mass exploded with a sharp report and the watch-glass was broken into a score of pieces. In another instance while brushing some of the carbide from a filter-paper with a camel's hair brush into a dish, the particles adhering to the paper exploded with a loud report and flame and the filter-paper was badly torn but the bulk of the material, which was not over an inch or two away, was not exploded by the concussion. The same fact was noted in the first explosion above in which case the watch-glass was standing beside a crucible containing quite a large amount of dry gold carbide.

No other aurous solutions were tested with a view to obtaining gold carbide. From auric chloride in aqueous solution metallic gold is precipitated by acetylene.

A solution of auric chloride made alkaline with potassium hydroxide does not give a precipitate under similar conditions, nor does an aqueous or ammoniacal solution of potassium auric cyanide give a precipitate when acetylene is passed into it.

THE NATURE OF THE CHANGE FROM VIOLET TO GREEN IN SOLUTIONS OF CHROMIUM SALTS.

BY F. P. VENABLE.

Received January 22, 1900.

IN a recent number of this Journal[1] Whitney has reported further work upon this problem and at the same time criticized an article by Venable and Miller which had previously appeared upon the same subject.[2] As Mr Miller is no longer at work with me and I was, in the main, responsible, for the presentation and discussion with which Dr. Whitney finds fault, my name appears alone in this reply.

Whatever disinclination I may have felt to accept as final the previous efforts at determining the presence of free sulphuric acid in the green solutions, I can have none as to this recent admirable and conclusive direct determination of the acid by Whitney. It is, of course, of little importance to explain why an opinion was formed, unless truth is advanced by such explanation. I shall therefore only refer to two or three of the facts stated by Whitney as sufficient to convince one that free sul-

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[1] This Journal, 21, 1075-1084.

[2] *Ibid.*, 20, 484-496.

phuric acid is present. I do this because I cannot verify them as facts.

1. Dr. Whitney states that the green solutions are acid to the usual indicators. We could draw no conclusions as to the difference between the solutions from this because both violet and green solutions are thus acid. This statement was made by us in the original article and has been carefully verified by me since reading Whitney's article. It is also supported by the experiments of Baubigny and Pechard. Furthermore, the mere fact that barium chloride is prevented from precipitating all of the sulphuric acid in the green solution cannot be taken as proving the presence of free sulphuric acid.

2. Whitney cites Recoura as stating that the "distillation of the green solution results in an acid distillate, while the violet salt may be heated above 100°C. without loss of acid." My experiments failed to verify this. I took 15 grams of the alum and dissolved it in 200 cc. of distilled water. This was then carefully distilled from an ordinary distilling flask connected with a condenser and the distillate treated in successive portions of 50 and 25 cc. until only about 25 cc. were left, without finding any acid. Beyond this point the temperature began to rise, portions splashed upon the sides became overheated, and acid distilled over. This was repeated with chromium sulphate with the same result. It was also repeated with ordinary potash alum with the same result. As the solution became very concentrated the temperature rose, portions were splashed upon the hot sides and acid distilled over. Lastly, it was repeated with 5 cc. of sulphuric acid in 200 cc. of water and no acid distilled over until most of the water had been driven off and the temperature had risen above 100°C. Manifestly this experiment of Recoura's can throw no light upon the presence or absence of free acid.

3. Krüger's statement that alcohol poured in a layer over the green solution takes up acid (something that gives an acid reaction) from the solution is only part of the truth for alcohol will do precisely the same thing when poured over the violet solution. In the course of a few hours the reaction is quite perceptible from both solutions. There is no change apparent in the color of the violet solution after four or five days' standing under the layer of alcohol.

After weighing the evidence then at hand I reached the conclusion that a satisfactory explanation of the change could scarcely be deduced from these and the other experiments.

And they did not seem to me to justify the construction of an equation and an elaborate formula for a hypothetical substance which was assumed to cause the green coloration, even if the presence of the free acid should be granted.

The exception is well taken by Whitney to our experiment with the decinormal solution of ammonia and explains a result which greatly puzzled us in the interpretation of our later work. We scarcely knew what value to attach to the experiment and so merely stated that "these experiments therefore agree with those of Baubigny and Pechard, but are at variance with the conclusions of the other authors mentioned." The agreement was, of course, only to the extent that "both solutions are acid" and that was all that was claimed for the experiment.

It seemed to us necessary to get under hand for analysis the body which gave the green coloration before any formula could be established for it. We therefore abandoned what we styled "indirect methods giving results capable of other explanations." We thought it more material to secure this body than to settle the question as to whether free acid or an acid sulphate was formed. Certainly any other line of research would always leave the body in question hypothetical. Hence in the latter part of the paper[1] the sentence occurs, "as the alcohol left is decidedly acid it must contain either free acid or an acid sulphate" and there was no further effort at settling this point.

The method which most commended itself to us for securing this compound was precipitation by means of alcohol. In this precipitate, in the case of the alum, we obtained the potassium sulphate along with the chromium compound and this blinded us to the true formula. A recalculation of the results of Mr. Miller's analyses, eliminating the potassium sulphate, and taking the mean of the experiments, gives as the ratio of the chromium to SO_4, 18.23 : 41.62. Now the ratio, calculated for the formula $Cr_4O.(SO_4)_4.SO_4$, is 18.23 : 41.99. Having then the direct determination of the free sulphuric acid from Whitney's last experiments and the gravimetric determination of the chromium

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[1] This Journal, 20, 496.

and SO_4 in the basic chromium sulphate from Miller's analysis, there can no longer be any reason for not accepting the equation given for the change:

$$2K_2SO_4.Cr_2(SO_4)_3 + H_2O = 2K_2SO_4 + Cr_4O(SO_4)_4.SO_4 + H_2SO_4.$$

The conclusion drawn in the article by Miller and myself was conservative and still stands; namely, that the color of the green solutions was due to the formation of basic salts of chromium, green and uncrystallizable, thus confirming the explanation first suggested by Berzelius. To this must now be added that this formation is accompanied by the liberation of a portion of the combined acid, in the case of the alum corresponding to one-half of the total.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, No. 18].

ON THE DECOMPOSITION OF NICKEL CARBONYL IN SOLUTION.

BY VICTOR LENHER AND HERMANN A. LOOS.

Received January 12, 1900.

IT has been shown by Berthelot that nickel carbonyl in contact with moisture suffers decompositions of a more or less complex character. When nickel carbonyl is mixed with water according to Berthelot[1] there is formed a green compound which consists of hydrate of the oxide free from carbon. A portion of the nickel carbonyl at the same time escapes and is oxidized in moist air to a whitish compound. This same white compound Berthelot prepared in larger quantity by the slow oxidation with air and found it to contain 5.3 per cent. carbon, 53.3 per cent. nickel oxide (NiO), and 40.1 per cent. water.

Mond[2] considers the green body formed when nickel carbonyl is exposed to damp air to be a carbonate of nickel of varying composition.

The deportment of nickel carbonyl in solution is different from that in the pure condition or as a gas, as is seen, for example, from the fact, that it will decompose in solution at 60°, whereas in the gaseous condition, it will not decompose until about 150°.

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[1] *Compt. rend.*, 112, 1343; 113, 679.

[2] *Chem. News*, 64, 108; also *J. Soc. Chem. Ind.*, 11, 750.