up. The samples of the alcohols employed for this purpose melted at 24.6° and −11.1°, respectively, the butyl alcohol being a reserve material which was somewhat less pure than that used in the preceding molecular weight determinations. The freezing points of these solutions were then measured and found to be in all cases intermediate between those of the two alcohols. The results can be seen plotted in Fig. 2. They lie very consistently upon a curve which is typical of a system that forms mixed crystals on freezing. There is no indication of a eutectic point, such as would be necessary if pure crystals of the two components were separating out.

Of course, the application of Equation 1 to such a system, in which mixed crystals are formed on freezing, is not legitimate, and this fact explains our erratic molecular weight results for *t*-amyl alcohol and also, in all probability, for the propyl and butyl secondary alcohols.

Summary

The suitability of tertiary butyl alcohol as a solvent for molecular weight determinations by the freezing point method has been studied. From thermodynamic data and from the freezing point depressions of solutions of six typical solutes a value of 8.25 has been suggested for the cryoscopic constant. The molecular weights of twenty-eight compounds dissolved in tertiary butyl alcohol have then been determined. The results indicate that this solvent is satisfactory in cryoscopic determinations for most types of organic compounds, including primary alcohols and all classes of hydrocarbons. However, it cannot be used when certain closely related secondary and tertiary alcohols are the solutes because of the formation of mixed crystals on freezing.

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RECEIVED DECEMBER 17, 1934

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

The Estimation of Iron in the Presence of Titanium: An Aeration Process[1,2]

BY WILLIAM M. THORNTON, JR., AND REUBEN ROSEMAN[3]

A number of years ago Gooch and Newton[4] published an interesting volumetric process for estimating iron in the presence of titanium. This method depends upon the fact that, if to a sulfuric acid solution containing bivalent iron and trivalent titanium solid bismuth trioxide be added, the titanium is completely oxidized to the quadrivalent state while the ferrous iron is not appreciably affected. After filtration from the surplus bismuth oxide and the precipitated bismuth, the iron can be titrated with a standard solution of potassium permanganate.

Now it is known that sulfuric acid solutions of ferrous sulfate undergo atmospheric oxidation but very slowly at room temperatures.[5] Thus, Baskerville and Stevenson[5] found that on passing air for twelve hours through a solution of Mohr's salt, acidulated with sulfuric acid, there resulted only 0.0001 g. of Fe^{+++} out of a total of approximately 0.71 g. of Fe^{++}. On the other hand, titanous sulfate solutions of ordinary acidity are extremely unstable in air. Accordingly, while reduction of titanium in the Jones reductor proceeds quantitatively to the trivalent condition, the deoxidized substance is usually collected under a protective solution (ferric sulfate), whereby the titanium is converted immediately to the quadrivalent state with the formation of an equivalent amount of the more stable ferrous sulfate.[6]

This greater stability toward atmospheric oxidation on the part of ferrous sulfate 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

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(1) From Ph.D. dissertation of Reuben Roseman, Johns Hopkins University, June, 1933.

(2) For a preliminary report of this work see Thornton, Roseman and Katzoff, THIS JOURNAL, **54**, 2131 (1932).

(3) Holder of the J. T. Baker Chemical Company Research Fellowship in Analytical Chemistry (Eastern Division), 1930–1931.

(4) Gooch and Newton, *Am. J. Sci.*, [4] **23**, 365 (1907).

(5) See, for example, McBain, *J. Phys. Chem.*, **5**, 623 (1901); Peters and Moody, *Am. J. Sci.*, [4] **12**, 369 (1901); Varinskii and Laska, *Ann. chim. anal. appl.*, **14**, 45 (1909); Baskerville and Stevenson, THIS JOURNAL, **33**, 1104 (1911); Hillebrand, U. S. Geol. Survey, *Bull.* **700**, 199 (1919); Jilek, *Chem. Listy*, **15**, 105, 138 (1921); Banerjee, *Z. anorg. allgem. Chem.*, **128**, 343 (1923); Posnjak, *Am. Inst. Mining Met. Eng.*, No. **1615D** (1926); Friend and Pritchett, *J. Chem. Soc.*, 3227 (1928); Lamb and Elder, THIS JOURNAL, **53**, 137 (1931); Lundell, Hoffman and Bright, "Chemical Analysis of Iron and Steel," John Wiley & Sons, Inc., New York, 1931, p. 115.

