A return of the strong, irritating odor indicates that the purifiers have become exhausted.

The purification of acetylene by means of moist chloride of lime or sodium hypochlorite, as suggested by Odernheimer[1] and Lunge[2] or as modified by Wolff[3], is impracticable because of the instability of the solutions and because chlorine and chlorination products of acetylene are produced, which must then be removed by lime. Frank's method,[4] using strongly acid solutions of copper or iron chloride, does not seem very efficient, nor is the employment of bromine as a purifier convenient for laboratory use. The combination of Hempel's and Ullmann's methods seems to meet all the requirements and is easily and conveniently arranged.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, NO. 17.]

THE CARBIDE OF GOLD.

BY J. A. MATHEWS AND L. L. WATTERS.

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EXPLOSIVE compounds resulting from the action of acetylene or coal-gas upon alkaline solutions of cuprous, argentous and mercuric salts have been known for many years. These compounds are for the most part flocculent precipitates which retain water with more or less tenacity, and at temperatures which will render them anhydrous they are apt to explode violently. The earlier investigators of these acetylides did not recognize them as true carbides and their analyses show the presence of hydrogen and oxygen, which are reported as constituent atoms of the molecule. Berthelot,[5] who did a great deal of work upon acetylene derivatives, speaks of copper acetylide as "cupro-acetyloxide," and gives it the formula $(C_2Cu_2H)_2O$. Reboul[6] gives silver acetylide as $(C_2HAg)_2+Ag_2O$ and Blochmann[7] gives respectively, $C_2H_2Cu_2O$ and $C_2H_2Ag_2O$. All of these might better

[1] *Chem. Ztg.*, **22**, 21.

[2] *Ztschr. angew. Chem.*, 651 (1897).

[3] *Chem. Ztg.*, **22**, 281; Wolff treats the gas first to remove ammonia and then with hypochlorite, thus eliminating the danger of forming nitrogen chloride, which he says is possible.

[4] *Ztschr angew. Chem.*, 1050 (1898).

[5] *Ann. chim. phys.* [4], **9**, 425.

[6] *Compt. rend.*, **54**, 1229.

[7] *Ann. Chem.* (Liebig), **173**, 176, 177.

be written C_2Cu_2 or C_2Ag_2 plus more or less water. Miasnikoff[1] gives silver acetylide as $C_2H_2Ag_2$. Keiser[2] showed, however, that when properly dried these two acetylides are simply C_2Ag_2 and C_2Cu_2, and later[3] produced mercuric acetylide, HgC_2, which is also hydrated at the time of its formation.

Berthelot[4] seems to be authority for the statement which appears in a number of old chemical works, but for which these do not give him credit, that by passing acetylene through aurous thiosulphate, a yellow explosive precipitate is formed. He gives no analyses of the product and does not give any suggestions as to its probable constitution.

We have recently investigated this interesting compound, which proves to be analogous to the copper and silver compounds, its formula being aurous carbide, Au_2C_2.

In the preparation of aurous sodium thiosulphate we followed the method of Fordos and Gélis.[5] Pure auric chloride was dissolved in 50 parts of water; 3.2 parts of sodium thiosulphate were dissolved in the same amount of water. The solution of gold was added to the thiosulphate very slowly and with constant stirring. A slight odor of sulphur dioxide was noticed and a little sulphur separated.

The solution was filtered and the sodium aurous thiosulphate was precipitated with absolute alcohol. It was not recrystallized. The principal reaction is said to be

$$8Na_2S_2O_3 + 2AuCl_3 = 2Na_3Au(S_2O_3)_2 + 2Na_2S_4O_6 + 6NaCl.$$

This compound forms a colorless precipitate, very soluble in water but insoluble in alcohol. To form aurous carbide an aqueous solution of the sodium aurous thiosulphate is made strongly alkaline with ammonia and a slow stream of acetylene passed through. The solution remains colorless for a short time and then becomes yellow and finally a yellow flocculent precipitate appears. In this respect it differs from silver and copper carbides, which form almost instantly and hence are used to test for the presence of minute quantities of acetylene. The precipitate is filtered off, washed with water and alcohol and dried in a desiccator over sulphuric acid.

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[1] *Ann. Chem.* (Liebig), 118, 330.

[2] *Am. Chem. J.*, 14, 285.

[3] *Ibid.*, 15, 535.

[4] *Ann. chim. phys.* [4], 9, 425.

[5] *Ibid.*, [3], 13, 394, 1845.

Properties.—When thoroughly dried, the carbide of gold is highly explosive either upon rapid heating, by a blow or even by brushing with a camel's hair brush. The explosion generates sufficient heat to produce flame and the gold is left in an extremely finely divided condition and black. Carbide of gold is easily decomposed by hydrochloric acid giving acetylene and leaving a black residue of aurous chloride. The presence of acetylene was shown by passing it into ammoniacal silver nitrate, in which it produced silver acetylide. The aurous chloride was tested by boiling, which gave auric chloride and metallic gold. By boiling gold carbide with water it is decomposed into its constituents, no acetylene being produced. Cupric sulphate and neutral ferric chloride do not decompose it in the cold; when anhydrous it becomes darker in color and of a brown tint and if heated very gradually decomposes without explosion. This fact was made use of in the determination of gold. The sample to be analyzed was heated in the air-bath very slowly until a temperature of 180° to 200° was indicated, and then ignited in the flame of a Bunsen burner. The black mass becomes yellow by the burning off of the carbon and annealing of the gold. The analyses resulted as follows:

	Weight of sample.	Gold found.	Gold. Per cent.	Theory for Au_2C_2.
I	0.029	0.0273	94.14	94.25
II	0.0174	0.0164	94.25	94.25

One sample of aurous carbide after two days in the desiccator lost no weight at 100° C. nor was loss experienced on renewed heating up to 120° C. Another sample that had not stood so long over sulphuric acid lost 0.0004 gram at 100°. By rapid heating in the air-bath explosions were obtained at various temperatures from 83° to 157° C. No attempt was made to secure especially uniform heat at all parts of the air-bath, but the thermometer bulb was in all cases very close to the dish containing the explosive compound. It seems then that the rate of heating has most to do with effecting the decomposition of gold acetylide. The violence of the explosion was shown by several unexpected explosions. In one case about 15 or 20 milligrams of the substance were on a watch-glass. In trying to remove a small fragment with the point of a knife, the whole 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.

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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.