

is reduced by the presence of that salt to $(1.1 \times 10^{-5})^2 = 1.21 \times 10^{-10}$. Substituting these values, the calculated E.M.F. of the silver cell at 15°C is

$$\pi = -0.0002 \times 288 \times \log_{10}(1.21 \times 10^{-9}) = 0.52 \text{ volts}$$

a result which agrees sufficiently well with the observed value 0.51 volts.

An analogous explanation may be offered for the "abnormal" behavior of silver in a solution of silver potassium cyanide.* In a cell of

Silver | Silver-potassium cyanide | Lead nitrate | Lead

not only does the E.M.F. observed bear no apparent relation to that of silver against lead in a solution of their nitrates, but its very sign is changed; and whereas in the latter case the lead is negative with reference to the silver, in the cyanide cell it is the silver that dissolves. "Abnormal" cases such as this, which have contributed largely to the overthrow of the older electrochemical theories, and which seemed to argue against the possibility even of a definite order for the metals in the "Electrochemical Series," may, by means of the methods explained in this paper, be brought under the same category as the others, and their E.M.F. may be calculated without the introduction of any new hypotheses.

In this paper, an endeavor has been made to show how the introduction of the conception of "osmotic pressure" in conjunction with the first and second main principles of thermodynamics has led to the evolution of a theory of solutions, which includes a quantitative account of the relations existing between phenomena so diverse as are the vapor tension, freezing and boiling points of solutions, their electrical conductivity, and its dependence on dilution, and the alteration in their concentrations produced by the passage of a current, and which lends itself to the solution of problems in connection with the E.M.F. of various voltaic batteries in a manner as accurate as it is simple and straightforward. It must not be supposed, however, that more than a mere sketch of the subject has been attempted, or that even the points of contact between the new theory and the electrical phenomena have been extensively reviewed; the temperature

*Such a solution contains extremely few Ag ions. See *Leblanc and Noyes*, Ueber vermehrte Löslichkeit, *Z. Ph. Ch.*, VI., 397, 1890.
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