(6) Lundell and Knowles, THIS JOURNAL, **45**, 2620 (1923); *Ind. Eng. Chem.*, **16**, 723 (1924). *Cf.* Newton, *Am. J. Sci.*, [4] **25**, 130 (1908).

conversion of the Ti^{+++} to 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.

Experimental

The titanic sulfate solution (approximately 0.1 N) was prepared from purified chemicals in conformity with the procedure recommended in a foregoing paper,[7] and its titer was set with the aid of the reductor, following essentially the instructions of Lundell and Knowles.[6]

The iron solution was made from a sample of ferric ammonium sulfate, which had been procured from a well-known, and supposedly reliable, manufacturer, in such a way as to guard against the presence of ferrous salt.[8] This solution, likewise about 0.1 N, was similarly standardized by the reductor method.[6]

The 0.1 N potassium permanganate solution was scrupulously freed from organic matter and hydrated manganese dioxide, whereupon its exact concentration was determined by means of the certified sodium oxalate of the National Bureau of Standards in accordance with the technique of McBride.[9]

The titanic sulfate and ferric alum solutions in admixture with each other (or alone) were drawn through the Jones reductor in the approved manner,[6] and then air was bubbled through them for varying periods of time,[10] the duration of the operation depending upon the amount of titanium present. The solutions thus aerated were titrated with the standard permanganate in the usual way.

To aerate a solution, the 1-liter flask (with side tubulure) containing it was first closed with a rubber stopper, through which passed a piece of glass tubing. One end of this tube dipped well into the liquid. Having made the customary connections, a stream of air was pulled rapidly through the solution by running water at full speed, or nearly so, through a Chapman filter pump; meanwhile a rotary motion was imparted to the contents of the flask by hand at frequent intervals.

The wide difference between ferrous sulfate and titanous sulfate as regards resistance to oxidation by air was first confirmed. The results of Table I show that ferrous sulfate, in a solution slightly acidified with sulfuric acid, is scarcely affected by thirty minutes of aeration; while titanous sulfate, under like conditions, is almost, though not quite, completely oxidized. It appears, however, that when the two salts are present in the same solution they are not without influence, one upon the other, while undergoing oxidation at the expense of a series of air bubbles. Thus in the experiments recorded in Table II, in which sulfuric acid solutions containing known quantities of iron and titanium were subjected to the treatment delineated above, the findings are reasonably near to the true values (those found by standardization). Yet it may be well to introduce the proviso that the procedure is most apt to succeed when the iron is equal to, or preponderates over, the titanium.

Table I

Relative Stability of Sulfuric Acid Solutions of Ferrous Sulfate and Titanous Sulfate toward Air Oxidation

Test solutions passed through reductor prior to aeration

0.1 N $NH_4Fe(SO_4)_2$ taken, cc.	0.1 N $Ti(SO_4)_2$ taken, cc.	Aeration, min.	0.1 N $KMnO_4$ required, cc.
24.96	..	0	25.00
24.96	..	30	24.98
29.92	..	0	29.99
29.92	..	31	30.00
...	10	15	0.27
...	25	20	.09
...	50	30	.45

Table II

The Estimation of Iron in the Presence of Titanium

0.1 N $NH_4Fe(SO_4)_2$ taken, cc.	0.1 N $Ti(SO_4)_2$ taken, cc.	Aeration. min.	Iron taken, g.	Iron found, g.
24.96	5	10	0.1555	0.1557
24.97	10	15	.1556	.1555
24.97	20	15	.1556	.1555
1.00	25	20	.0062	.0065
4.99	25	25	.0311	.0318
24.97	25	20	.1556	.1554
24.97	30	20	.1556	.1553
24.97	40	25	.1556	.1554
24.97	50	30	.1556	.1560

As to the interfering action of such elements (other than titanium) as are likely to be present in the material under examination—for example, a titaniferous iron ore—both manganese and chromium have been studied experimentally, but no tests have as yet been made with vanadium. Bivalent manganese seems to have no effect upon the ferrous salt when the titanous sulfate is oxidized by the passage of air through the solution.[11] Small amounts of chromium were found to behave in much the same way as titanium, but when the chromium was present in large quantity as compared with the iron it proved very difficult to convert the chromous sulfate completely to the corresponding chromic compound. However, no

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[7] Roseman and Thornton, This Journal, **57**, 328 (1935).

[8] Thornton, "Titanium," The Chemical Catalog Company, Inc., New York, 1927, p. 227.

