

RELATION OF VOLTAGE OF DRY CELLS TO HYDROGEN-ION CONCENTRATION

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I. INTRODUCTION

In connection with the testing at the Bureau of Standards of materials to be used in the manufacture of dry cells, it became necessary to measure the potentials of some carbon-manganese-dioxide electrodes, such as are used in dry cells. It was originally planned to make a thorough study of the oxides of manganese in their rôle as depolarizers in dry cells, with particular attention to the shelf-life of the cell; but, since it was necessary to discontinue the work for a time, it was felt that the results thus far obtained would be useful to manufacturers of dry cells and might be suggestive to other workers in this field.

Several important papers have been published on the manganese-dioxide electrode. Tower¹ and Smith² studied the electrolytically prepared oxide as a means for measuring the hydrogen-ion concentration of organic acid salts. Thompson and Crocker³ noted the effect of alkalies and acids upon the

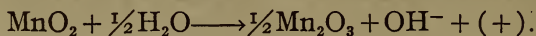
¹ Tower, *Zeit. phys. Chem.*, 18, p. 17; 1895. Tower, *Zeit. phys. Chem.*, 32, p. 566; 1900.

² Smith, *Zeit. phys. Chem.*, 21, p. 93; 1896.

³ Thompson and Crocker, *Trans. Am. Electrochem. Soc.*, 27, p. 155; 1915.

potential of electrodes prepared from a mixture of granulated carbon and pyrolusite.

Allmand⁴ states that the reaction of manganese dioxide as a depolarizer may be represented by an equation such as



According to Nernst's equation, the electrode potential at 25° C would then be

$$\begin{aligned} E &= \text{constant} + 0.059 \log \frac{[\text{MnO}_2]}{[\text{Mn}_2\text{O}_3]^{\frac{1}{2}}[\text{OH}^-]} \\ &= \text{constant} - 0.059 \log [\text{OH}^-] = \text{constant} + 0.059 \log [\text{H}^+] \end{aligned}$$

in which the potential is a logarithmic function of the hydrogen-ion concentration.

No experimental data have been published to show whether this relation is true. While the authors previously mentioned recognized that a logarithmic relation exists and suggested equations representing it, they did not establish their conclusions by measurements with a hydrogen electrode. Moreover, no one has pointed out the significance of the hydrogen-ion concentration as explanatory of variations in the open-circuit voltage of dry cells and the part it plays in the polarization of a dry cell during discharge.

It is, therefore, the purpose of this paper to present experimental data showing (1) that the potential of a manganese-dioxide electrode prepared from certain ores is a logarithmic function of the hydrogen-ion concentration of the solution in contact with it; (2) that chemically prepared manganese dioxide does not show the logarithmic relation; (3) that the relation between the potential of the manganese-dioxide electrode and hydrogen-ion concentration serves as a partial explanation of variations in the open-circuit voltage and polarization of dry cells.

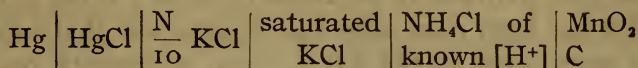
II. EXPERIMENTAL WORK

I. METHOD OF MEASUREMENT.—The method used for measuring the potential of the carbon-manganese dioxide electrode in different solutions was briefly as follows:

The electrode was introduced into a 2-ounce bottle containing the solution of known hydrogen-ion concentration. Into this solution dipped a siphon containing a saturated solution of potassium chloride which led to a tenth-normal calomel electrode.

⁴ Allmand, *Applied Electrochemistry*, p. 206; 1912.

This set-up is shown in Fig. 1. The electromotive force of this chain



was then measured with a potentiometer.

