THE POTENTIAL OF DRY CELLS WITH MAGNESIUM CHLORIDE ELECTROLYTE.

By V. L. R. Vepa.

INTRODUCTION.

The type of dry cell which is most used contains 20 to 25% of ammonium chloride solution, a little zinc chloride and often some calcium chloride. These cells are found unsatisfactory in tropical climates chiefly due to:—(*a*) creeping of ammonium chloride which not only results in a loss of electrolyte but also in the corrosion of the brass cap of the cell, and (*b*) the drying up of the electrolyte which retards the chemical action of the cell and lowers its life. To avoid these defects several organic as well as inorganic chemicals[1,2,3] have been tried to replace the ammonium chloride in the cell. Of these, magnesium chloride has found favour not only due to its greater hygroscopic properties but also its cheapness as compared with ammonium chloride. Besides this, it has been found that magnesium chloride cells give higher initial e.m.f., greater service, and longer shelf life as compared with ammonium chloride cells.

The potential of an electrode is largely determined by the nature and the pH value of the electrolyte in which it is immersed. So far, the importance of pH variation in dry cells has not been fully investigated and only a few papers [4,5,6,7,8] have been published which deal with this subject but most of these relate to cells with ammonium chloride as electrolyte. Martin and Helfrecht[6] found that the P.D. between the manganese dioxide—carbon electrode and 20% ammonium chloride solution varied from 0·3760 to 0·2903 as pH value of the solution was varied from 1·2 to 7·9, *i.e.*, a change in potential of 0·086 volt for a change in pH of 6·7. Owing to the suitability of

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[1] Thompson and Crocker, *Trans. Am. Electrochem. Soc.*, 1915, **27**, 155.

[2] Kostjejev, *Trans. Am. Electrochem. Soc.*, 1930, **58**, 305.

[3] Felix Kainz, *Chemiker-Zeitung*, 1932, **56**, 691.

[4] Holler and Ritchie, No. 364, Scientific Paper, *Bull. B. Stds.*, 1919-20, **15**, 659.

[5] Farrington Daniels, *Trans. Am. Electrochem. Soc.*, 1928, **53**, 52.

[6] Martin and Helfrecht, *Ibid.*, 1928, **53**, 83.

[7] Allmand, *Applied Electrochemistry*, 1924, p. 213.

[8] Keller, *Zeits. f. Electrochem.*, 1931, **37**, 342–348.

magnesium chloride cells for tropical climates and the absence of data relating to the variation of P. D. with pH of the electrolyte, this investigation was undertaken to examine the variation of P. D. of cells containing magnesium chloride electrolyte of various pH values.

EXPERIMENTAL.

Preparation of Electrode.—For experiments given here, Indian pyrolusite ore of 60 to 80 mesh containing 76% of manganese dioxide and flake graphite containing 97% of carbon were used. The carbon rods were each of 55 mm. length and 10 mm. diameter. Finished core was of 35 mm. diameter and 40 to 42 mm. high. The proportions, by weight, in this bobbin were 4 parts of pyrolusite ore to 1 part of flake graphite. The mass was wetted with a small amount of distilled water to facilitate moulding. It was tamped around a carbon rod under hydraulic pressure which was gradually raised up to 800 lbs. per square inch and the whole mass was then wrapped in a muslin cloth. The electrodes were then dried for 48 hours in a current of hot air, at about 100°C. obtained from an electrically operated air oven. A copper wire was soldered to the brass cap fitted on to the carbon rod to serve as a lead to the potentiometer terminal.

Preparation of Solutions.—Solutions of magnesium chloride having concentrations of 15, 20, 25 and 50% were prepared. Then solutions of different pH values from strongly acidic (pH 1 to 2) to slightly alkaline (pH 7 to 8) were obtained by adding definite amounts of acid or alkali to the above solutions.

Method of Measurement.—The pH value of the electrolyte in which manganese dioxide—carbon electrode was immersed was first determined with the help of quin-hydrone electrode. Next the potential of the electrode itself was measured against the saturated calomel cell in the solutions described above.

The schematic representation of the arrangement used in this set of experiments is:—

$$\text{Hg} \;:\; \text{HgCl} \left| \begin{array}{c}\text{Sat. KCl}\\ \text{solution}\end{array} \right| \begin{array}{c}MgCl_2\text{ of}\\ \text{known }(H^+)\\ \text{concentration}\end{array} \left| \; MnO_2\text{–C} \right.$$

The e.m.f. of this chain was measured with the potentiometer. The pH of the electrolyte was calculated from the potentiometer reading by using the well-known formula:

$$\text{pH} = \frac{E - E_{\text{std.}} - E_{\text{obs.}}}{0\cdot058}$$

where $E = (0\cdot7175 - 0\cdot00075\ t°\text{C.})$ volts.

The apparatus used is shown diagrammatically in Fig. 1.

