III.—*Note on the Solubility of Sulphate of Baryta in Hydrochloric Acid.*

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IN the Proceedings of the Royal Society, vol. viii. p. 532, there is an abstract of a paper "On Chemical Affinity, and the Solubility of Sulphate of Baryta in Acid Liquors," by Mr. F. Crace Calvert. The author says that "the insolubility of this salt is affected even by the weakest nitric or hydrochloric acids," and that "in future the practice of rendering liquors acid with either of these acids must be discontinued when sulphates are to be determined." In the abstract of Mr. Calvert's memoir, as it appears in the "Proceedings," the only experiments quoted relate to the solubility of sulphate of baryta in *nitric* acid; whether he extended his researches to hydrochloric acid, it is not stated; it is to be concluded that he did so, since, in a practical point of view, it is of far greater consequence to establish the fact, and the degree of the solubility of this sulphate in the latter acid than in

the former, the great majority of sulphur and of sulphuric acid determinations in mineral analyses being made in liquids containing excess of hydrochloric acid.

That sulphate of baryta is soluble to some extent in nitric acid, or at any rate that sulphuric acid may exist in nitric acid, both strong and dilute, and still no precipitate or even cloudiness be produced by the addition of a barytic salt, has, I believe, been known for some time to many chemists. Speaking for myself, I have certainly been aware of the fact for upwards of two years. I do not claim it as a discovery of my own, though I am quite unable to say from whom I derived my information. I have reason to believe, however, that the discovery originated with Mr. Nicholson, though the first public announcement of it is probably in Mr. Calvert's paper.

It is easy to prove that almost all the fuming nitric acid of commerce contains sulphuric acid, though it may retain a perfect transparency, when largely diluted with water, and treated with a barytic salt. All that is necessary is to evaporate an ounce or so of the acid, in a platinum capsule, down to about a drachm, then add water and nitrate or chloride of barium, upon which a greater or less turbidity will ensue. That very grave errors have been committed in sulphur determinations in organic compounds, in consequence of a want of the knowledge of this important fact, cannot be doubted, fuming nitric acid having been very generally employed as the oxidising agent to convert the sulphur into sulphuric acid: thousands of mineral analyses must, for the same reason, be considered erroneous as regards the determination of this particular element; and I consider myself fortunate that I was made aware of the almost invariable impurity of nitric acid, previous to the commencement of my own iron and cinder analyses, and thus have been enabled to guard against it. It is quite otherwise, however, as regards hydrochloric acid; and I must certainly confess that I read the abstract of Mr. Calvert's paper with considerable discomfort; for if his statement be true, then my own, and many thousand other sulphur determinations, have been made in vain, since in separating sulphur from phosphorus in crude iron and forge cinders I have almost invariably done so in an acid solution, and that acid has been *hydrochloric*. Being thus so immediately interested, and in the absence of all experimental evidence in the abstract of Mr. Calvert's paper, it was natural that I should forthwith commence a series of experiments to satisfy myself as to the justice or injustice of Mr. Calvert's con-

clusions; it being sufficiently evident that if the insolubility of sulphate of baryta is affected by the weakest hydrochloric acid, the usual course of mineral analyses must be somewhat modified. The results of my experiments I beg briefly to lay before the Society; they have proved the groundlessness of my fears, and may have the effect of relieving the minds of some other practical chemists as they have relieved mine. They show that though, under certain circumstances, the insolubility of sulphate of baryta is affected by weak hydrochloric acid, yet that the error likely to be thereby introduced into analysis is either altogether *nil*, or so exceedingly small as to be in most cases unworthy of consideration.

FIRST SERIES OF EXPERIMENTS.

