When the titration of zinc is carried on in an ammoniacal solution, a strong citric acid solution of ferric chloride, when used as a spot-test, gives a very satisfactory end-point and is preferable to copper sulphate. As the normal zinc ferrocyanide is always formed in an ammoniacal solution, whether zinc or ferrocyanide be in excess, this method has the advantage that it is possible to run over with a standard ferrocyanide solution and then titrate back with zinc solution, which is not possible when the titration is done in an acid solution on account of the variation in the composition of the precipitate.

QUANTITATIVE LABORATORY,
June 18, 1904.

ON THE REACTION BETWEEN CARBON DIOXIDE AND SOLUBLE NITRITES.

BY RICHARD B. MOORE.

Received June 15, 1904.

SEVERAL years ago, while working on the preparation of the nitrosulphides and nitroprussides, C. Marie[1] and R. Marquis found that carbon dioxide would liberate nitrous acid from a solution of sodium nitrite. More recently Meunier[2] denied that such a reaction takes place, whereupon Marie[3] and Marquis repeated the following experiments in proof of their contention: (1) Pure carbon dioxide was passed into a solution of sodium nitrite containing potassium iodide and starch paste. A blue color indicated the fact that iodine had been liberated by nitrous acid. (2) A solution of sodium nitrite containing potassium iodide, when shaken with chloroform, gave no coloration, but a similar solution saturated with carbon dioxide turned the chloroform violet. (3) Carbon dioxide was passed through a solution of sodium nitrite and then into a solution of potassium iodide and starch paste, which was turned perceptibly blue.

Meunier claims that the results obtained in the first two experiments were due to the presence of potassium iodide. In order to show this he saturated a solution of sodium nitrite with carbon

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[1] *Compt. Rend.*, **122**, 137 and 473.

[2] *Ibid.*, **137**, 1264; **138**, 502.

[3] *Ibid.*, **138**, 367.

dioxide and divided it into two portions. To one of these portions he added a little potassium iodide. After standing some time the solution containing the potassium iodide turned slightly yellow and gave the characteristic tests for iodine with chloroform and with starch. The other portion, which did not contain potassium iodide, at no time gave a test with iodized starch paper, no matter how long it was allowed to stand. With reference to the third experiment of Marie and Marquis, Meunier thinks that the sodium nitrite used contained small quantities of halogen salts, which behaved in a similar manner to the potassium iodide in the first two experiments.

In order, if possible, to obtain conclusive evidence as to whether carbon dioxide does or does not liberate nitrous acid from a solution of potassium or sodium nitrite, the writer performed the following experiments: Three small bottles were taken and partially filled with the following: (*a*) Distilled water, (*b*) and (*c*) strong solution of potassium nitrite. Into (*a*) and (*b*), but not into (*c*), pure carbon dioxide was passed until the liquids were saturated. A strip of iodized starch paper was then suspended in each bottle one-quarter of an inch above the liquid which it contained. Care was taken that the paper should not come in contact with the liquid or sides of the vessel. At the end of three minutes the paper in bottle (*b*) showed a decided change in color, and after six minutes was quite blue. The paper in the two other bottles did not change, even after standing several hours.

The potassium nitrite used was freshly prepared by heating Kahlbaum's special grade of potassium nitrate. The solution was boiled before using.

The above experiment was repeated, only, instead of iodized starch paper, strips of filter-paper, dipped in a solution of metaphenylene-diamine hydrochloride, were used. In bottle (*b*), which contained the solution of potassium nitrite saturated with carbon dioxide, the paper acquired a deep orange-red color in less than two minutes. In the two other bottles the paper showed no change in color at the end of two hours.

On repeating the experiment with solutions of sodium and silver nitrite, instead of potassium nitrite, similar results were obtained.

Filter-paper dipped in a solution of ferrous sulphate was also tried. In bottle (*b*) the paper turned to a yellowish brown in thirty minutes. In bottles (*a*) and (*c*) the paper was entirely unaffected. That the color was not due to oxidation of the ferrous sulphate is shown by the fact that the change took place in (*b*) in an atmosphere of carbon dioxide, but the paper was unaffected in (*c*), which contained air.

The coloration of a solution of *a*-naphthylamine and sulphanilic acid in acetic acid, noted by Marie[1] and Marquis, was confirmed. Hence the evidence points decidedly towards the conclusion that nitrous acid is liberated from a solution of potassium, sodium or silver nitrite by carbon dioxide.

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THE COLORIMETRIC ESTIMATION OF MAGNESIUM.[2]

BY OSWALD SCHREINER AND WILLIAM S. FERRIS.

Received May 11, 1904.

IN THE course of certain investigations the problem of the determination of small amounts of magnesium in aqueous solutions was presented. It was thought that a possible solution of the difficultly could be found in precipitating the magnesium as magnesium ammonium phosphate, as is done in the ordinary gravimetric procedure, and after washing, to redissolve the precipitate in nitric acid and then to estimate the magnesium indirectly by determining the phosphate with ammonium molybdate, according to the well-known colorimetric method.[3] The idea was tested by evaporating 50 cc. of a magnesium salt solution to a very low bulk or to dryness and using sodium hydrogen phosphate in excess as precipitant, and ammonium hydroxide as wash-liquid. The results were discouragingly high, owing, no doubt, to the difficulty in washing out the sodium hydrogen phosphate from the precipitate and the filter. The more soluble potassium phosphate was, therefore, substituted with far more encouraging results, as will be seen in Table I. In the first two columns in the table are given the actual amounts of magnesium present and found in the tests of 50 cc. of solution used, and in the last two columns the parts of

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[1] *Compt. Rend.*, **138**, 694.

[2] Published by permission of the Secretary of Agriculture.

[3] See West-Knights : *Analyst*, **5**, 197 (1880) : Lepierre : *Bull. Soc. Chim.* (3), **15**, 1213 (1896) ; Jolles and Neurath : *Monatsh. Chem.*, **19**, 5 (1898) ; Jolles : *Arch. f. Hygiene*, **34**, 22 (1899) ; Woodman and Cayvan : This Journal, **23**, 96 (1901) ; Woodman : *Ibid.*, **24**, 735 (1902) ; Veitch : *Ibid.*, **25**, 169 (1903) ; Schreiner : *Ibid.*, **25**, 1056 (1903).