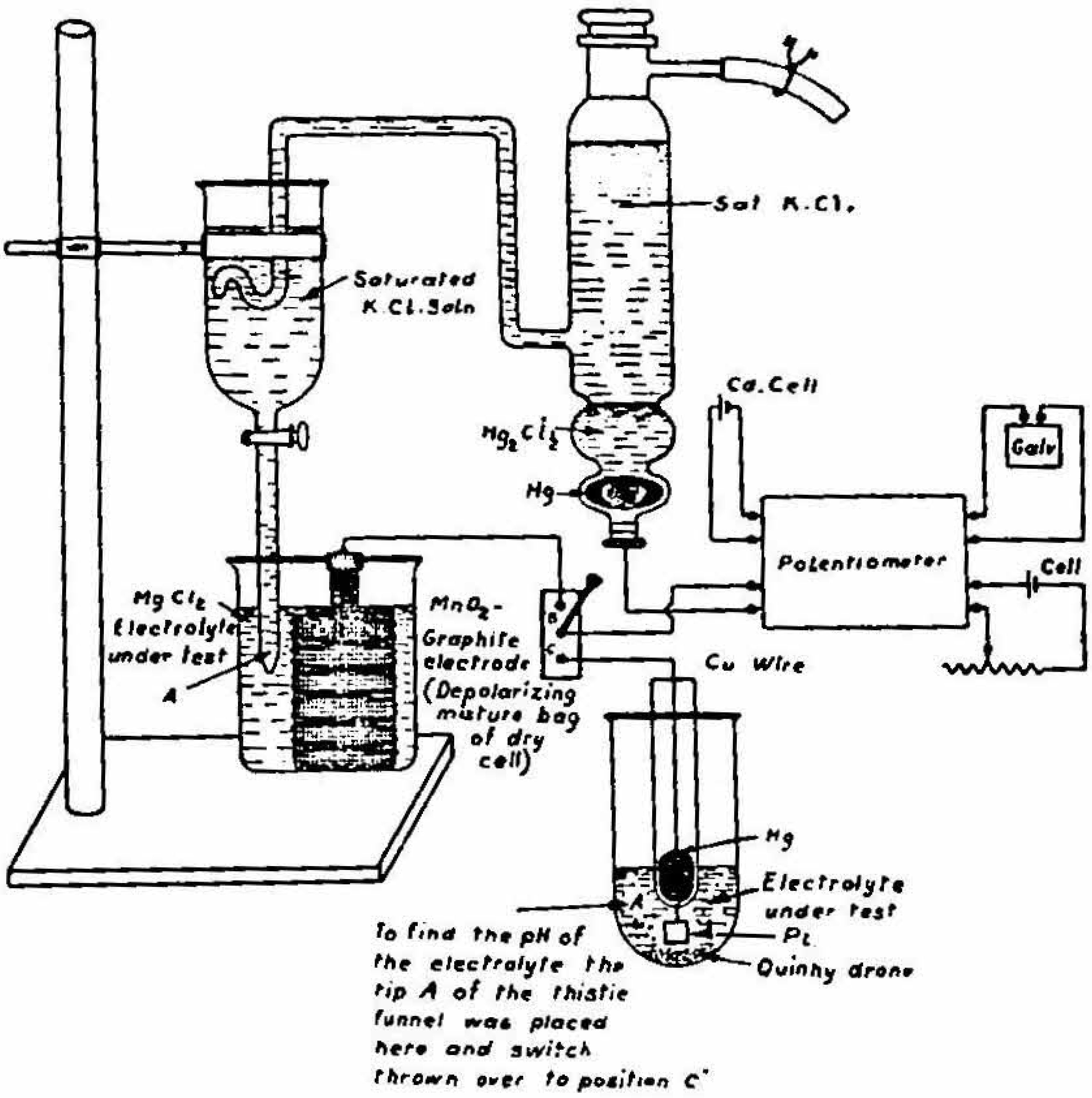

Fig. 1.

The arrangement of apparatus set up to measure the pH of magnesium chloride electrolytes and the P. D. of the manganese dioxide—carbon electrode.

Test Results.—Curves 1, 2, 3 and 4 in Fig. 2 show the results obtained from tests for magnesium chloride solutions of strength marked against the respective curves. Curve 5 in Fig. 2 is reproduced from a paper by Martin and Helfrecht[6] for comparison, as it relates to an electrode composed of caucasian pyrolusite ore containing 74·8% manganese dioxide which is nearest to the ore (76% manganese dioxide) used in the present experiments. The electrolyte used by Martin and Helfrecht was 20% ammonium chloride solution.

Variation of Potential with pH.—An examination of the curves in Fig. 2 shows that all the cells have a common characteristic, *viz.*, rapid falling of potential for pH values 1 to 3, a slight variation for pH values 3 to 6·5, a pronounced rise in every case for a pH value of about 6·5 and then again a rapid fall on entering the alkaline region. It is interesting to note that for all the four solutions tested, the maximum potential occurs at a value of pH lying between 0·75 and 1·5, and the point of maximum potential occurs further up on the pH scale as the percentage concentration of the solution is decreased.

