

done with the molybdenum derivative, although by analogy we might deduce a similar structure. We tried the action of ammonia upon wolframyl chloride suspended in ether (it is not soluble in this menstruum), and also in chloroform, but obtained green colored decomposition products.

Our experiments demonstrate: (1) that wolframyl chloride behaves very differently from molybdenyl chloride at the ordinary temperature when exposed in an atmosphere of ammonia; (2) that the reaction product is not a true amide, but in all probability a union of disintegrated amide molecules; and (3) that metallic tungsten is present in the product.

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DETERMINATION OF ORGANIC MATTER BY MOIST OXIDATION.

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ANY chemist who has carried out combustions by the ordinary dry process knows how much time is required, and what care must be observed, to obtain results of practical value. In technical work, where time is limited, the combustion process is resorted to only when nothing else will give the desired result.

Many attempts have been made to shorten and simplify the general process of organic elementary analysis, but for carbon and hydrogen we have, as yet, no process which accomplishes what the Kjeldahl method does for nitrogen.

I have tried to solve this problem by employing a wet method in place of the ordinary dry one. The advantages of a wet process are evident. First, the trouble of preparing the copper oxide, or substitute, would be saved. Besides this, it would not be necessary to have the substance in the dry condition, and finally, much simpler apparatus could be used. Instead of the combustion tube and the combustion furnace, a simple burner and a flask may be used.

I am sorry to say that, at the present time, the methods of combustion by the wet process have not been improved so much that all substances can be determined. What has been

accomplished in solving the problem, I will explain in the following:

There are two substances which are used as oxidizing materials for combustions by the wet process—permanganate of potash and chromic acid—the latter as free chromic acid and in the form of bichromate of potash. Both oxidize in presence of sulphuric acid. The permanganate is used only for a few special purposes, namely for the oxidation of oxalic acid, the well known quantitative method for determination of glycerine according to Planchon, whereby the oxidation is not a complete one, and finally, for determination of the organic matter in water, a method which does not give absolute, but only relative results. More generally chromic acid is employed.

The oldest directions in regard to employment of a chromic acid and sulphuric acid mixture for the determination of carbon seem to be those of the Rogers brothers, published in 1847. The authors mentioned worked with a highly concentrated sulphuric acid, namely five parts of acid and one part of water, and used bichromate of potash. They employed the method only for determination of carbon in graphite, which can be oxidized only with great difficulty by the dry process. The carbonic acid developed was absorbed by an absorption apparatus and was weighed.

Ullgren improved this method by using free chromic acid instead of bichromate, in order to prevent the formation of sulphate of chromium and potassium, which covered the particles of carbon so that the mixture could not act upon them. Ullgren employed this method also for the determination of carbon in iron and steel. He worked with a mixture less strong than that used by Rogers. His method is found in all manuals of quantitative analysis, and is preferred in general to the dry combustion process.

It was only one step further to employ these methods in the determination of the carbon in carbon compounds. Bossingault first did this. Unfortunately, I have not been able to find any of the particulars of his method.

Messinger used no new principle in this method as applied by him. He worked usually with 0.15–0.35 gram sub-

stance, five to six grains chromic acid or bichromate, and thirty-three cc. sulphuric acid. He heated only slightly. He says that he got good results with almost all substances; only with very volatile substances he did not succeed. He varied his method according to circumstances, and prescribed special methods for substances containing sulphur, phosphorus, arsenic, antimony, chlorine, bromine, and iodine. In all cases he weighed the carbonic acid.

Legler used the chromic acid mixture only for a special purpose, namely for determination of glycerine. He took 0.75-1 gram of the substance, and heated for each one-fourth gram one hour. In contradistinction to the methods mentioned above, Legler operated in the so-called "two flask" apparatus, whereby the carbonic acid was calculated from the loss of weight. This seems, at first, to be of no importance, but is really of great importance.