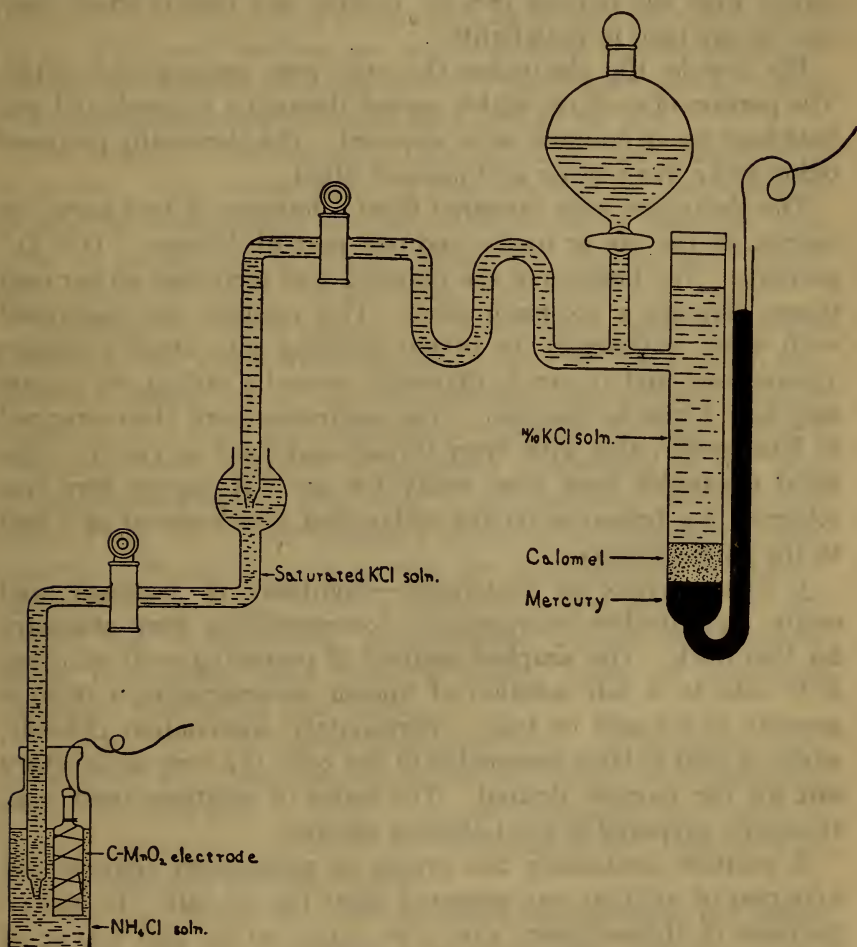


FIG. 1.—Set up for measuring the potentials of the carbon manganese dioxide electrode in different solutions of known hydrogen-ion concentration

2. PREPARATION OF ELECTRODES.—Because of the variety of manganese ores used at the present time in making dry cells, it was decided to select for this investigation several ores typical of those in use. For this purpose some of the manufacturers furnished⁵ a number of ores, of which three were selected for this work.

⁵ Acknowledgment is made of the courtesy of the Burgess Battery Co., and the National Carbon Co., who furnished the samples of ores.

The materials selected were a Caucasian ore, which is considered to be the best material in all respects for dry cells; a Brazilian ore, which has been used since the importation of the Caucasian ore, was interrupted by the war in 1914; a domestic ore; and a chemically prepared oxide. The latter is used in large proportions mixed with the natural ores for making dry cells of small sizes, such as are used in flash lights.

For use in the electrodes the ores were ground and sifted. The portion of each ore which passed through a 65-mesh and was held back by an 80-mesh sieve was used. The chemically prepared oxide was a fine powder and was not sifted.

The electrodes were prepared from a mixture of two parts, by weight, of the ore or oxide, and one part of Acheson "D A G" graphite. The fineness of the graphite was such that 99 per cent passes through a 200-mesh sieve. This mixture was moistened with water sufficiently to permit molding into small cylinders 33 mm long and 12 mm in diameter, around a carbon rod 25 mm long and 5 mm in diameter. The electrodes were then wrapped in filter paper, tied with linen thread, and dried at 110° C. The dried electrodes were then ready for use. A copper wire was soldered to a brass cap on the carbon rod, which served as a lead to the potentiometer.

3. PREPARATION OF SOLUTIONS.—Solutions of constant and easily reproducible hydrogen-ion concentrations were necessary for this work. The simplest method of preparing such solutions is to add to a salt solution of known concentration a definite amount of its acid or base. Fortunately, ammonium chloride, which is used in large proportion in dry cells, is a very satisfactory salt for the purpose desired. The series of solutions used was, therefore, prepared in the following manner:

A solution containing 200 grams of ammonium chloride per kilogram of solution was prepared from the cp salt. To 100 cc portions of this solution, 1 cc, 5 cc, 10 cc, 50 cc, and 100 cc of tenth-normal hydrochloric acid or ammonium hydroxide were added. The hydrogen-ion concentration of each one of these solutions was determined by the bell type of hydrogen electrode suggested by Hildebrand⁶ and measured against a tenth-normal calomel electrode.