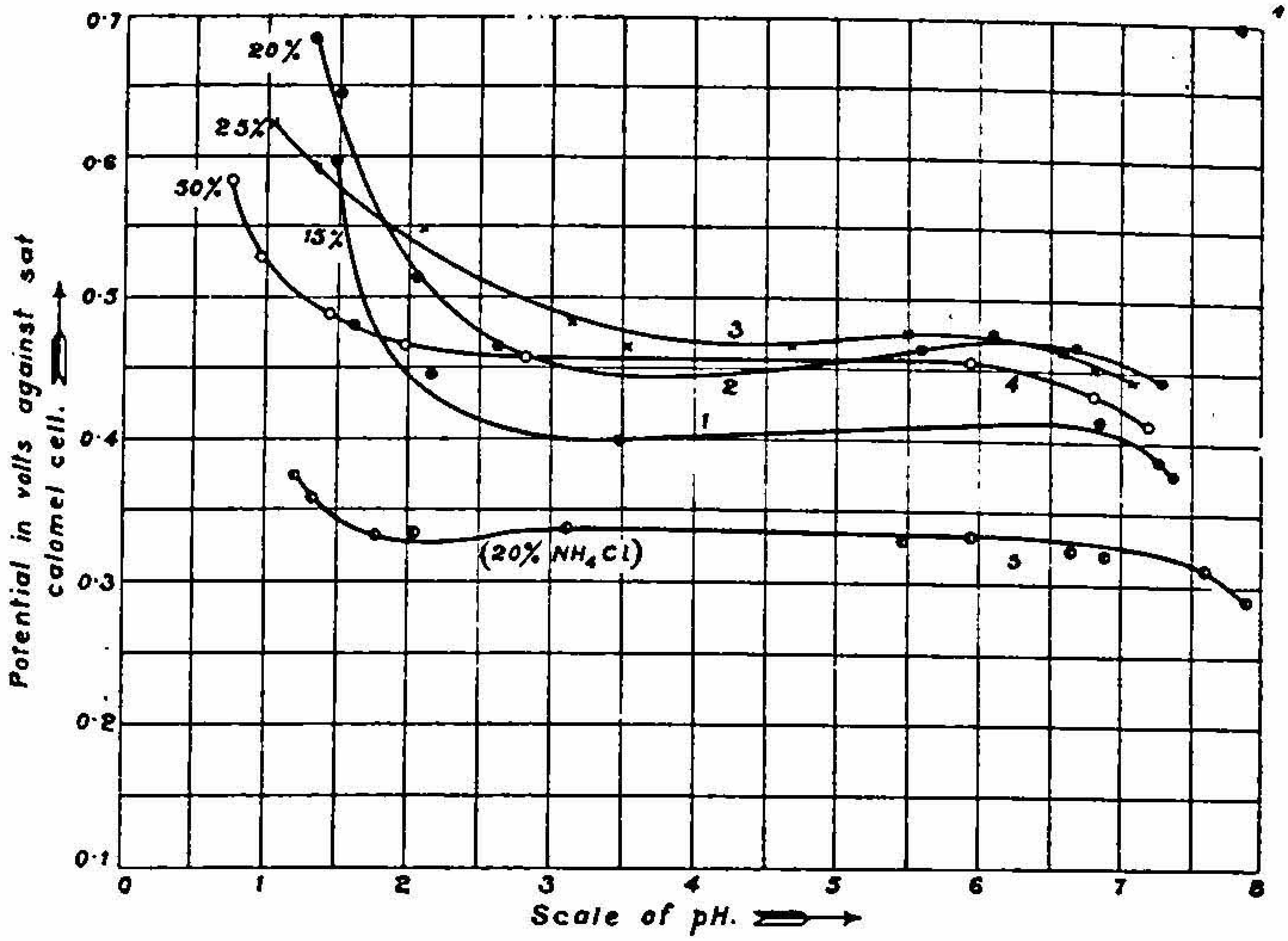

Fig. 2.

Graphs showing the variation in potential of manganese dioxide—carbon electrode with pH and strength of electrolyte.

It will be observed that with highly acidic solutions, a high initial potential is obtained but this is offset by the rapid drop in potential as the pH value approaches 2·5, and the destructive effect of the solution on the zinc of the cell. From considerations of steady potential and for minimising the corrosive effect of the electrolyte, it is advisable to start with a pH value of about 2·5. Comparing the four cells in the region of pH 2·5 to 6·5 which appears to be the most suitable working range, it will be seen that the maximum potential is obtained with 25% solution and the variation of potential during the life of this cell is quite satisfactory. A decrease in the strength of solution results not only in a decrease in the maximum potential but also a greater variation of potential during the life of the cell. With a 50% solution the potential is steadier during the life of the cell than with other solutions but the average potential is the lowest.

From considerations of economic production, high initial voltage and steady P. D. of the cell during its active life, it would appear that 25% solution is the most suitable.

CONCLUSIONS.

1. Average potential during the life of a magnesium chloride cell is higher than that of an ammonium chloride cell.

2. Maximum potential and change of potential during the life of a cell varies with the strength of the electrolyte.

3. From considerations of economic production, high initial voltage and steady P. D. of the cell during its active life, 25% solution is the most suitable.

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