganese dioxide electrode (as observed), $MnO_2 + 4H^+ + 2e \longrightarrow Mn^{++} + 2H_2O$.

The "normal potential," E_0, of the manganous-manganese dioxide

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[1] Tower, *Z. physik. Chem.*, **18**, 17 (1895).

[2] Smith, *ibid.*, **21**, 93 (1896).

[3] Brown and Tefft, THIS JOURNAL, **48**, 1128 (1926).

electrode can be calculated from the electromotive force, E_c, which is the observed value corrected to 76 cm. for hydrogen, and the activities, a, of the hydrogen ion and manganous ion at the given concentrations, by using the equation $E_0 = E_c - 0.05915/2 \log a_{\mathrm{H}^+}{}^2/a_{\mathrm{Mn}^{++}}$.

This equation requires the activity coefficients for manganous salts and of perchloric acid when they are in solution with each other. To eliminate the use of these doubtful values, an attempt was made to make all observations on solutions in which the manganous perchlorate and the perchloric acid were of equal molality (Table I). The value E' may be calculated from the equation

$$E' = E_c - 0.05915/2 \log m_1{}^2/m_2 = E_c - 0.05915/2 \log m$$

and E_0 may be determined by extrapolating the values for E' to zero molality if observations can be made at high dilution. It was discovered that at greater dilutions than 0.05 molal a dark deposit appeared on the hydrogen electrode and caused fluctuations in the observed values large enough to introduce considerable error in the plotting of the curve. However, the mean of these inaccurate values was near the curve extrapolated to 1.235 volts.

In order to meet the difficulty a second series (Table II) of measurements was made in which the perchloric acid was kept at tenth molal while the concentration of the manganous perchlorate was varied. The standard potential E_0 was calculated on the assumption that the activity coefficient for the manganous perchlorate followed the values given by Lewis and Randall[4] for similar salts and that the $Mn(ClO_4)_2$ in the experimental electrode could be considered as $2HClO_4$ for the purpose of determining a, the activity. Of course, for the more dilute solution this correction becomes practically zero and is a very small correction for the two more concentrated solutions.

Experimental Part

Manganese dioxide was prepared by slowly decomposing at 150°, the best manganous nitrate obtainable, treating the residue at that temperature four times with nitric acid, pulverizing, washing several times with conductivity water and finally heating at 250–300° for four hours. Analysis of the dioxide thus prepared showed it to be at least 99.9% pure. Water was the only detectable impurity.

The wash water from the manganese dioxide was tested for manganese; since none was found we assumed all to be changed to dioxide. There was a slight reduction of a dilute permanganate solution due to oxides of nitrogen. The washed dioxide was heated to 250–300° and tested as given above; the results were negative. By analysis this final product contained 100 ± 0.1% of manganese dioxide. To determine the possible presence of

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[4] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, **1923**, p. 362.

oxides of nitrogen, we heated a considerable portion to a high temperature; a slight deposit of moisture was all that was observed. Our observations indicate that the manganese dioxide has a great adsorptive capacity for water and oxides of nitrogen. Heating directly to 250–300° did not remove the latter.

Manganous perchlorate was prepared by the action of perchloric acid on the best grade of manganous carbonate. The strength of this solution was determined by decomposing a weighed sample by the method given above and weighing the manganese dioxide.

In all cases efforts were made to have chemicals specially purified. Conductivity water was used to prepare all solutions.

The powdered manganese dioxide and the electrode solution were rotated at 25° for three hours before they were placed in the electrode vessel.

The half cell consisted simply of a test-tube with a sealed on side arm to serve as a liquid connection to the hydrogen electrode, and a one-holed stopper through which was inserted a glass tube with a platinum foil sealed in it at the lower end and filled with mercury to make contact. The platinum foil is always completely immersed in the solution.

Since the same solution appears throughout the cell, the hydrogen electrode was separated from the manganese dioxide electrode only by a stopcock to prevent possible diffusion of hydrogen. This was opened only while measuring.

The potentials were measured at 25° with a Leeds and Northrup Type K potentiometer, an L and N Type 2500 galvanometer, and a new standard cell calibrated by the Bureau of Standards was employed to check the reference cell.

The cells prepared as described above show no radical fluctuations; some of them were observed for a month and no change greater than two millivolts was observed. The cells were usually measured over a period of a few days before the final reading was taken. If the solution was not rotated with the manganese dioxide, a steady change of the electromotive force took place for a period of days. The initial value was low by about 0.1 volt, rose to a maximum usually several millivolts above the final equilibrium values, and then decreased to constant value.

TABLE I

EXPERIMENTAL RESULTS

m $HClO_4$ and m $Mn(ClO_4)_2$	E_c, mv.	E
0.3	1.2402 ± 0.8	1.2557
.2	1.2336 ± 0.3	1.2543
.1	1.2202 ± 0.5	1.2498
.05	1.2054 ± 0.3	1.2439

By extrapolating the curve for E, the value 1.235 is obtained.

TABLE II

EXPERIMENTAL RESULTS

m $HClO_4$	m $Mn(ClO_4)_2$	E_e, mv.	E_0
0.0940	0.050	1.2360 ± 0.1	1.238
.0992	.010	1.2525 ± 0.6	1.238
.0978	.005	1.2580 ± 0.4	1.237
.0983	.002	1.2663 ± 0.4	1.236
.0983	.001	1.2726 ± 0.4	1.234
		Average	1.237

Based on these results the value +1.236 for the normal potential of the electrode $MnO_2 + 4H^+ + 2e \rightleftharpoons Mn^{++} + 2H_2O$ is probably correct within 2 mv.

II. The Manganous–Permanganate Electrode.—Using the value +1.586 determined by Brown and Tefft[3] for the potential of the manganese dioxide–permanganate electrode and the value as determined above, the calculated value for the manganous–permanganate electrode in the presence of an acid at unit activity is +1.446 volts.

Summary

A value of +1.236 volts was obtained for the oxidation potential of the reaction $MnO_2 + 4H^+ + 2e \rightleftharpoons Mn^{++} + 2H_2O$ in perchloric acid solution. For the oxidation potential of the reaction $MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{++} + 4H_2O$, the value +1.446 volts was calculated.

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CHLORIDE-FREE FERRIC OXIDE HYDROSOLS AND THE BURTON–BISHOP RULE

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Introduction

Although the general validity of the Burton–Bishop rule[1] relative to the effect of concentration of colloid on the flocculation values of electrolytes seems to be quite well established in the case of the widely studied arsenic trisulfide sols, it is quite as definitely discredited by the behavior of ferric oxide hydrosols. Kruyt and van der Spek[2] have shown that for colloidal hydrous ferric oxide the precipitation values of all electrolytes, monovalent as well as di- and trivalent, decrease with dilution of

[1] Burton and Bishop, *J. Phys. Chem.*, **24**, 701 (1920).

[2] Kruyt and van der Spek, *Z. Kolloidchemie*, **25**, 3 (1919).