

THE ANALYST.

NOVEMBER, 1879.

SOCIETY OF PUBLIC ANALYSTS.

THE next Meeting of this Society will be held at Burlington House, Piccadilly, on Wednesday evening, the 19th November.

ON THE OXIDATION OF SULPHUR IN GAS BY COMBUSTION.

By W. C. YOUNG, F.C.S.

IN No. 8 of *THE ANALYST** I published an account of some experiments, made for the purpose of ascertaining whether sulphurous or sulphuric acid was produced by the combustion of gas containing sulphur, the results of which led me to the conclusion that practically the whole of the sulphur present was converted immediately into sulphuric acid. This conclusion was afterwards borne out by Silliman and Sadler in a paper "on the volumetric determination of sulphur and ammonia in illuminating gas," which appeared in *The Journal of Gas Lighting*, vol. 29, p. 461, and subsequently by Heisch and Wigner in this journal.† Having this conviction, it seemed to me possible to absorb the acid fumes by passing the products of combustion over zinc in a fine state of division, by which means a very simple method of estimating the sulphur would be found as the difference in weight of the apparatus before or after use would be due solely to sulphuric acid. In attempting to put this into practice, I was surprised to find that the zinc was quite unaffected, except in places where moisture had condensed, and there sulphate had formed. I noticed, moreover, in the course of numerous experiments that wherever sulphate was, there also was carbonate to be found. This result casting some doubt on my former conclusions, I determined to investigate the subject farther, and avoid using any alkaline or basic substance as an absorbent of the acid. Accordingly, I first determined the amount of sulphuric acid contained in the water condensed in the gas referees' apparatus, used without carbonate of ammonia before and after oxidation with nitric acid, when I obtained an average of .5 grains of sulphur per 100 cubic feet consumed, but in no case did I find an increase when the liquor was boiled with nitric acid previous to precipitation. As it was possible that the condenser was too hot to admit of the absorption of the acid by the condensed water, I next caused a fine stream of water to flow on to the glass balls in the cylinder by means of a modification of Bischof's constant level apparatus, used in his method of water analysis. A drawing of this apparatus will be found in a paper, by me, printed in *The Journal of Gas Lighting*, vol. 29, p. 464. It consists of an inverted flask, the neck of which is fitted into a tube narrowed towards the end to a fine bore, and fitted near its extremity with a stop-cock; on to this tube is blown at right angles another tube bent up again so as to be parallel with the former, and furnished near the top with a stop-cock. To use this apparatus, the flask is filled and the tube fitted firmly into its neck, the whole inverted and the lower stop-cock opened; when the flow of water ceases the delivery can be regulated to any desired rate by means of the upper stop-cock.

* Vol. I., p. 43.

† Vol. III., pp. 133, 138.

The following results were obtained in this way :—

	Sulphur condensed as H_2SO_4 in grains per 100 cubic feet of gas consumed.				Total Sulphur in gas in grains per 100 cubic feet.			
1.	·90	12·9
2.	·65	14·8
3.	·80	11·9
4.	1·26	12·8
5.	1·26	15·4
6.	1·31	14·6
7.	1·53	12·7
8.	·98	13·2

It seems, therefore, that either by using a larger quantity of water, or by cooling the cylinder, the amount of sulphuric acid condensed was somewhat increased but not to the extent expected, as fully half the space in the cylinder was kept quite cool during the progress of the experiment. This experiment was varied by carrying the end of the eduction tube of the referees' apparatus into the neck of another cylinder, on to the glass balls in which the water was run, so that the condensing power of the apparatus was vastly increased whilst using the same quantity of water as before.

The results thus obtained are as follows :—

	Sulphur condensed as H_2SO_4 in grains per 100 cubic feet of gas consumed.				Total Sulphur in gas in grains per 100 cubic feet.			
1.	1·02	12·8
2.	1·01	16·1

A second estimation of the sulphur in the liquor obtained in these experiments was made after oxidation, but no increase was obtained. It was clear, therefore, that the means adopted were inadequate for the purpose of the complete absorption of the sulphur acids formed, but it seemed to me that if only sulphuric were formed these means were competent to arrest it; and to assure the presence of that acid only, I substituted bromine water for the water, using only one condenser, when the following results were obtained :—

	Sulphur in grains per 100 cubic feet of gas consumed.				Total Sulphur in gas in grains per 100 cubic feet.			
1.	3·28	13·8
2.	5·20	12·4
3.	8·22	13·1

In these experiments the sulphur obtained as sulphuric acid increased with the bromine water employed, which in the last one was a saturated solution; as, however, a considerable portion of the sulphur had escaped condensation, a trial was made with the double apparatus before described, substituting bromine water for the water, when very similar results were obtained, as will be seen below :—

	Sulphur obtained in grains per 100 cubic feet of gas consumed.				Total Sulphur in grains per 100 cubic feet of gas.			
1.	7·25	10·80
2.	7·32	9·48

It being evident that sulphuric acid could be absorbed from the mixture of gases by means of water, the inference drawn from the failure to obtain the whole of the sulphur was that the remainder escaped in the form of sulphurous acid, the means employed not being sufficient to oxidise the whole; accordingly I again varied the experiment by placing bromine under water beneath the burner, dispensing with the dripping apparatus, and substituting a reservoir of bromine under water in the upper cylinder, formed by removing the tube in the bottom and plugging the hole.

In this way I obtained more sulphur in the form of sulphuric acid, per 100 cubic feet of gas consumed, than was given by the method employed for estimating the total quantity of that impurity in the gas, as will be seen below :—

Sulphur as H_2SO_4 found by experiment as above described in gas per 100 cubic feet of gas.				Total Sulphur in gas by "Referees" method in gas per 100 cubic feet.			
1.	14.2	12.5
2.	13.8	12.4
3.	12.5	11.3

As some of the sulphur obtained may have been derived from the vulcanized rubber connections employed in these experiments they were repeated, cork being substituted for the rubber, when the results obtained were practically the same as those given by the usual method of estimating the sulphur.

Repeat of last experiment, cork connections substituted for vulcanized rubber :—

Sulphur as H_2SO_4 in grains per 100 cubic feet.				Sulphur by "Referees" method in grains per 100 cubic feet.			
1.	13.00	13.4
2.	9.28	9.2
3.	13.20	13.3

These results show beyond doubt that sulphurous acid only is formed when gas is burned in a Bunsen burner under the "Gas Referees'" apparatus, as the small quantity condensed as sulphuric acid by water alone may reasonably be assumed to have been oxidised during its passage through the apparatus. It is remarkable, however, that in all the experiments I have made where alkali or alkaline carbonate was used as the absorbent no trace of sulphite could be detected; that sulphurous acid cannot be detected in the water condensed in the cylinder, by the ordinary tests, and that when the cylinder is packed with zinc, or copper turnings, the whole of the sulphur is arrested, the resulting compound being invariably sulphate, and especially so in face of the circumstances that the air in the apparatus was formed to contain, on an average, only 12 per cent. of oxygen when the gas was burning at the rate employed, which was .5 cubic feet per hour; but if any doubt could have remained as to the power of the current of hot air to oxidise the alkaline and other sulphites formed (by the action of sulphurous acid on carbonate of zinc or copper), the result of the following experiment must have entirely removed it. An alkaline solution of sulphite of soda, containing the equivalent of 5 per cent. of sulphur, was slowly run on to the glass balls in the cylinder of a Gas Referees' sulphur apparatus, the flame of a small spirit lamp being employed in the place of a Bunsen burner to produce the current of air, when it was found that the whole of the sulphite was oxidised into sulphate before it reached the bottom of the apparatus.