THE ELECTROMOTIVE FORCE OF CELLS CONTAINING DILUTE HYDROCHLORIC ACID

Sir:

In a recent paper Carmody [THIS JOURNAL, **54**, 188 (1932)] has published the results of some very accurate measurements of the e. m. f. of cells containing dilute solutions of hydrochloric acid. Mainly owing to the use of silica vessels these results differ from those of Linhart [THIS JOURNAL, **41**, 1175 (1919)] and of Nonhebel [*Phil. Mag.* [7] **2**, 1085 (1926)] but it can be shown that the results of these earlier workers are not incompatible with those of Carmody.

It has been suggested elsewhere [*J. Phys. Chem.*, **31**, 1647 (1927)] that the conductivity data for strong acids and bases in dilute solution can be corrected for the effect of impurities by the equation

$$\Lambda = \Lambda_0 - bc^{1/2} - k/c$$

where b is a constant calculable from Onsager's theory or determinable experimentally and k is a measure of the amount of acid removed by the
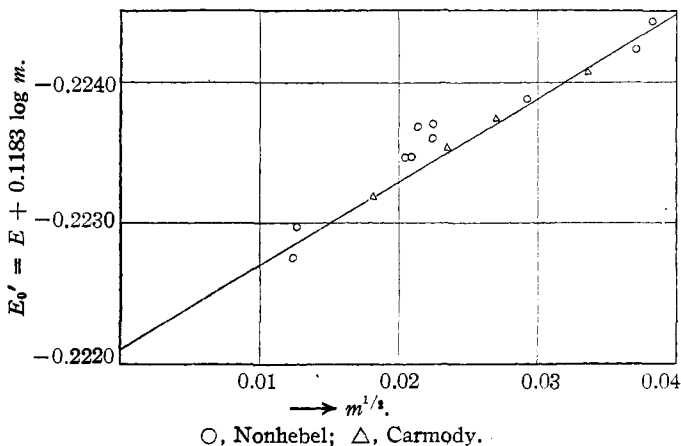

O, Nonhebel; △, Carmody.

Fig. 1.

impurities which either have dissolved from the glass or were originally present in the water. By the courtesy of Sir Harold Hartley, F.R.S., I have been able to avail myself of some measurements by Marshall on the conductivity of dilute solutions of hydrochloric acid in cells of similar glass and water of comparable conductivity to those employed by Nonhebel. Using the above equation, I have calculated from these data that Nonhebel's results are about 0.0010 volt high at 0.0001 molal and 0.0001 volt high at 0.001 molal. Even Carmody's results require a slight correction which can be calculated from the recent conductivity data of Jeffery and Vogel [*J. Chem. Soc.*, 400 (1932)], who employed silica cells and water of

about the same conductivity as that used by Carmody: the correction lowers Carmody's most dilute point by 0.00012 volt.

The corrected data are plotted in the accompanying diagram and the straight line is drawn with the slope required by the limiting equation of Debye and Hückel. It is evident that the agreement is satisfactory and that the most probable value of E_0 is 0.2221 volt, which is the value previously adopted by Randall and Young [THIS JOURNAL, **50**, 989 (1928)].

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THE ESTIMATION OF IRON IN SOLUTIONS CONTAINING BOTH BIVALENT IRON AND TRIVALENT TITANIUM

Sir:

It is known that sulfuric acid solutions of ferrous sulfate undergo oxidation but very slowly at room temperatures.[1] Thus, Baskerville and Stevenson[2] found that upon passing air for twelve hours through a sulfuric acid solution of Mohr's salt, there resulted but 0.0001 g. of Fe^{+++} out of a total of approximately 0.71 g. of Fe^{++}.

Furthermore, titanous sulfate solutions of ordinary acidity are extremely unstable in air. Thus, while reduction of titanium in the Jones reductor proceeds quantitatively to the trivalent condition, the deoxidized substance is usually collected under a protective solution, such as ferric sulfate, whereby the titanium is immediately converted to the quadrivalent state with the formation of an equivalent amount of the more stable ferrous sulfate.[3]

These facts, namely, the stability of acidified ferrous sulfate solutions and the instability of acidified titanous sulfate solutions toward atmospheric oxidation, suggested the possibility of estimating Fe^{++} in the presence of Ti^{+++} by subjecting the solution containing these ions to an air-bubbling process. It was hoped that in the time required to effect the complete oxidation of the Ti^{+++} the amount of Fe^{++} oxidized would be negligible, so that titration of the aerated solution with standard potassium permanganate would give a value corresponding to the iron alone.

This hope has indeed been realized and we have found that results obtained by the method outlined above are in good agreement with those obtained by the well-known method of Gooch and Newton,[4] wherein the Ti^{+++} is oxidized by bismuth trioxide, which does not affect the Fe^{++}, the metallic bismuth thus precipitated and excess bismuth oxide removed by

[1] McBain, *J. Phys. Chem.*, **5**, 623 (1901).
[2] Baskerville and Stevenson, THIS JOURNAL, **33**, 1104 (1911).
[3] Lundell and Knowles, *ibid.*, **45**, 2620 (1923); *Ind. Eng. Chem.*, **16**, 723 (1924).
[4] Gooch and Newton, *Am. J. Sci.*, **23**, 365 (1907); Newton, *ibid.*, **25**, 343 (1908).