

THE INFLUENCE OF ALUMINIUM SALTS ON THE ESTIMATION
OF SULPHATES.—BY H. JERMAIN M. CREIGHTON, M. A.,
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During an experience extending over three years, in the estimation of sulphur in coal gas, the writer at various times observed the presence of a flocculent white precipitate in the liquid which resulted from the condensation of the vapours formed by the burning of the gas. The following investigation was therefore carried out with a view to determining the nature of this precipitate and the influence its presence had on the estimation of the sulphur present in the liquid. It may be mentioned here that the amount of sulphur in coal gas was determined by burning a known volume of the latter in a special burner which was surrounded with lumps of ammonium carbonate. Over the burner fitted a large glass tube, up which the gases of combustion passed into a glass tower filled with glass balls. On coming in contact with the cold balls, the sulphur dioxide, ammonia, water vapour, etc., condensed and were caught in a beaker placed beneath the tower. After oxidation, the sulphur in this liquid was determined by precipitation with barium chloride. It was in this liquid which I shall refer to as the "sulphur solution," that the white flocculent precipitate referred to was frequently observed.

It should be pointed out that the coal from which the gas was generally made was that supplied by the Dominion Coal Co., in Cape Breton; and that analysis showed it to be very often high in sulphur. On several occasions where different American coals low in sulphur were used, no such precipitate occurred.

This white precipitate readily dissolved in dilute hydrochloride acid, and was re-precipitated by ammonium hydroxide

but not by sodium hydroxide. On heating some of the washed precipitate on charcoal, allowing it to cool, and heating again after moistening with cobalt nitrate solution, the mass became sky blue on cooling a second time. A qualitative analysis proved this precipitate to contain aluminum only.

As the only source of aluminium seemed to be the glass balls in the condensing tower, many of the bottom ones being greatly corroded, an analysis of them was made. The sodium carbonate used for fusing was free from aluminium. These balls were found to contain a quantity of aluminium.

The weight of this white precipitate which was present in the alkaline "sulphur solution" in the form of hydroxide, usually varied from 10 to 40 milligrams.

Peckham* has observed that when sulphates are precipitated by barium chloride in the presence of aluminium, the precipitate is contaminated with aluminium, and hence its weight is greater than that which corresponds to the actual amount of sulphur present. This case is similar to that which occurs in the precipitation of sulphates in the presence of ferric salts. The following experiments were carried out to determine whether the amounts of aluminium usually present in the "sulphur solutions" caused any marked error in the sulphur estimation.

Two sets of experiments were carried out. On the one hand, varying amounts of an aluminum salt were added to constant amounts of sulphate solution; on the other hand, constant amounts of the aluminium salt were added to varying quantities of the sulphate solution. The sulphate in each case was determined by precipitation with barium chloride.

The sulphate used was the ammonium salt. The strength of this solution was about ten grams per litre. The object of using the ammonium salt was to reproduce as far as possible the conditions existing in the above mentioned sulphur estimation.

The aluminium salt used was the chloride. This solution, which was prepared by dissolving pure aluminium in hydro-

*Peckham J., Arner. Chem. Soc., 1899, 21, 772.

chloric acid, contained one gram per litre; or 1 cc. was equivalent to one milligram of the metal.

The precipitation of the sulphate was carried out at 100° C., and the precipitate was allowed to digest in the hot (80—90° C.) liquid for three or four hours before filtering.

The results given in the following tables are the means of three analyses.

The experimental error in this work is ± 0.0008 grams.

In the first table are given the results obtained by adding various amounts aluminium chloride solution to 50 cc. of ammonium sulphate solution.

TABLE I.

Volume of Ammonium Sulphate Solution used.	Volume of Aluminium Chloride Solution used.	Weight of Barium Sulphate Precipitate.	Increase in Weight due to the presence of Aluminium.
cc.	cc.	grams	grams
50.00	0.8649
50.00	10.00	0.8651	0.0006
50.00	15.00	0.8672	0.0023
50.00	20.00	0.8699	0.0050
50.00	25.00	0.8714	0.0065
50.00	35.00	0.8710	0.0061
50.00	50.00	0.8711	0.0062

The second table gives the results obtained by adding a constant volume of aluminium chloride solution to different volumes of ammonium sulphate solution.

TABLE 2.

Volume of Ammonium Sulphate used.	Volume of Aluminium Chloride used.	Weight of Barium Sulphate Precipitate.	Increase in Weight due to the presence of Aluminium.
cc.	cc.	grams	grams
10.00	0.1729
10.00	25.00	0.1738	0.0011
30.00	0.5193
30.00	25.00	0.5235	0.0042
50.00	0.8650
50.00	25.00	0.8714	0.0064
80.00	1.3838
80.00	25.00	1.3950	0.0112
100.00	1.7362
100.00	25.00	1.7501	0.0139

From the foregoing results, it is seen that the effect of the presence of small quantities of aluminium chloride is to produce a material increase in the weight of the barium sulphate precipitate. With increasing amounts of aluminium chloride and a constant amount of sulphate present, the weight of aluminium taken up by the barium sulphate at first increases and then remains constant, while in the second case, where the amount of sulphate is varied, the degree of contamination of the barium sulphate is proportional to the weight of sulphate used. These results are similar to those obtained by Schneider* for iron. In a solution containing 0.5 gram of ammonium sulphate and 0.025 gram of aluminium there would be an error of about 1 per cent. in the estimation of the sulphur present, as carried out in the ordinary way.

Although it is well known that ammonium carbonate cannot be kept in clay or stoneware jars on account of its action upon them, the presence of ammonium carbonate round the gas burner is not sufficient to explain the corrosion of the glass balls in the

*Schneider, E. A., Zeit. f. physik. Chem., 1892, 10, 425

condensation tower; for if such were the case one would expect to find aluminium hydroxide continually present in the "sulphur solution" instead of only occasionally. It is important to note that this aluminium precipitate only occurs when the gas contains a large quantity of sulphur, which I may mention is mostly present in some organic form. This consideration leads me to believe that there is probably a connection between the formation of this aluminium hydroxide and the amount of sulphur, and the condition in which it exists, in the coal; more especially as the Cape Breton coals contain, for the most part, a large percentage of sulphur organically combined, and consequently not completely removed in the purification of the gas, while this is not the case with the American coals referred to. It is hoped in a future paper to give a complete explanation of this behaviour. In conclusion, I would point out the advisability of using glass balls that are free from aluminium, in determining sulphur in coal gas by the method here described.

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