Twelve liquors were prepared of uniform bulk,—the first consisted of 1000 grain measures of distilled water; the second of 900 grains of water + 100 grain measures of hydrochloric acid, sp. gr. 1.153; the third of 800 grains of water + 200 grain measures of the same acid; the fourth of 700 grains water + 300 grain measures of acid; the fifth of 600 grains water + 400 grain measures of acid; the sixth of 500 grains water + 500 grain measures of acid; the seventh of 400 water + 600 acid; the eighth of 300 water + 700 acid; the ninth of 200 water + 800 acid; the tenth of 100 water + 900 acid; the eleventh of 1000 grain-measures of the acid without any water: 5 grains of neutral and thoroughly dried sulphate of potash were dissolved in each of these liquors; and, while boiling, solutions of 10 grains of nitrate of baryta in 300 grains of water were poured into each; they were allowed to remain at rest for twenty-four hours, then filtered, and the sulphate of baryta washed, dried, ignited, and weighed. In the twelfth experiment, the 5 grains of sulphate of potash were dissolved in 500 grain measures of hydrochloric acid, and the 10 grains of nitrate of baryta were boiled for some time with another 500 grain measures of the acid; little, if any, of the salt was dissolved, but abundance of chlorine was disengaged, and the liquor became dark yellow from the absorption of nitrous vapour. The acid liquor was decanted and added to the acid solution of the potash salt, sufficient boiling water was then added to dissolve the baryta-salt, and the liquors were then mixed, boiled, and the sulphate of baryta allowed to subside. The quantities of barytic sulphate obtained in the twelve experiments are given in the following table. The quantity of nitrate of baryta required theo-

retically to precipitate 5 grains of sulphate of potash is 7·5 grains, and the quantity of sulphate of baryta produced should be 6·70 grains.

Number of experiment.	Number of grain measures of water.	Number of grain measures of hydrochloric acid. Sp. gr. 1·153.	Quantity of sulphate of potash used.	Quantity of nitrate of baryta used.	Quantity of sulphate of baryta produced.
1.	1000	0	5 grs.	10 grs.	6·74
2.	900	100	do.	do.	6·70
3.	800	200	do.	do.	6·71
4.	700	300	do.	do.	6·72
5.	600	400	do.	do.	6·69
6.	500	500	do.	do.	6·71
7.	400	600	do.	do.	6·78
8.	300	700	do.	do.	6·77
9.	200	800	do.	do.	6·76
10.	100	900	do.	do.	6·78
11.	0	1000	do.	do.	6·78
12.		500	do.	do.	6·78

It is seen that so far from there being a loss of sulphate of baryta, there is in the last six experiments a small apparent excess; this doubtless arose from a small portion of undecomposed nitrate having been carried down mechanically in the strongly acid liquor with the sulphate, from which it was not subsequently thoroughly removed by washing. It is well known that nitrate of baryta does adhere most pertinaciously to the sulphate when thus carried down, and requires long-continued washing to detach it; it is also well known that nitrate of baryta is very sparingly soluble in highly acid liquids. The precipitates were in all cases washed with the same quantity of boiling water, and the experiments show clearly, I think, that in this particular bulk of liquid, — viz. about 1000 grains measure, — the precipitation of sulphuric acid is complete in whatever proportion hydrochloric acid exists, — whether it forms the entire volume of the liquid, or whether it is absent altogether.

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But Mr. Calvert says, "The solubility of sulphate of baryta is affected in a higher degree by the *bulk* of the acid than by its strength," and the table that he gives for nitric acid fully proves this to be the case. It became necessary to examine this position in relation to hydrochloric acid.

SECOND SERIES OF EXPERIMENTS.

5 grains of sulphate of potash were dissolved in 9000 grains of distilled water + 1000 grains of hydrochloric acid, sp. gr. 1.153, and precipitated as before, while boiling, with a solution of 10 grains of nitrate of baryta. Three precisely similar experiments were made, and the following quantities of sulphate of baryta were obtained:—

I.	II.	III.
5.81 . . .	5.72 . . .	5.90
Mean . . .	5.81 grs.	

Here, then, there is a distinct loss of .89 gr. of sulphate of baryta, but does this arise from a solution of the salt in the acid liquor, or is it the result of dilution? To determine this point, the same quantities of sulphate of potash were dissolved in the same bulks of acid and water, but double the quantity, viz. 20 grains of the precipitant, were employed: the proportions of sulphate of baryta now obtained in three experiments were—

I.	II.	III.
6.52 . . .	6.51 . . .	6.50
Mean . . .	6.51 grs.	Loss19 gr.

Three other solutions were then made and precipitated by 30 grs. of nitrate of baryta. The quantities of sulphate of baryta obtained were—

I.	II.	III.
6.71 . . .	6.69 . . .	6.71

the exact theoretical quantity. I must observe, that in these last six experiments the washings were continued for some hours, in order to avoid any possible error arising from the adhering of a portion of the precipitant to the precipitated salt.