All methods described suffer from a fundamental error. The merit of detecting this error belongs to Cross and Bevan, who worked in company. They tried to oxidize cellulose by the chromic acid mixture, and did that first in the "two flask" apparatus according to Legler, and then for control, according to Ullgren. The results of these two methods did not agree. They assumed that in the process of oxidation, not only carbon dioxide, but also the monoxide, was formed. They tested, therefore, the gas developed by both methods, and found carbon monoxide in both cases. Of course, the error must be larger in those methods in which the carbonic acid is weighed in an absorption apparatus, than in those in which it is shown by the loss of weight. In the latter, only the second atom of oxygen, which ought to oxidize the monoxide to dioxide, escapes observation, while in the first the whole of the carbon monoxide escapes. The errors must be in the proportion of 16 : 44. Cross and Bevan prevented this error in theory perfectly by measuring the gases, as carbon monoxide and carbon dioxide contain the same amount of carbon in the same volume. In practice there were some difficulties. A concentrated mixture of chromic and sulphuric acid develops oxygen when heated, and that had to be prevented. Therefore, they determined

the proportion of the ingredients in which the evolution of oxygen below 100° C. did not take place. At the end of the operation the liquid has to be heated to accomplish oxidation and to remove carbon dioxide from the solution. A little will remain, nevertheless, because the solution will not boil at 100° C., as it contains sulphuric acid and salts. For this reason a correction for the absorbed carbon dioxide is necessary.

The method is, briefly, as follows :

Take enough of the substance to develop 90-100 cc. gas. The substance is dissolved in nine cc. sulphuric acid, and chromic acid is added in excess of thirty per cent. First, the temperature is kept between 60° - 70° , then raised to 100° . Cross and Bevan published very good results. Only fatty acids and bases containing nitrogen could not be oxidized completely.

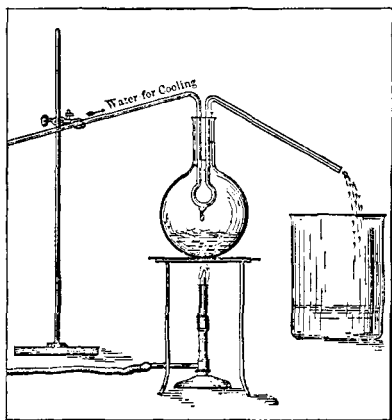
Cross and Bevan's discovery of the carbon monoxide in the products of oxidation called the attention of Professor Fresenius to the same point. Fresenius engaged Widmer to criticize Ullgren's method. Widmer found that also in the oxidation of graphite carbon monoxide is formed. He proved that by passing the gases leaving the absorption apparatus over heated copper oxide, carbon dioxide was produced. He determined the quantity, and found the surprising result that the error amounted to 6.58 per cent. to 4.72 per cent. in a graphite containing about ninety per cent. of carbon. In order to get correct results, it is necessary to oxidize the carbon monoxide in the current of gas before it reaches the absorption apparatus, by passing the same through a small combustion tube.

Helmer, who, like Legler, employed the chromic and sulphuric acid mixture for determination of glycerine, introduced a new principle in these methods. He did not weigh or measure the products of oxidation, but determined the amount of oxygen used for oxidation. Helmer took 0.4 gram substance, dissolved in twenty-five cc., added 40-50 cc. of a concentrated solution of bichromate and fifteen cc. sulphuric acid. This mixture was heated two hours in a water bath. Then it was diluted, and the chromic acid, which remained intact, determined. He convinced himself that glycerine, in this way, was completely oxidized, and found at the same time that the soluble fatty acids remained intact.

Kjeldahl has recently published a method of combustion by chromic acid, but I am not acquainted with the details as worked out by him.

I wish now to explain the method as employed by myself. In some respects it resembles the Helmer method, and was first carried out in detail in the laboratory of Dr. Eudemann, in New York, some three years ago, although work had been done on it several years earlier.

I employ in this process: (1) A $\frac{N}{5}$ solution of potassium bichromate; (2) chemically pure sulphuric acid; (3) the usual volumetric apparatus for titration; (4) solutions of potassium ferricyanide and ferrous sulphate or ammonium ferrous sulphate; (5) the apparatus shown in the cut, the characteristic feature of which is the condenser. This is inserted in the neck of the boiling flask, so that the condensed vapors come



in contact with glass only; (6) the solution of the substance to be examined, which should not be stronger than $\frac{N}{5}$.

The method is carried out as follows: Twenty-five cc. of the solution of the substance is mixed with thirty cc. of the $\frac{N}{5}$ solution of potassium bichromate, and then thirty-three cc. concentrated sulphuric acid are added. The whole mixture is heated

on a wire gauze until it begins to boil. Then the flame is regulated so that the liquid boils up from time to time. During the heating, the return condenser is kept in action. Most of the vapors are condensed; small losses of the volume are of no importance. After boiling is continued for ten minutes the flask is removed from the flame, and the excess of chromic acid is determined in the usual manner. I must mention here that it is not necessary to cool or to dilute the solution before titration.