⁶Jour. Am. Chem. Soc., 35, p. 864; 1913.

III. DISCUSSION OF RESULTS

I. HYDROGEN-ION CONCENTRATIONS.—In Fig. 2, curve *V* represents the series of ammonium-chloride solutions the preparation of which was previously described. The zero ordinate represents the neutral 20 per cent ammonium-chloride solution. Additions of tenth-normal ammonium hydroxide to a volume of 100 cc of the salt solution are indicated from zero to the right, and similar additions of tenth-normal hydrochloric acid to 100 cc of the salt solution are indicated from zero to the left.

The range in hydrogen-ion concentration thus obtained is 10^{-1} to 10^{-8} . The uncertainty of the potential of the hydrogen electrode in ammoniacal solutions, due to loss of ammonia produced by passage of hydrogen, makes the alkaline part of the curve a little doubtful, but the error is believed to be small.

The alkalinity of the ammonia is considerably reduced by the presence of the ammonium chloride. Thus, in the solution prepared by adding 100 cc of tenth-normal ammonium hydroxide to 100 cc of 20 per cent ammonium-chloride we really have a twentieth-normal solution of ammonia containing 10 per cent of ammonium-chloride and with a hydrogen-ion concentration (curve *V*) of 10^{-8} . The hydrogen electrode in twentieth-normal ammonia without the salt showed the hydrogen-ion concentration to be 10^{-10} . That is, the presence of 10 per cent of the salt reduced the hydrogen-ion concentration by one hundredfold. Similar calculations were made by Blum,⁷ using the ionization constants of ammonia and water.

2. POTENTIAL OF MANGANESE-DIOXIDE ELECTRODE.—The potentials of the three samples of ores and oxide are represented by the curves in Fig. 2, curve *I* for the Caucasian ore; curve *II* for the domestic ore; curve *III* for the Brazilian ore; and curve *IV* for the chemically prepared oxide.

In the case of the ores, although the parallelism is not exact, it appears that the potential is a logarithmic function of the hydrogen-ion concentration. Thus, while the potential of the hydrogen electrode in curve *V* decreases (-0.39 to -0.79) 0.40 volt, the potential of the Caucasian ore decreases ($+0.62$ to $+0.15$) 0.47 volt; the domestic ore ($+0.67$ to $+0.11$) 0.56 volt; and the Brazilian ore ($+0.64$ to $+0.19$) 0.45 volt. That is, for

⁷ Blum—Bull. Bur. Stand., 13, p. 521; 1916.

