

siderable amount of water. The pink sulphide is a mixture in varying proportions of the gray and red sulphides.

The difference in color between the red and green modifications must be due to a difference in molecular structure, the green being probably the more complex. This view is supported by the following facts:

(a) The pink or red modification is invariably first formed by precipitation, the green being a transformation product of one of these sulphides.

(b) The green modification is more distinctly crystalline and larger-grained.

(c) The green sulphide is by far the most stable substance.

Although we have never obtained either sulphide free from sulphur, which can be extracted by carbon disulphide, we do not believe that this sulphur forms part of the molecule of either sulphide, as the properties of neither modification seem to be modified when this sulphur is extracted.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN, N. Y.]

DETERMINATION OF MANGANESE AS THE GREEN SULPHIDE.¹

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Two sulphides of manganese have been generally known up to the present time. One of these is pink or flesh colored, while the other is green. These sulphides differ markedly in their physical properties. The pink variety is finely divided, stays suspended in the liquid and passes through the pores of the filter-paper very persistently. The green sulphide is much larger grained, so that it settles readily from the mother-liquor and can be readily filtered and washed.

In quantitative work, therefore, it is very desirable to obtain the green sulphide. As manganese can be weighed with the greatest accuracy as sulphide, this method of determining the element would be much more largely used, if the green modification could be invariably obtained on precipitation. This method of deter-

¹ Read before the New York Section of the American Chemical Society, April 8, 1904.

mination has the advantage over the phosphate method that it separates manganese from the alkaline earth metals, while it is superior to the precipitation of manganese as dioxide in that the latter compound invariably carries down other bases, even the alkalies and, still further, the composition of the ignited oxide is variable.

Practically only two methods for obtaining the green sulphide for quantitative work have been published. The first method was published by F. Muck,¹ in 1869. He obtained the green sulphide by adding ammonium sulphide in excess to a hot solution of the pink sulphide in ammonium oxalate or sulphate. The precipitate first formed was pink, but changed rapidly to green. He states that ammonium chloride in considerable amounts hindered the precipitation and the change from pink to green. If the change did take place, however, the precipitate became very dark and pulverulent. He also states that the green sulphide can not be formed by the use of sodium or potassium sulphide as precipitant.

We repeated his experiments with the ammonium oxalate and found that with a minimum of 0.1 gram of ammonium oxalate for 0.5 gram of manganese chloride the pink sulphide turned green after five minutes heating. When more of the oxalate was present the change was more rapid. This method could very evidently not be used, if the alkaline earth metals were present, as they would also be precipitated. We have also verified his statements in regard to the influence of ammonium chloride and sodium sulphide. Cleremont and Guiot have also repeated Muck's experiments and obtained the same results.²

The second method of obtaining the green sulphide by precipitation has been published by several workers, among whom are Alex. Classen³ and Fresenius.⁴ These investigators recommend to precipitate the manganese from a hot solution, using an excess of ammonium sulphide and to continue heating the solution until the transformation has taken place. A small amount of ammonium chloride must be present to insure complete precipitation of the manganese, but the presence of this salt hinders the conversion of the pink to the green sulphide. The presence of potas-

¹ *Ztschr. Chem.*, 1869, p. 680.

² *Bull. Soc. Chim.*, 1877, p. 353.

³ *Ztschr. anal. Chem.*, 15, 319.

⁴ *J. prakt. Chem.*, 82, 265.

sium or sodium sulphide also hinders the transformation, and if ammonium sulphide is entirely absent, the pink is not transformed into the green modification. We have tried this method also and have found that in about half of the trials the green sulphide is obtained.

In our experiments a solution of manganese chloride was made of such a strength that 0.55 gram of the salt was present in 5 cc. This amount was used in each case. The volume was always made up to 100 cc. and the precipitations were carried out in Erlenmeyer flasks of 250 cc. capacity. The solutions were heated to the boiling-point before precipitation and if the precipitate did not immediately turn green, the solution was kept almost boiling for one-half hour.

The ammonium sulphide solution was made as follows: Concentrated ammonia was diluted with twice its volume of water. One-half of this solution was completely saturated with hydrogen sulphide, the flask being cooled with tap-water or ice to prevent the formation of the yellow sulphide. The other half of the dilute ammonia was then added. In the preliminary experiments the strength of this solution was assumed to be that calculated from the amount of ammonia present. It was soon suspected that it varied considerably in strength and the following method of titration was adopted: A standard solution of copper sulphate was made by weighing out 15.945 grams of the pure salt and diluting to 1 liter. A measured volume of this solution was warmed and the ammonium sulphide solution added until lead acetate paper was given a brown tinge when held over the nearly boiling solution.

The ammonium chloride solution used contained 265 grams of the dry salt per liter and was, therefore, of five times normal strength.

At first the precipitations were carried out by adding the ammonium sulphide to the boiling hot solution of the manganese and the ammonium chloride made up to 100 cc. In twenty-nine experiments, carried out in this manner, the green sulphide was obtained in only nine cases. In these cases the ammonium sulphide was present in large excess (20 to 37 cc. instead of the 5 to 8.5 cc. necessary for precipitation). The presence of the largest amount, however, did not render its formation certain, an equal

number of pink precipitates being obtained. The presence of even 30 or 40 cc. of 5N ammonium chloride did not seem to prevent the formation of the green sulphide.