The above mentioned proportions of the solution of the sub-

stance of chromic acid solution and sulphuric acid are not accidental, but are the result of a number of experiments in regard to which I want to say a few words, as they are of importance.

It is desirable to use as much sulphuric acid as possible in order to act energetically upon the organic substances, and to get high temperatures. On the other hand, a decomposition of chromic acid by the sulphuric acid alone must be prevented. To find the proper proportion I heated mixtures of $\frac{N}{3}$ potassium bichromate and sulphuric acid alone for thirteen minutes. I started with very large quantities of sulphuric acid and reduced the same gradually, until the point was found where the decomposition was so small that it could be neglected.

For instance, I took in a first experiment 23 cc. $\frac{N}{3}$ $K_2Cr_2O_7$ + 30 cc. H_2SO_4 . The decomposition corresponded to 2.65 cc. $\frac{N}{3}$ $K_2Cr_2O_7$. Then I took 23 cc. $\frac{N}{3}$ solution + 20 cc. H_2SO_4 . The decomposition amounted to 0.25 cc. $\frac{N}{3}$. Finally, I took 23 cc. $\frac{N}{3}$ + 15 cc. H_2SO_4 . The decomposition was 0.05 cc. $\frac{N}{3}$ $K_2Cr_2O_7$.

Purposely I stopped here, and did not reduce the sulphuric acid any more, as, firstly, an error of one-half tenth of one cc. is very small and it may be neglected with safety; secondly, as the error must be still smaller in practical determinations, because the main quantity will be reduced inside of the first minute. Therefore, the decomposition of chromic acid by action of the sulphuric acid alone can take place only in the excess of added chromic acid. This excess is about five cc. or one-fifth of the quantity used in the blank experiment. Therefore, the decomposition cannot be larger than one-fifth of five-hundredths on one cc. or one-hundredth of one cc.

Further, these five cc. are present in a volume of 25 + 30 + 33 = 88 cc. in a practical determination, while the twenty-five cc. in the blank experiment was present in 25 + 15 cc. = 40 cc. The dilution in the first case is eleven times larger than in the latter one. I will not say that the error is only one-eleventh of 0.01 cc., but I am sure it is not larger than 0.01 cc. An error of 0.01 cc. may be neglected without scruple.

Speaking of the practical use of the method, I do not claim that it is suitable for general use. On the contrary I would

wish to have it considered only as an empirical one. Quantitative oxidation is possible only with a small number of substances, but almost quantitative results are obtained with very many substances. The method has, in my own opinion, about the same value as Allihn's method for determination of sugar with Fehling's solution. In a very similar manner it will be necessary to make tables in which the results empirically found are registered. I have commenced already to do this. I found that the oxidation is the more complete the larger the excess of chromic acid has been. In general, the figures run so close that it was sufficient to determine two points of the table, namely for 100 per cent. and for 40 per cent. All other points may be obtained near enough by interpolation.

For the advantages of my method in comparison with other ones, I may mention that it is a quick one, and requires only very small quantities of substance. In parallel determinations I obtain very close results, which is due to the fact that all the conditions of the experiment can be easily followed. In conclusion, I will give a short table of results by way of illustration.

Name of substance.	Oxidized by a concentration equivalent to	
	$\frac{N}{5}$	$\frac{2N}{3}$
Oxalic acid.....	100.00 per cent.	100.00 per cent.
Tartaric acid(1)	99.48 "	99.75 "
" "(2)	99.56 " "
Dextrose	98.45 "	99.90 "
Corn starch, commercial:		
With 11.66 per cent. moisture..	84.8 "
" 10.34 " " ..	85.6 "
" 12.09 " " ..	84.4 "
" 12.15 " " ..	85.2 "
Average, 11.56 " " ..	85.0 "
Purest glycerine from Schering....(1)	97.50 "
" " " "(2)	97.73 "
" " " "(3)	97.65 "
Acetic acid.....	0	0
Alcohol ¹	33.6 "
Alpha-naphthol	75.0 "
Beta-naphthol	83.0 "
Benzoic acid	Very little more than 90 per cent.	
Salicylic acid	" " " " " "	
Morphine	61 per cent.	

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¹ This experiment was made with a measured quantity, therefore not absolutely correct. I assume that alcohol will be oxidized exactly to acetic acid, and the result will be just 33½ per cent.