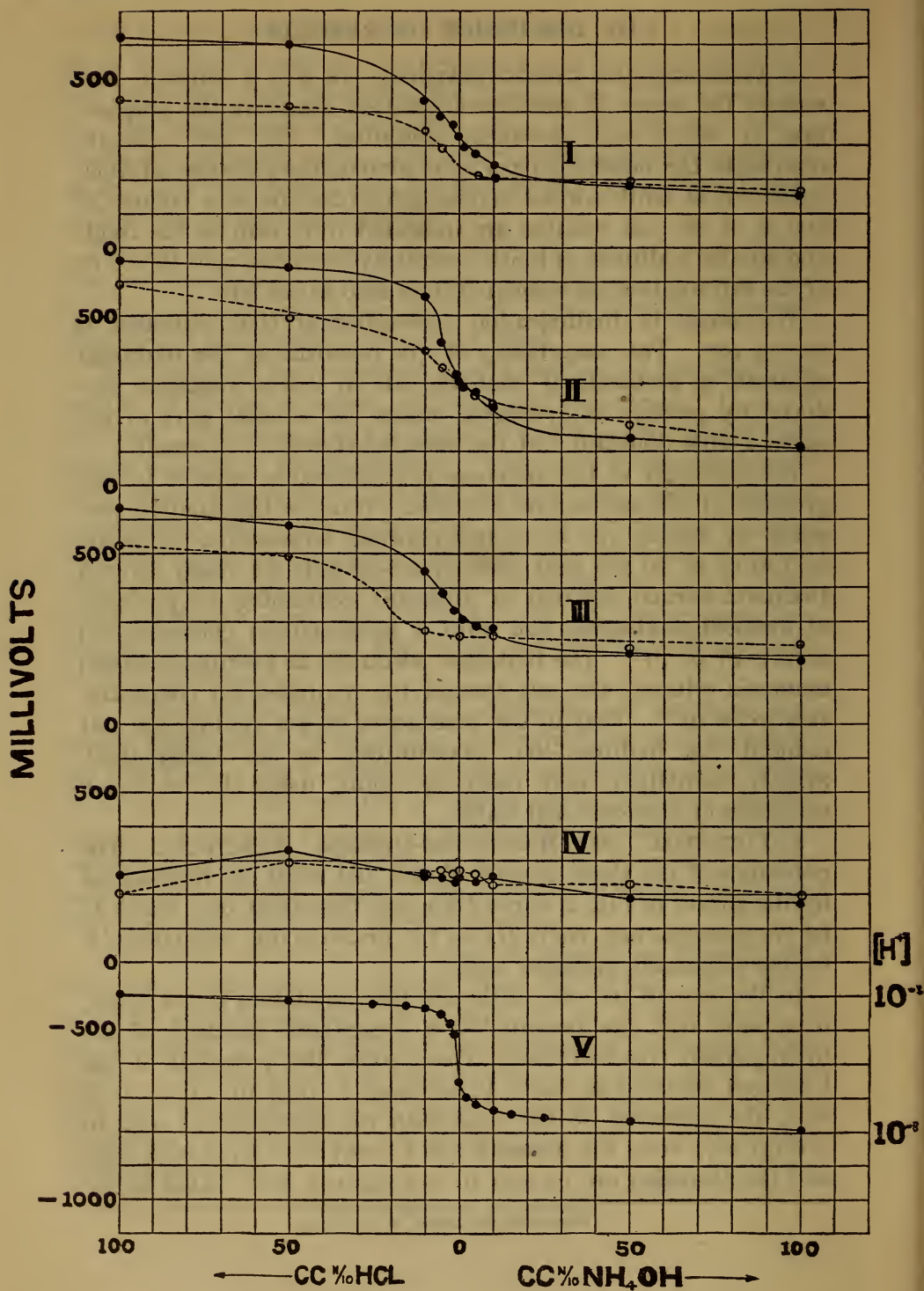


FIG. 2.—The potentials of different manganese ores and an oxide as measured in series of NH_4Cl solutions of known hydrogen-ion concentration are represented by above curves I, Caucasian ore; II, domestic ore; III, Brazilian ore; IV, chemically prepared oxide; V represents the curve of the series of NH_4Cl solutions used in this work, the hydrogen-ion concentration ranging from 10^{-1} to 10^{-8} .

each tenfold decrease in hydrogen-ion concentration, the potential of the Caucasian ore decreased $\left(\frac{0.47}{7}\right)$ 0.067 volt; the domestic ore $\left(\frac{0.56}{7}\right)$ 0.080 volt; and the Brazilian ore $\left(\frac{0.45}{7}\right)$ 0.064 volt.

The potential of the chemically prepared oxide appears to be independent of hydrogen-ion concentration, for which no explanation is offered. This difference from the ores was entirely unexpected and requires further study.

3. EFFECT OF TIME.—The increase in potential produced by increased acid concentration would suggest a simple means of increasing the voltage of a dry cell, and it has been said to have been used by dishonest makers to “boost” the voltage and “flash point” of their dry cells. It has the disadvantage, however, that the voltage drops from day to day. This is indicated by the dotted curves in Fig. 1, which represents, the potentials at the end of one week. Thus it is seen that the potential gradually decreased in acid solutions and increased slightly in alkaline solutions. These results would indicate that the shelf-life⁸ of a cell containing acid would probably be short, entirely apart from the action of the acid solution upon the zinc.

