

1922

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Recommended Citation

Hendrixson, W. S. and Verbeck, L. M. (1922) "Electrometric Titration of Sulfurous Acid with Permanganate," *Proceedings of the Iowa Academy of Science*, 29(1), 361-364.

Available at: <https://scholarworks.uni.edu/pias/vol29/iss1/75>

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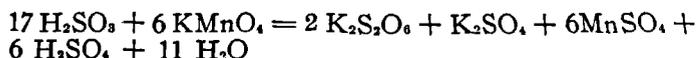
Contribution from the Chemical Laboratory of Grinnell College

ELECTROMETRIC TITRATION OF SULFUROUS ACID
WITH PERMANGANATE

W. S. HENDRIXSON AND L. M. VERBECK

The purpose of this work was to determine whether sulfurous acid in acid solution is completely oxidized to sulfuric acid by an excess of permanganate as stated in the literature. If so the excess of permanganate should be easily and accurately determinable electrometrically with potassium iodide thus giving a simple method for determining sulfur dioxide, sulfurous acid or sulfites. The results show that with a small or large excess of permanganate only about 90 per cent is oxidized to sulfuric acid, the remainder of the sulfurous acid probably forming dithionic acid.

The practicability of titrating sulfurous acid with permanganate seems so obvious that it is not surprising that it has been attempted by many chemists, though the results have many times been shown to be too low and discordant. For this fact two causes have been assigned, loss of sulfur dioxide and the incomplete oxidation to sulfuric acid by permanganate whether in excess or not. Nearly forty years ago Honig and Zatzek¹ stated that permanganate did not oxidize sulfurous acid completely to sulfuric acid in acid solution, but only in neutral or alkaline solution. In titrating sulfurous acid with permanganate Dymond and Hughes² obtained as the average 88.9 per cent of oxygen used as compared with theory for complete oxidation. By separate experiments on a large scale they definitely proved the formation of dithionic acid when they at the same time ran permanganate and sulfur dioxide into cold water, keeping the sulfur dioxide in excess. They regarded the formation of the dithionic acid as an essential part of the reaction, and due to a stage in the reaction, namely, the reduction of MnO_2 to MnO . Their equation is,



¹ Honig and Zatzek, *Monatshefte, f. Chem.*, 4, 738.

² Dymond and Hughes, *Jour. Chem. Soc.* 71, 314 (1897).

which would require 88.2 per cent of the oxygen required for complete oxidation to sulfurous acid. They say, however, "When a solution of sulfurous acid is poured into an excess of permanganate only sulfuric acid is found."

Pinnow³ carried out several series of titrations of sulfite with permanganate in parallel with titrations by the iodine method. The oxidation to sulfuric acid was never found to be complete. Temperature, concentration and acidity had little influence. His results vary from 90.9 per cent in acid to 97.2 in alkaline solution. He also assigned the discrepancy to the formation of varying amounts of dithionate.

Possibly encouraged by the statement quoted from Dymond and Hughes two papers have appeared which propose the determination of sulfurous acid by oxidation with an excess of permanganate. Milbauer⁴ added a very dilute solution of the sulfurous acid to ten times the requisite permanganate to oxidize it to sulfuric acid according to theory and determined the excess with oxalic acid. Even though the oxidation were complete it would be difficult to determine the fact by difference in his method owing to the large magnification of the unavoidable error in determining such a great excess of permanganate. Sweeney, Autcault and Withrow⁵ added sulfur dioxide or sulfite to an excess of permanganate and determined the excess colorimetrically. They insist on an excess of permanganate at all times. This permanganate was standardized with specially purified sodium sulfite. However, a later communication⁶ from the same laboratory showed the impossibility of preparing in weighable condition pure sodium sulfite and called in question all determinations of sulfite basis on sodium sulfite as a standard.

Though the preponderance of evidence seemed to be against the complete oxidation of sulfurous acid in acid solution by a moderate excess of permanganate, the question seemed to merit a more rigorous test than had apparently been applied to it, and the electrometric method, as one of us⁷ had applied it in the determination of nitrous acid, seemed to meet the requirements.

The starting point was a solution of sodium sulfite placed in an atmosphere of hydrogen by use of an apparatus practically the same as that used by Thornton and Chapman.⁸ After stand-

³ Pinnow, *Zeit. Anal. Chem.*, 43, 91 (1904).

⁴ Milbauer, *Zeit. Anal. Chem.*, 47, 17.

