

A NEW METHOD OF DETERMINING IRON, NITRITES, ETC.

JOHN W. CALVIN.

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In the experiments reported below an effort was made to determine substances such as ferrous iron, nitrites, etc., that reduce hydrogen per-oxide quantitatively, by titrating them directly against a standard solution of hydrogen peroxide, using a titanium solution as an indicator. It was to determine whether or not it is possible to use a titanium solution as an indicator to show when the oxidation is complete, that the experiments were taken up.

The fact that a yellow or orange color is produced when hydrogen peroxide is added to a titanium solution, was discovered by Schon, and has long been known as a delicate test for both hydrogen peroxide and titanium. Although this reaction has been known about thirty years, in examining the literature on the subject, very little is found. In the Journal of the Chem. Soc., 1874, the yellow or orange color formed when a solution of titanium, made by digesting titanium oxide in concentrated sulphuric acid, is added to a solution of hydrogen peroxide, is given as a delicate test for the latter. In the Chemical News, Vol. 47, Edward Jackson gives an article in which he says in substance, if hydrogen peroxide is added to a solution of the chloride or sulphate of titanium, a fine yellow color is formed which is a delicate test for both the peroxide and titanium; the test being so delicate that $\frac{1}{50,000}$ th part of titanium or $\frac{1}{25,000}$ th part of hydrogen peroxide is sufficient to produce the color. In an abstract in the Journal of the Chem. Soc. from the Ber. d. Deutsch Chem. Ges., 1882, Weller gives a method of determining small amounts of titanium colorimetrically by means of the yellow color produced when hydrogen peroxide is added to the solution of titanium. The color produced

in the unknown solution is compared with that produced by a standard solution made by dissolving pure potassium titanofluoride.

Experiments were made using ferrous salts, nitrites, and sulphites. A solution to be used as an indicator was made by digesting titanium oxide with about three times its weight of potassium acid sulphate and a little concentrated sulphuric acid. After digesting this mixture for twenty minutes, the oxide dissolved. The solution was then diluted with water. On the addition of a small amount of water a white precipitate was formed, but on the addition of more water and warming, the precipitate redissolved. About one gram of titanium oxide was used for 150 c.c. of the solution.

Some preliminary experiments were made, using a stock solution of ferrous ammonium sulphate which contained small amounts of sulphuric acid and ammonium sulphate. Several portions of this solution were measured out with a pipette and to each was added about 200 c.c. of water, 5 c.c. of phosphoric acid to remove the yellow color of the iron solution, and 5 c.c. of indicator solution. The hydrogen peroxide was run in from a burette. It was found that the indicator gave a sharp end point that could be easily detected after a little practice. On the addition of a slight excess of the peroxide a yellow color appeared which disappeared if a drop of the iron solution was added. In these experiments the duplicates agreed closely. Next some experiments were made using weighed portions of ferrous ammonium sulphate. Four portions of the iron salt were weighed out from a weighing bottle and dissolved in about 200 c.c. of water. To each was added about 5 c.c. of sulphuric acid, 5 c.c. of phosphoric acid, and 5 c.c. of the indicator. The hydrogen peroxide was run in from a burette. The results of these experiments, shown in table I., do not agree. The only explanation that could be thought of for this

TABLE I.

Weight of salt.	Amt. H_2O_2 used.	Amt. H_2O_2 required for 1 gm. salt.	
0.1985 gm's.	5.73 c.c.	1 gm.	28.86 c.c.
0.4480 "	12.44 c.c.	1 gm.	27.77 c.c.
0.3405 "	9.86 c.c.	1 gm.	28.96 c.c.
0.4641 "	13.16 c.c.	1 gm.	28.36 c.c.

disagreement, when the first experiments did agree, was that the ammonium sulphate used in the stock solution must play some part in the reaction. To test this supposition, seven portions of the iron salt were weighed out and treated the same as the above, except that to each about 1gm. of ammonium sulphate was added. The results of these experiments, shown in Table II. agree within the limit of experimental error.

Gms. salt taken.	c.c. peroxide required.	Amt. of H_2O_2 required for 1 gm.	
0.1902	3.09 c.c.	1 gm.	16.24 c.c.
0.3420	5.54 c.c.	1 gm.	16.19 c.c.
0.4918	7.90 c.c.	1 gm.	16.07 c.c.
0.6258	10.11 c.c.	1 gm.	16.15 c.c.
0.5374	8.74 c.c.	1 gm.	16.25 c.c.
1.1133	17.82 c.c.	1 gm.	16.11 c.c.
1.4645	23.45 c.c.	1 gm.	16.01 c.c.

As the strength of the hydrogen peroxide used in the above experiments was not exactly known, some experiments were made in which the peroxide used was standardized against iron in the same way as the above experiments, and also against a standard solution of potassium permanganate. In these experiments the normality of the peroxide as shown by the iron was .1498, while the normality as shown by the permanganate was .1507. From the above experiments we can draw the

conclusion first, that it is possible to use titanium salts as an indicator for such reactions as that between ferrous iron and hydrogen peroxide; and second, that the presence of the ammonium sulphate plays some part in the reaction.

While making the above experiments it occurred to the writer that the method used in them would be an easy way of determining the strength of hydrogen peroxide solution. The end point is easily seen and a small trace of organic matter would doubtless not affect the results as it does in the permanganate method.

Some experiments were made with sodium sulphate, but it seemed that the sulphites were not oxidized quantitatively by hydrogen peroxide. Some experiments were then made with the nitrites. An approximately .5 normal solution of sodium nitrite was used. Portions of this solution were measured from a burette and diluted. Owing to the fact that the acid of the indicator liberated oxides of nitrogen, a trial portion was first taken, the indicator added, and the peroxide run in until a yellow color appeared. By this portion the approximate quantity of peroxide necessary to add, was found. Other portions were then taken and nearly enough hydrogen peroxide added to complete the reaction, then the indicator was added and enough peroxide added to complete the reaction. The results gotten by this method were fairly close, but not entirely satisfactory. If more time had been put on the method, good results could doubtless have been gotten.

SUMMARY.

First, it is shown that by using a titanium solution as an indicator, substances which are oxidized quantitatively by hydrogen peroxide, can be determined by titrating them directly against a standard peroxide solution.

Second, that ammonium sulphate plays some part in the reaction

between ferrous ammonium sulphate and hydrogen peroxide.

Third, that by the use of a titanium solution as an indicator, and a standard iron solution, the strength of hydrogen peroxide solution can be easily determined even in the presence of small traces of organic matter.