4. RELATION OF HYDROGEN-ION CONCENTRATION AND OPEN-CIRCUIT VOLTAGE OF DRY CELLS.—Experiments showed that the potential of a zinc electrode in the solutions corresponding to curve V varies less than 0.02 volt; that is, the zinc potential is practically independent of the hydrogen-ion concentration of the solution. But since the potential of the carbon-manganese dioxide is dependent upon the hydrogen-ion concentration, the open-circuit voltage of the dry cell, containing a given ore, is, therefore, determined by the hydrogen-ion concentration of its electrolyte. It would be possible, then, to vary the open-circuit voltage, when the cell is new, by 0.4 or 0.5 volt by simply adding acid or alkali to it.

Measurements of the hydrogen-electrode potential in solutions containing 12.5 to 50 per cent of ammonium chloride and up to 40 per cent of zinc chloride gave values from 0.52 to 0.59 volt against the tenth-normal calomel electrode, corresponding to hydrogen-ion concentrations from 10^{-3} to $10^{-4.5}$. Since the slope

⁸ At the beginning of this investigation it was hoped that the change in potentials over a short period of time might serve as an indication of the probable shelf-life of a dry cell containing the ore or oxide tested. The results obtained, however, were not sufficient to justify the conclusion that it is possible to predict the shelf-life of an ore by such a method.

of the curves for the ores near the neutral point is much less than that for the hydrogen electrode, the variation in the open-circuit voltage, caused by differences in hydrogen-ion concentration of ammonium and zinc chlorides solutions, would be somewhat less than 0.07 volt.

5. RELATION OF HYDROGEN-ION CONCENTRATION AND POLARIZATION OF A DRY CELL.—There is no means of measuring the hydrogen-ion concentration of the electrolyte in a dry cell with a hydrogen electrode. From the previous discussion it appears that the potential of the manganese dioxide electrode gives about as true value of the hydrogen-ion concentration in a dry cell as it is possible to obtain.

While it is true that zinc chloride would reduce the alkalinity produced by ammonia formed during discharge of the cell, it is probable that the alkalinity would at least amount to that represented in curve V; that is, $[10^{-8}]$. Assuming this to be true, then, the decrease in hydrogen-ion concentration from that of the neutral ammonium-chloride solution to about 10^{-8} would cause a drop of 0.17 volt in the voltage of a cell containing the Caucasian ore; 0.21 for the domestic ore; and 0.14 volt for the Brazilian ore. Roughly, then, a drop in voltage of at least 0.15 to 0.20 volt may be due to decreased hydrogen-ion concentration. At least a portion of the polarization of a dry cell is, therefore, probably due to the layer of electrolyte on the surface of the electrode becoming impoverished in hydrogen ions.

To determine the relative change in potentials of the electrodes of a dry cell, during discharge, a No. 6 cell was discharged continuously through a resistance of 10 ohms, and the potentials of the electrodes were measured at frequent intervals with a tenth-normal calomel electrode and a potentiometer (Fig. 3). It is noted that after the first 50 hours the potential of the zinc is very constant for the remaining 170 hours, while during the latter period of time the manganese dioxide electrode dropped 0.28 volt (from +0.04 to -0.24). From the previous discussion it is reasonable to assume that the reduced hydrogen-ion concentration is responsible for 0.15 or 0.20 volt of this drop. It, however, must not be forgotten that the chemical changes (reduction of the oxide) at the surface of the electrode during discharge would also lower the potential.