The experiments were then repeated with the modification that the manganese solution was poured into the boiling hot solution of the ammonium chloride and sulphide. These experiments were frequently carried out side by side with the preceding experiments so as to secure identical conditions except that of the solution which was poured in. In twenty-eight experiments the green sulphide was always formed when the amount of ammonium sulphide present was from 15 to 64 cc. instead of 2.5 cc., as required for complete precipitation. With smaller amounts of ammonium sulphide a large amount of ammonium chloride prevented the formation of the green sulphide. When the amounts of ammonium sulphide given were present, the presence of even 30 or 40 cc. of 5N ammonium chloride did not prevent the formation of the green sulphide, which, however, was formed more slowly and was of a darker green and more pulverulent.

The method as we have adopted it for quantitative work is as follows: For 150 mg. of manganese 10 cc. of a five times normal solution of ammonium chloride or $2\frac{3}{4}$ grams of the dry salt and five times the theoretical amount of ammonium sulphide are used. The concentrated solution of the manganese (10 cc.) is *poured into* the boiling hot solution of the ammonium salts (90 cc.) contained in a 250 cc. Erlenmeyer flask. The solution is frequently shaken vigorously and the heating continued until the transformation of the pink (which is always first formed) into the green sulphide is complete. A grayish color is at first noticed, which, on shaking and heating, becomes more and more greenish, until the pink color has entirely disappeared. Failure to secure the transformation has repeatedly been shown to be due to the absence of a sufficient excess of ammonium sulphide.

In order to insure the presence of an excess of ammonium sulphide a number of precautions are absolutely necessary. In the first place the solution must not be boiled for any length of time before the manganese is added, since the ammonium sulphide boils away very rapidly. The reagent must also be prepared immediately before use, as it rapidly turns yellow on standing. Such a solution tends to redissolve the manganese sulphide. 25 cc. of

the ammonium sulphide, prepared as previously directed (page 1624), contains the necessary excess for the precipitation of 0.15 gram of manganese. The precipitate should be digested for about one-half hour. Longer digestion causes the manganese to redissolve because of the formation of the yellow sulphide of ammonium and the volatilization of the excess of the salt. When a large amount of ammonium chloride is present, necessitating long digestion, 40 cc. or more of the ammonium sulphide should be used. After the first half hour's digestion it may be necessary to add 10 or 15 cc. more. The precipitate settles readily, leaving a perfectly clear solution. It is washed with distilled water containing a moderate amount of ammonium sulphide and chloride.

After drying, the precipitate is detached from the paper, which is then burned. The precipitate with the ash is placed in a weighed Rose or porcelain crucible and mixed with two or three times its bulk of sulphur. It is ignited in a stream of dry hydrogen which is free from arsine. A Bunsen burner is used which gives a flame at least six inches high. If the crucible is not heated sufficiently hot, brown manganese dioxide will remain in the precipitate, which should be entirely green. Oxygen or moisture in the hydrogen also tends to form the oxides of manganese. It is cooled in the stream of hydrogen and weighed. We have carried out the entire determination, including the preparation of the ammonium sulphide in about four hours.

In a series of determinations in which 10 cc. of a manganese solution were used the following weights of manganese sulphide were obtained: 0.2248, 0.2248, 0.2244, 0.2248, 0.2246, 0.2248 gram. The average of several determinations of the manganese in 10 cc. portions of the same solution by the Volhard method gave a value corresponding to 0.2243 gram of manganese sulphide, giving a difference between the two methods of 0.4 mg., or about 0.2 per cent. of the weight of the sulphide.

The manganese in another solution was determined¹ by precipitation as the green sulphide. Two 5-gram portions of this solution gave the following weights of manganese: 0.1440, 0.1436, 0.1435, 0.1435, 0.1437, 0.1439, 0.1443, 0.1433 gram. The average of these results is 0.1437 gram. The phosphate determination of the amount of manganese is 25-gram portions of the same solu-

¹ These determinations were made by Mr. W. S. Rapalje.

tion gave the following results: 0.1452, 0.1431, 0.1430, 0.1442, 0.1409, 0.1433 gram. The average of these determinations is 0.1433 gram. The difference between the results by the two methods is 0.4 mg. of manganese. It will be noticed, however, that the maximum difference between the results obtained by the phosphate method is 4.3 mg., while the corresponding difference for the sulphide method is only 0.7 mg.

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QUALITATIVE DETECTION OF SACCHARINE IN WINE.

BY ED. MACKAY CHACE.

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THERE appeared in a recent issue¹ of *La Revue Commerciale et Coloniale*, of Bordeaux, an article by Dr. P. Carles, announcing the discovery of a substance occurring in many French wines which responds to the salicylic acid test for saccharine. In testing for the latter substance by the following method he obtained strong indications of its presence in wines of known purity. Two hundred and fifty cc. of wine were extracted in 50 cc. portions with the same 50 cc. of ether, the ether evaporated and the extracted matter fused with sodium hydroxide for fifteen minutes. The fused mass was dissolved in water, acidified with sulphuric acid and extracted with low boiling-point gasoline. The gasoline extract was tested for salicylic acid with a dilute solution of ferric alum. In his investigation he used several types of French wines and found the substance in all of them, varying in degree from the red wines to those of the sauterne type, which gave the best reactions.

In order to avoid this substance, which he terms "False saccharine," the same writer, in a later publication,² offers a method for testing for saccharine by taste; it is sensitive, however, to but 20 mg. per liter.

It has been known for some time that wines extracted by ether alone would respond to the salicylic acid test for saccharine. C. Schmitt³ called attention to this fact; he thought the trouble due

¹ December 12, 1903.

² Abstract in *Report de Pharm.*, No. 3, 1904, p. 110.

³ *Report der Anal. Chim.*, 1887, p. 439.