
Bachelors Theses

Student Theses and Dissertations

1913

Volhard's volumetric method for manganese

John A. Murphy

Follow this and additional works at: https://scholarsmine.mst.edu/bachelors_theses



Part of the [Physical Sciences and Mathematics Commons](#)

Department:

Recommended Citation

Murphy, John A., "Volhard's volumetric method for manganese" (1913). *Bachelors Theses*. 96.
https://scholarsmine.mst.edu/bachelors_theses/96

This Thesis - Open Access is brought to you for free and open access by Scholars' Mine. It has been accepted for inclusion in Bachelors Theses by an authorized administrator of Scholars' Mine. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact scholarsmine@mst.edu.

VOLHARD'S VOLUMETRIC METHOD FOR MANGANESE

by

John A. Murphy.

A

T H E S I S

submitted to the faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

in partial fulfillment of the work required for the

D E G R E E O F

BACHELOR OF SCIENCE IN GENERAL SCIENCE

Rolla, Mo.

1913

Approved by

W. S. Gotschalk

Professor of Chemistry.

Table of Contents.

- A Introduction, page 1.
- B Experimental, page 3.
Apparatus, page 4.
Manganese determination, page 3, table 1.
Available oxygen determination, page 5, table 2.
Zinc determination, pages 7 and 8, table 3.
- C Conclusions, page 8.
- D Resume, page 10.

Bibliography.

- American Journal of Science. Vol. 6, 1898.
" " " " " 8, 1899.
Journal of the Am. Chem. Soc. " 21, 1899.
Chemical News, Vol. 24, 1871.
School of Mines Quarterly, Vol. 11, 1899-1900.
Miller's Quantitative Analysis
Olson's Quantitative Analysis, 1908.
Tredwell, Vol. 2, 1900.
American Chemist (Leiberg) 198, 310.
Chemical News, 40, 207.
Journal Chem. Society. 38, 141.
Journal Iron and Steel Industry, 1880, 355.

(I)

VOLHARD'S VOLUMETRIC METHOD FOR MANGANESE.

A Introduction.

Volhard's volumetric method for manganese is based upon the following reaction which takes place in a hot neutral solution containing zinc sulphate or nitrate in which the manganese is present as a sulphate or nitrate:



This well known method was first proposed by Guyard in 1863. It was not until 1879 however, that the proposed scheme was investigated. Volhard tried it out completely and found it to be a safe process under proper conditions.

Since that time the method has been the subject

(2)

of much work and various discussions. To quote Miller in his "Quantitative Analysis"; page 63, "Many modifications of the original method have been proposed, such as neutralizing with barium carbonate, sodium carbonate, etc., but probably the only improvement which has been made is Stone's use of nitric acid in the case of spiegels."

Among the accounts for the causes of error, and these have been many, we find arguments to show that the using of iron standard permanganate solution and the difficulty of removing all organic matter tend to shift the results up or down; these things in all probability do cause the varying of results.

The purpose of this article and the data contained is an attempt to show how the percentage of manganese varies with different amounts of zinc salt present. It was also intended to determine the ratio of manganese to oxygen and zinc in the brown precipitate obtained upon the titration of manganese sulphate against a permanganate solution in the presence of varying quantities of zinc, but through an oversight the data is insufficient for this purpose.

(3)

B Experimental.

A solution of manganese sulphate was made up to work from, containing 16 grams of crystalized manganese sulphate, roughly weighed up, in a liter of water.

Portions of 50 c.c. measured in a pipet were used which contained quantities of zinc sulphate from zero grams to 35 grams inclusive.

Table I.

No.	Grams zinc.	No.c.c. KMnO4	Grams manganese.
1	0	32.20	.1953
2	5	32.71	.1972
3	10	33.50	.1974
4	15	33.58	.2024
5	20	33.63	.2028
6	25	34.80	.2097
7	30	34.40	.2074
8	35	34.18	.2059

1c.c. KMnO4 = 0.02056 grams iron.

Factor^{for} manganese is 0.2951

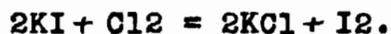
From the above results it would appear that the apparent manganese content increased as the amount of zinc sulphate except in the case of numbers 6 and 7 where the increase is a little too rapid; number 8 is found still increasing in the proper relation with regard to numbers 1,2,3,4,5.

(4)

The solution was filtered after titration and the brown precipitate of manganese dioxide was removed from the filter paper to a watch glass and dried in a heating oven at 105 degrees C. this drying was done simply to put the material into a suitable shape for handling. It was then placed in a Bunsen apparatus with hydrochloric acid and heated to boiling. The flask containing the manganese dioxide was connected with a receptacle containing a solution of potassium iodide. The manganese dioxide acted on the hydrochloric acid, liberating chlorine as follows:



The chlorine in its turn passes over to the potassium iodide solution, liberating free iodine:



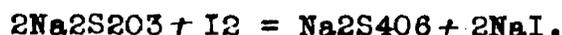
The Bunsen Apparatus.

This apparatus consisted of one 50 c.c. flask and a second 300 c.c. flask. In the first flask the manganese dioxide was placed and dissolved in hydrochloric acid. The chlorine liberated passed over to the second flask which contained the potassium iodide solution.

(5)

These reactions have been described.

After it could be seen that all of the manganese dioxide was dissolved, the flask containing the free iodine was removed, its contents carefully washed into a beaker and titrated against a solution of sodium thio sulphate.