[9] McBride, This Journal, **34**, 393 (1912).

[10] It is important to continue the air stream for ten to fifteen minutes after the color of the titanous ion has vanished.

[11] Unpublished experiments by S. I. Katzoff.

experiments, in which both chromium and titanium were associated with the iron, were carried out.[12]

In addition to the work that has just been recorded, an attempt was made to substitute the air-bubbling process for the treatment with bismuth oxide in Newton's method[13] for determining iron, wherein the ferric salt is deoxidized by means of a previously prepared solution of titanous sulfate, the rest of the procedure being the same as that of the Gooch and Newton[4] process. Strangely enough, it was found that the outcome of the experiments depended somewhat upon the way in which the titanic sulfate had been reduced, in order to obtain the desired reagent. When the necessary valence change was brought about with the aid of a reductor,[14] the resulting solution could be used in the procedure and relied upon to yield a result in satisfactory agreement with the standard value.[15] When, on the other hand, the refined electrolytic process[7] was employed for the deoxidation of the titanic compound, the solution so obtained gave rise to results that were noticeably too low. It would seem, therefore, that the matter requires further investigation.

Summary

As the differential oxidizing agent ordinary air has been substituted, with a fair degree of success, for bismuth trioxide in the Gooch and Newton process for estimating iron in the presence of titanium.

(12) Unpublished experiments by B. W. Allan.

(13) Newton, *Am. J. Sci.*, [4] **25**, 343 (1908).

(14) Van Brunt, THIS JOURNAL, **36**, 1426 (1914); Bray, Simpson and MacKenzie, *ibid.*, **41**, 1363 (1919); Lundell and Knowles, *ibid.*, **45**, 2620 (1923).

(15) Reductor values taken as correct.

BALTIMORE, MD. RECEIVED DECEMBER 19, 1934

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Hydrides of Boron. IV. The Methyl Derivatives of Diborane

BY H. I. SCHLESINGER AND A. O. WALKER[1]

Although diborane has an atomic arrangement similar to that of ethane, as shown by x-ray data[2] taken at low temperatures, the bonds in the two compounds must differ in certain fundamental respects, for the molecule of diborane does not contain enough valence electrons to establish doublet bonds between the atoms involved. Many suggestions have been made concerning the structure of diborane;[3] although all of these lack the support of an adequate experimental basis, those assuming some type of single electron bond between boron and hydrogen seem at present most satisfactory as working hypotheses. To account for the molecular formula of diborane, four of the six hydrogen atoms are usually thought of as bound by ordinary doublet bonds; each of the two remaining hydrogen atoms is bound by a single electron bond to each of the two boron atoms.[4]

For a molecule so constituted, one need not assume that the same two hydrogen atoms are at all times held by single electron bonds. The situation is, however, different in a compound in which four of the hydrogen atoms are replaced by other atoms or groups, for boron compounds containing no boron to hydrogen linkages have, in general, formulas consistent with the ordinary present-day concepts of valence.

The present investigation was undertaken to obtain data which might be of value in deciding to what extent the idea of the single electron bond might aid in suggesting new lines of investigation and in interpreting observations in the chemistry of the boron hydrides. It was hoped that the methyl derivatives might be stable enough to allow the preparation and isolation of all of those capable of existence. Should there be marked differences in properties and stability of the tetra-

(1) Taken from a dissertation submitted by A. O. Walker to the Faculty of the Division of the Physical Sciences of the University of Chicago in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Mark and Pohland, *Z. Krist.*, **62**, 103 (1925).

(3) Eastman, THIS JOURNAL, **44**, 438 (1922); Robinson, *Trans. Faraday Soc.*, **18**, 298 (1922); Main-Smith, *Chem. News*, **135**, 81 (1927); Sugden, *J. Chem. Soc.*, 1173 (1927); Wiberg, *Z. anorg. allgem. Chem.*, **173**, 199 (1928); Sidgwick, "The Electronic Theory of Valency," Oxford Press, 1927; Pauling, THIS JOURNAL, **53**, 3225 (1931).

(4) According to Mullikan, *Phys. Rev.*, **43**, 765 (1933), a molecule so constituted should possess magnetic properties which a preliminary investigation, carried out in this Laboratory, fails to disclose. Since the work has not yet been extended to low temperatures, and since the theoretical basis for the conclusion is as yet uncertain, this discrepancy will, for the present, be neglected.