⁵ Sweeney, Autcault and Withrow, *J. Ind. and Eng. Chem.*, 9, 949 (1917).

⁶ Shenefield, Vilbrandt and Withrow, *Chem. and Met. Eng.*, 25, 953 (1921).

⁷ Hendrixson, *Jour. Amer. Chem. Soc.*, 43, 1309.

⁸ Thornton and Chapman, *Jour. Amer. Chem. Soc.*, 43, 91.

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ing three or four days it was standardized by the iodine method. In all titrations recently boiled water was used and the titrating vessel was kept full of carbon dioxide. Loss of sulfur dioxide was prevented by use of series of bulbs containing iodine and potassium iodide solutions in the standardizations, potassium permanganate in the titrations with permanganate. On account of the rapid change in the concentration of the sulfite solution it was restandardized by the iodine method on the same days that its concentration was determined with permanganate. Though protected in the apparently perfectly working apparatus which maintained an outward pressure of hydrogen equal to about 20 cms. water pressure, the sulfite solution lost about 1 per cent of its reducing power daily. This would require for the average amount of solution stored, the access of about 40 cc. of air daily, which seems impossible, and the facts incline one to the view of Shenefield, Vilbrandt and Withrow⁹ that the salt suffers auto-oxidation.

In carrying out the electrometric determinations with permanganate a weighed amount of this solution was placed in the titration vessel, an amount of dilute, recently boiled and cooled sulfuric acid was added to make the acid concentration about normal at the end of the experiment and a rapid stream of purified carbon dioxide was run through the solution for several minutes. The current of gas was slowed down, the mechanical stirrer was started and sufficient sulfite solution was run in to use about half of the permanganate in series (1), nearly all in series (2), and to the end point in series (3). In series (1) and (2) the excess of permanganate was destroyed by a slight excess of known potassium iodide and then permanganate was run in till the voltage showed the end point had been reached. The high degree of uniformity attained by essentially the same method in the determination of nitrous acid¹⁰ was not reached in the titration of sulfurous acid, indicating that the reaction in the latter case is

SERIES (1)

TITRATION OF SULFUROUS ACID WITH A LARGE EXCESS OF PERMANGANATE

	KMnO ₄ reduc. cc.	Excess KMnO ₄ cc.	Na ₂ SO ₃ cc.	H ₂ SO ₄ to 1 cc.
1.	37.61	39.64	24.50	0.00325
2.	38.86	41.74	24.95	0.00329
3.	51.27	30.88	33.25	0.00326
4.	31.28	16.73	20.00	0.00330
			Average	0.003275

variable, depending upon small differences in conditions that cannot be easily discovered or controlled. Only a few representative determinations are selected for each series. The value of the permanganate was found by $\text{Na}_2\text{C}_2\text{O}_4$ to be $N/20 \times 1.033$.

The iodine method may not be perfect, but it is the best we have and is doubtless accurate enough for present purposes. Three determinations in parallel by the iodine method gave 0.00352 sulfurous acid in 1 cc. of the sulfite solution, which means that the permanganate gave only 93 per cent of its value.

SERIES (2)

TITRATION OF SULFUROUS ACID WITH SLIGHT EXCESS OF PERMANGANATE

	KMnO ₄ reduc. cc.	Excess KMnO ₄ cc.	Na ₂ SO ₃ cc.	H ₂ SO ₃ to 1 cc.
1.	36.39	4.10	24.95	0.00309
2.	37.10	2.84	25.00	0.00314
3.	53.20	3.39	36.20	0.00311
			Average	0.003113

The iodine method gave at the same date 0.003476, or the permanganate method gave 89.6 per cent of the sulfurous acid present.

Two titrations as shown in series (3) were made by running the sulfite solution into acidified permanganate to the end point, with the result that the percentage of oxidation was found not materially different.

SERIES (3)

TITRATION OF SULFUROUS ACID WITH PERMANGANATE TO THE END POINT

	KMnO ₄ reduced cc.	Na ₂ SO ₃ used cc.	H ₂ SO ₃ to 1 cc.
1.	44.72	30.50	0.00311
2.	63.18	42.60	0.00314
		Average	0.003125

The iodine method gave on the same day 0.00340, which is equivalent to 91.9 per cent of the sulfurous acid present.

The conclusion from our results and the records of the work of others on this subject, is that the development of an accurate method for the determination of sulfurous acid with permanganate is impracticable, perhaps impossible.

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