

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 Stevenson² 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).

filtration, and the filtrate, containing the Fe^{++} , titrated with standard permanganate in the usual manner.

Lundell and Knowles⁵ have shown that sulfuric acid solutions of uranous sulfate, like ferrous sulfate, exhibit marked stability toward air oxidation, and we hope to employ our differential oxidation procedure in the evaluation of uranium in solutions containing U^{++++} and Ti^{+++} .⁶ Other determinations, involving similar combinations, suggest themselves as possibilities in the further application of this method.

In the course of this work, a technique has been developed for the preparation of very pure solutions of titanous sulfate and titanous sulfate.

We expect to publish a complete account of this work in the near future.

⁵ Lundell and Knowles, *THIS JOURNAL*, **47**, 2637 (1925).

⁶ Cf. Newton and Hughes, *ibid.*, **37**, 1711 (1915).

⁷ J. T. Baker Chemical Company Fellow in Analytical Chemistry, 1930-1931.

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PENTAVALENT BORON

Sir:

A compound of boron has been prepared which has the formula BR_3Na_2 in which R is the α -naphthyl group. This compound seems to be of a type not heretofore known and to be of particular interest from the standpoint of valence theory.

The compound has been prepared by treating tri- α -naphthyl boron in ether solution with 40% sodium amalgam in the absence of air and water.¹ The solution turns first yellow and finally black as the reaction progresses. Upon hydrolyzing the ether solution and titrating with acid the number of mols of sodium was found to be twice (1.97-1.98) the number of mols of the tri- α -naphthylboron originally introduced into the solution. The compound was then prepared in crystalline form from a mixture of ethyl ether and petroleum ether. It is nearly black in color, somewhat resembling iodine in appearance. This material was analyzed for sodium and boron. A second crop of crystals was obtained from the mother liquor. This had the same appearance and gave the same analysis. The analyses indicated one molecule of ether of crystallization, which was removed quantitatively by evacuating and heating to 175°. The first analysis given below is for the first crop of crystals, the second for the crop

¹ A solution of this compound was undoubtedly first obtained by Krause and Nobbe [*Ber.*, **63**, 934 (1930)] but inasmuch as they did not analyze their product they naturally assumed that it was a monosodium addition compound as in the case of triphenylboron.