By the side of these last experiments I placed two others, in one of which the 5 grains of sulphate of potash were dissolved in 10,000 grains of boiling distilled water, and in the other in

20,000 grains, no acid being added in either case: the quantities of sulphate of baryta obtained were —

I.	II.
6·73 grs.	6·72 grs.

Lastly, the following experiment was made:—

5 grains of sulphate of potash were dissolved in a small quantity of water, and precipitated by 10 grains of nitrate of baryta; 10,000 grain measures of a mixture of 9 parts water and 1 part hydrochloric acid were then added, and the whole was boiled for 20 minutes; after 24 hours the resulting sulphate of baryta was weighed. Two precisely similar experiments were made, with the following results:—

I.	II.
4·4 grs.	4·5 grs.

Here, then, was a loss of 2·3 grains of sulphate of baryta, one-third of the entire quantity that should have been obtained. The solubility of sulphate of baryta in a large bulk of dilute hydrochloric acid is proved conclusively by this experiment, but in a practical point of view it is not a matter of any importance; since, in the first place, it is not usual to attempt precipitations in such bulky liquids, but always to concentrate as far as possible; and, in the second place, it is always the practice to add considerable excess of the precipitant, which, as has been shown above, counteracts the tendency of the barytic sulphate to dissolve in the acid liquor. On the whole, then, I think that we may, without fear, continue to make our sulphur determinations in strong hydrochloric acid liquors, and that the only thing that the analyst has to guard against is the possible existence of sulphuric acid in the nitric acid he may employ as his oxidising agent.

While on the subject of sulphur determinations, I may allude to a method I have lately adopted for estimating the amount of this element in crude iron, which, with certain precautions, gives very accurate results, and which possesses the great advantage of enabling the operator to work upon much larger quantities of material than in any of the usual methods. The pounded iron is digested in a flask with dilute hydrochloric acid, and the gases evolved passed through three Wolfe's bottles, each containing a solution of arsenious acid; the whole of the sulphur of the metal passes over as sulphuretted hydrogen, and is estimated as As_2S_3 . I have convinced myself, by repeated experiments, that the *whole* of

the sulphur is thus obtained in combination with the arsenic, and that the phosphorus which the crude iron invariably contains, though it is partly liberated, at the same time, in the form of phosphuretted hydrogen, does not interfere with the accuracy of the result. In what form the phosphorus combines with the arsenious acid, or whether it combines with it at all, I intend to make the subject of a special investigation; at present but little is known of the compounds of phosphorus with arsenic. I have, however, satisfied myself that no insoluble compound is formed under the circumstances of the above experiment. The only precautions to be observed are—1st, not to add too much hydrochloric acid to the water in which the arsenious acid is dissolved, the tersulphide not being so insoluble in hydrochloric acid as is generally supposed; nevertheless the solubility of arsenious acid in water is so greatly increased by the addition of a little hydrochloric acid, that a small quantity may be added with advantage; 2nd. the evolved gases must pass through at least three Wolfe's bottles, and it may occasionally be advisable to add a fourth; and, 3rdly, the connections between the bottles must be of *sheet* and not of *vulcanised* India rubber, it being almost impossible to keep the latter perfectly tight under the pressure to which they are subjected. I have occasionally employed solutions of nitrate and acetate of lead in the place of arsenious acid, but the objection to these salts is the great difficulty of washing thoroughly the bulky sulphide of lead: the results are, however, when carefully obtained, quite trustworthy.