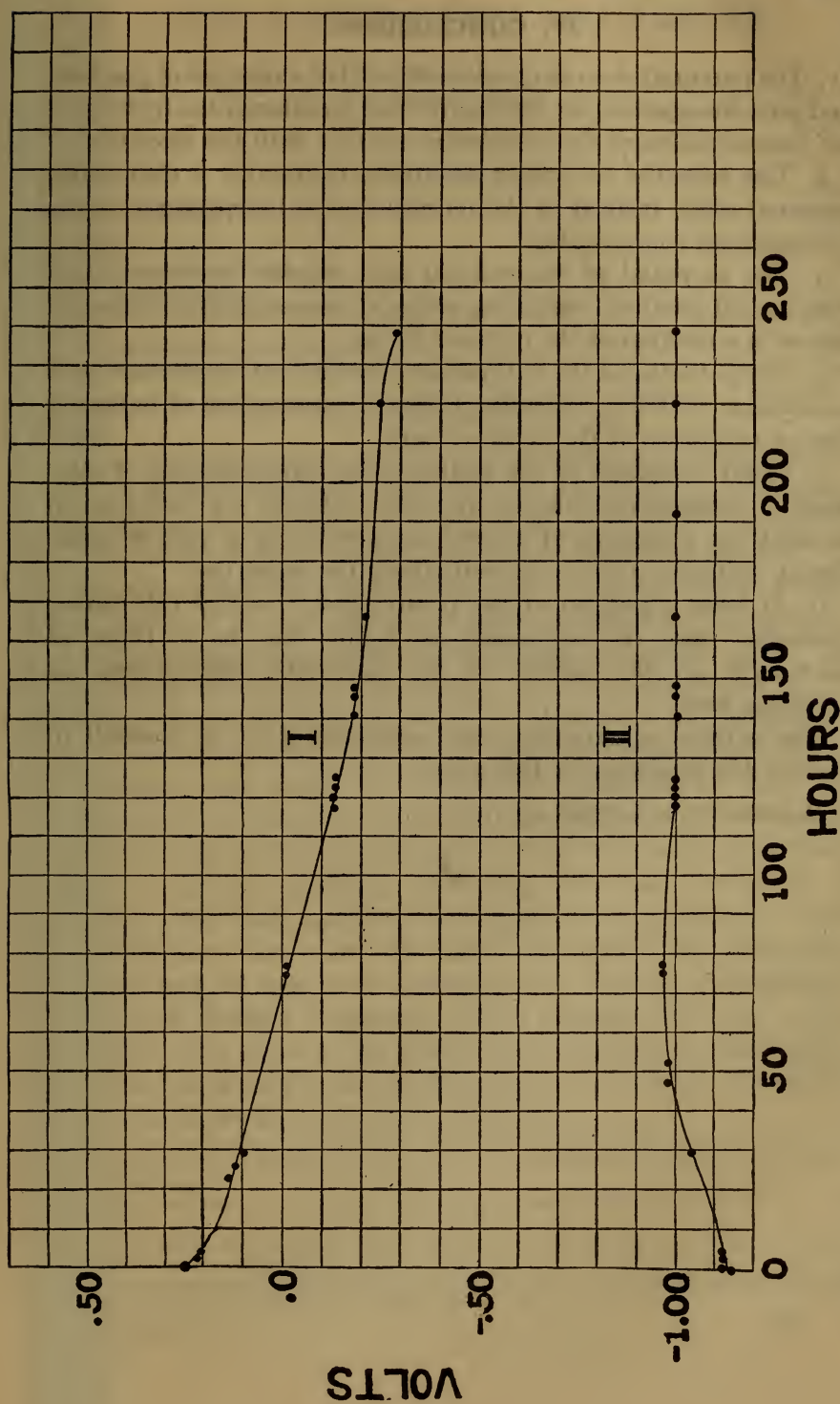


FIG. 3.—Relative change of the electrodes of a No. 6 dry cell when discharged through 10 ohms resistance and measured at frequent intervals of time with an N/10 calomel electrode and a potentiometer. Curve I represents the MnO₂ electrode and curve II the zinc electrode

IV. CONCLUSIONS

1. The potential of an electrode composed of a mixture of graphite and some manganese ores is a logarithmic function of the hydrogen-ion concentration of the solution in contact with the electrode.

2. The potential of similar electrodes containing a chemically prepared oxide instead of the natural ores is independent of the hydrogen-ion concentration.

3. The potential of the natural ores steadily decreased with time in acid solutions, indicating either a consumption of hydrogen ions or a reduction of the oxide or both.

4. The potential of the natural ores steadily but slowly increased in alkaline solutions, indicating either a consumption of hydroxyl ions or oxidation of the oxide or both.

5. Slight variations in the hydrogen-ion concentrations of solutions of ammonium chloride and zinc chloride are sufficient to account for variations of several hundredths of a volt in open-circuit voltages of dry cells containing the same ore.

6. At least a portion of the polarization of a dry cell during discharge may be explained as being due to a layer of electrolyte on the surface of the electrode impoverished in hydrogen ions.

The authors acknowledge the assistance of A. B. Goodall in making the drawings for this paper.

WASHINGTON, August 13, 1919.