From this the available oxygen was calculated.

Table 2.

No.	Solution	No. c.c. Na ₂ S ₂ O ₃	O 2I	Grams Oxygen.
1.	M	88.2	.08501	.0745
2.	M	96.4	"	.0819
3.	M	90.0	"	.0763
4.	L	118.0	"	.0825
5.	M	97.9	"	.0830
6.	L	121.0	"	.0847
7.	L	105.3	"	.0504
8.	L	111.2	"	.0532

In solution M 1 c.c. = 0.01347 grams iodine.
" " L 1 " = 0.01204 " "

The available oxygen of this table does not correspond to the manganese of table I; due to the failure to get satisfactory results from titrating the manganese from the zinc sulphide filtrate as described on page 6,7; the corresponding manganese values were not obtained.

(6)

The solution remaining in the 50c.c. flask of the Bunsen apparatus consisting of manganous chloride and zinc chloride was neutralized with sodium carbonate and the zinc and manganese separated by the Smith and Brunner method described in Tredwell Anal. Chem., Vol. 2, 1900, page 127. The solution after being neutralized with sodium carbonate is placed under the hydrogen sulphide generator and the gas passed in for about five minutes. A few drops of sodium acetate are added and the solution is then saturated with the gas, allowed to stand over night, filtered and washed with hydrogen sulphide water containing for every 100 c.c. two grams of ammonium chloride. The zinc is thrown down as a sulphide, while the manganese remains in solution. The zinc was then determined as zinc ammonium phosphate.

The determination of the manganese found in the filtrate from the zinc sulphide was unsatisfactory and is not given. This prevents the calculation of the ratio of manganese to oxygen to zinc because no pains were taken to collect and transfer the precipitate quantitatively. An attempt to analyse the manganese in the filtrate by Volhard's method gave more permanganate solution ~~than~~ in titrating the original sample of 50 c.c.

(7)

manganous sulphate, which was probably due to the presence of chlorides carried from dissolving the manganese dioxide. An attempt to rid the solution of the chlorides was made by neutralizing and precipitating the manganese with sodium hydroxide, filtering and washing and dissolving the precipitate in dilute sulphuric acid. The results were still unsatisfactory.

In a repetition of the work, the method described in Olson's Quantitative Chemical Analysis, 1908, page 82, of precipitating the manganese as a green sulphide would probably have been the best procedure at this point, followed by weighing as manganous sulphate.

The zinc ammonium phosphate was ignited in a crucible over a blast lamp. The salt gives up ammonia and water and goes to $Zn_2 P_2 O_7$ and from this the zinc was calculated.

Table 3.

$$\frac{-Zn}{ZnSO_4} = .2273 \text{ zinc in zinc sulphate.}$$
$$\frac{2Zn}{Zn_2 P_2 O_7} = .4289$$

(8)

No.	Grams of Zn ₂ P ₂ O ₇	Zn in prec. of Mn O ₂	Grams Zn used calculated from Zn S O ₄
1.	0.0000	0.0000	0.00
2.	0.0206	0.0088	1.14
3.	0.2886	0.1210	2.27
4.	0.6130	0.2629	3.42
5.	0.4070	0.1745	4.55
6.	0.7980	0.3422	5.68
7.	1.3950	0.5983	6.82
8.	0.3990	0.1711	7.95

The above results do not correspond to the manganese for the same reason spoken of on pages 6 and 7, but do correspond to the available oxygen of table 2, with the exceptions of numbers 4 and 8. There seems to be a proportionality between the zinc carried down and the concentration of the zinc in solution; the discrepancy might well be due to slight variations in conditions, a factor not examined in the work.

C Conclusions.

The statements in books on analysis that the precipitate in Volhard's volumetric method for manganese is not pure hydrated Mn O₂ is shown to be correct; a question as to the existence of manganites in this precipitate is not easily answered nor subject to simple experimental truth. The seeming proportionality between

(9)

the zinc ~~and~~ⁱⁿ the precipitate and the zinc in the solution is probably a case of solid solution or of adsorption. Although it may indicate formation of definite compounds (manganites) such as: $aZnO \cdot bMnO_2$.

The unexpected feature that the zinc in the precipitate does not strive toward a maximum but increases with the increase of concentration of zinc in solution rather favors the adsorption or solid solution conception; it seems not improbable that a series of properly designed experiments carried out similarly to those described in this paper would throw light on this subject although the methods of physical chemistry would have to be invoked for complete solution of the problem.

No explanation can be offered for the decrease in the available oxygen with the increase of zinc and manganese; chemically this would seem to indicate that the course of the reaction between permanganate and manganous salt is affected more vitally with the addition of zinc salts than has hitherto been assumed. On the other hand because of the oversight mentioned pages 6 and 7, this paper cannot be regarded as establishing this interesting behavior but suggests the urgent necessity of

(10)

examining this point more closely.

The effect of the addition of zinc on the apparant value for manganese however, is, in the sense, as required by the common statements, namely: the manganese content increases with increasing zinc content.

D Resume.

It has been found:

1. That the brown percipitate obtained in Volhard's volumetric method for manganese contained zinc.
2. That the zinc carried down by the percipitate increases more or less proportionally with the concentration of zinc in solution and does not reach a maximum.
3. That the addition of zinc to the solution increases the amount of permanganate consumption by a given quantity of manganous salt.
4. That the available oxygen obtained in the presence of zinc seems to decrease as the zinc content of the precipitate increases.