lyte is the perchlorate. Hence the weighed washings from the nitrate are usually greater than from the perchlorate.

Two series of comparisons have recently been made, one with the anodes in porous cups, and the other with the anodes wrapped in Baker & Adamson's washed filter paper. In the first series the deposits from the perchlorate average 0.023 per cent. heavier than that from the nitrate. In one case only did the nitrate give a deposit heavier by an insignificant per cent.

In the other series with the filter paper, the deposit from the perchlorate average only 0.013 per cent. heavier, and in half of the series of six determinations the nitrate gave the heavier deposit. Taken all together, the comparisons thus far appear to show a slightly heavier deposit from the perchlorate, and at the same time the indications are that no reduction or other products are formed from the perchlorate and no complex anodic compound is present. We do not thus far find any advantage in using the porous cup; in fact the porous cup is objectionable from several points of view. Ordinary filter paper cannot be used, but the washed paper appears not to be objectionable. Further investigation will be necessary in order to settle this point definitely.

A LECTURE EXPERIMENT IN ELECTROLYTIC THERMO-ELECTROMOTIVE FORCE.¹

BY HENRY S. CARHART.

IN the Helmholtz equation for the E.M.F. of a voltaic cell,

$$E = \frac{H}{Q} + T \cdot \frac{dE}{dT},$$

the second term is dependent on the temperature coefficient of the cell, and this coefficient is admittedly due to the thermo-electromotive forces at the several junctions of dissimilar substances in the cell. Whenever, therefore, the conditions are such that the heat of reaction is negligible, the first term, H/Q , becomes zero and only the second term remains. Such are approximately at least the conditions in a Helmholtz concentration cell. The E.M.F. of such a cell is thermoelectric in origin and should be represented by the second term of the Helmholtz equation.

A concentration cell with pure silver electrodes and solutions of silver nitrate, whose ratio of concentrations was 5.26, gave an E.M.F. at 30° of 0.0452 volt. The mean of two determinations of the temperature coefficient, dE/dT , was 0.000144. Whence E , calculated by the expression $T \cdot dE/dT$, is 0.000144 $\times$ 303 or 0.0436.

¹ Abstract of a paper presented at the Ithaca meeting of the Physical Society, June 29-July 3, 1906.

A similar concentration cell with cadmium amalgam and one-tenth and one hundredth normal cadmium sulphate solutions had an E.M.F. at 22.35° C. of 0.034 volt. The mean temperature coefficient was 0.0001085. Whence the calculated value of E is 0.0001085×295.35 or 0.032. The calculated value in both cases is below the measured E.M.F., indicating that there is a little heat of reaction, due perhaps to mixing the solutions.

From the curve obtained by the author,¹ expressing the relation between the thermo-electromotive forces of $\text{Zn} - \text{ZnSO}_4$ and the corresponding concentrations of the zinc sulphate solution, the following equation may be derived:

$$dE = a \cdot T \cdot \frac{dC}{C}. \quad \text{Whence } E = a \cdot T \log C.$$

This expression is the potential difference at a single electrode. For two electrodes immersed in solutions of different concentrations, the expression becomes

$$E = a \cdot T \cdot \log \frac{C_2}{C_1}.$$

This equation will be recognized as the one derived by Nernst from the theory of osmotic pressure. The derivative of E with respect to T is

$$\frac{dE}{dT} = a \cdot \log \frac{C}{C}.$$

Solve for the constant a , substitute in the above equation for E , and we get $E = T \cdot dE/dT$, the second term of the Helmholtz equation. We have thus the nexus between the Helmholtz and the Nernst equations, and at the same time it appears that the latter may be derived from thermo-electric data.

The lecture experiment of the paper is intended to illustrate electrolytic thermo-electromotive force. Two fine iron wires are soldered to the ends of a piece of "constantan" wire as a thermal couple. The junctions are placed in thin glass tubes and a little mercury is poured in to conduct heat. A helix of fine copper wire is wound closely around the end of each tube outside the junction of the iron and constantan. The tubes with their thermal junctions are then immersed in a concentrated solution of copper sulphate, and current is passed through by means of the copper wires. A sufficiently sensitive galvanometer shows that a difference of temperature is soon established between the copper electrodes, the anode, where the current encounters an opposing E.M.F., being the warmer. Heat is generated at the anode and absorbed at the cathode by the thermo-electromotive force.

¹ Transactions of the American Electrochemical Society, Vol. II., p. 123.