XVIII. Observations and experiments undertaken with a view to determine the quantity of sulphur contained in sulphuric acid; and of this latter contained in sulphates in general

Richard Chenevix Esq. F.R.S. M.R.I.A.

To cite this article: Richard Chenevix Esq. F.R.S. M.R.I.A. (1801) XVIII. Observations and experiments undertaken with a view to determine the quantity of sulphur contained in sulphuric acid; and of this latter contained in sulphates in general , Philosophical Magazine Series 1, 11:42, 112-118, DOI: [10.1080/14786440108675965](https://doi.org/10.1080/14786440108675965)

To link to this article: <http://dx.doi.org/10.1080/14786440108675965>

Published online: 18 May 2009.

Submit your article to this journal [↗](#)

Article views: 3

View related articles [↗](#)

some importance. But whatever reason there was to think, by arguing upon its chemical properties, that I had really succeeded in improving its medicinal virtues, it still remained to be proved, by actual experiment, that the hoped-for success was not merely conjectural. To ascertain this, I gave some of my powder to Dr. Crichton, Dr. Babington, and Mr. Abernethy; gentlemen whose extensive practice and acknowledged skill sufficiently enabled them to judge of its medical properties. They all concur in opinion, that, in its general effects, it agrees with Dr. James's powder and the *pulvis antimonialis*; but that it is more mild, and consequently may be given in larger quantities, seldom producing nausea or vomiting in doses of less than eight or ten grains.

XVIII. *Observations and Experiments undertaken with a View to determine the Quantity of Sulphur contained in Sulphuric Acid; and of this latter contained in Sulphates in general.* By RICHARD CHENEVIX, Esq. F.R.S. M.R.I.A.*

IN a paper which I had the honour to present to the Royal Society of London, and the subject of which was the analysis of some arseniates of copper and of iron, I had occasion, in examining many pyrites, matrices of those ores, to remark the very great inequality which prevailed in the results of repeated experiments, made with a view to determine the proportion of sulphur. But I soon perceived that the inaccuracy was caused by a partial combustion and acidification of the radical, through the means of the nitric acid employed to dissolve the ore.

Having therefore, in the usual manner, ascertained what quantity of that ingredient remained untouched, I was forced to seek the rest of it in the liquor which had washed the various precipitates. To obtain it, I poured a solution of nitrate of barytes into those washings when all the other substances had been carefully separated, and was thereby enabled to precipitate, in a state of purity, the sulphate of barytes, formed by that earth, and by the portion of sulphur originally acidified in the first treatment of the ore by nitric acid. To come at the knowledge of the proportion of sulphur contained in a given quantity of sulphate of barytes, I had recourse, in the first instance, to the quantity of sulphur said by Lavoisier to be contained in sulphuric acid; and, in the

* From the *Transactions of the Royal Irish Academy*.

next, to the proportions of the latter, announced in the synoptic tables of Fourcroy, as entering into the composition of sulphate of barytes. According to the former of those chemists, 100 parts of sulphuric acid contain 71 of sulphur and 29 of oxygen; and again, in adopting the proportions of the latter, we have 33 per cent. of acid in sulphate of barytes. But if 100 contain 71 of sulphur, 33 must contain 23.43. Consequently, for every 100 parts of sulphate of barytes, I was to allow 23.43 of sulphur. But, by the results of my analyses, I had such quantities of sulphate of barytes as induced me to doubt the accuracy of one or other of the statements by which I estimated the quantity of real sulphur contained in the ore.

No person is better acquainted than our celebrated president with the many difficulties that occur in the analysis of salts in general, particularly with regard to the quantity of real acid they may contain. It has been a work of trouble to the ablest chemists, and they have not always agreed in their results. The proportions announced by Fourcroy may therefore be doubted, in common with those of the other learned operators to whom I have alluded.

The real quantity of acid produced by the combustion of any acidifiable basis, can be determined by one or other of the following methods only: by direct combination in some salt, the proportions of which are already known; or by obtaining, in a state perfectly free from water, the acid resulting from such combustion. To the former method, the general objections against all analyses of salts must apply. The latter is still more defective. It is by no means certain that we have ever yet obtained any acid in a state of perfect fixity, unless we except the phosphoric and the arsenic; for even the crystallized vegetable acids retain a portion of water in their crystallization. It is not that I absolutely deny our having obtained them so; but I say merely that we have no proof. It would indeed be setting narrow bounds to the perfection of nature to assert, that no combustible body could, when saturated with oxygen, assume of itself the state of liquidity; or that the oxide of the particular substance called *hydrogen* must be present to confer that property. Doubtless sulphuric acid may, as well as water, contain in itself so just a proportion of specific heat, as to remain liquid at the temperature of our globe, and under the pressure of our atmosphere. But both water and sulphuric acid being easily volatilized, and having a powerful affinity for each other, it is not easy, if even possible, by distillation, to separate them with sufficient accuracy in experiments of delicate inquiry.

A second source of error, therefore, remained open in this branch of the calculation, which gave the proportion of 23.43 of sulphur, as that contained in 100 parts of sulphate of barytes.

However, before I would allow myself to call in question such authorities as those I have quoted, I instituted the following experiments:—In a tubulated glass retort I put 100 parts of purified sulphur, and poured upon them strong nitric acid. A quilled receiver, plunging into a Woulfe's apparatus, was adapted to the retort; and all being well luted, I proceeded to distil. The liquor which came over was poured back several times upon the sulphur, until the whole was dissolved. The water which had come over, and that through which the nitrous gas, produced during the operation, had passed, were essayed for sulphureous acid, and no traces of it could be found. No sulphur had been volatilized, therefore no suspicion could remain that all was not converted into sulphuric acid. The liquors which were in the various parts of the apparatus were united, and to them was added a sufficient quantity of nitrate of barytes. The whole was evaporated gently; because, though I am well acquainted with the very little solubility of sulphate of barytes, I well know that nitric acid will retain a small portion of it, particularly when formed in a liquor where that acid abounds. In a first experiment I obtained 694 from 100 of sulphur; in a second, 348 from 50; and, in a third, 347 from the same quantity. But the simple rule of three reduced these quantities to 14.6 or 14.4 per cent. of sulphur contained in sulphate of barytes; a difference wholly to be neglected. If, therefore, we take 14.5 as the average for the quantity of sulphur contained in 100 parts of sulphate of barytes, we shall not be far from the truth. From the accordance of these experiments, repeated and varied, I had now no doubt but concerning the source where I was to seek the error, which gave 23.43 as the just proportion.

To ascertain this point, I operated in the following manner:—I prepared some lime as pure, I believe, as chemical means can procure it. I digested white marble in muriatic acid; and, by leaving an excess of the earth, was certain that, by the superior affinity of lime for that acid, nothing else had been taken up. Upon trying the solution with ammonia, no precipitate took place. By means of carbonate of potash, I separated the lime in the state of carbonate; and, after well washing the precipitate, exposed it in a platina crucible to a violent heat till the weight no longer diminished. I am acquainted with no more efficacious method

to prepare lime fit for the delicate purposes of scientific chemistry.

One hundred parts of this lime were dissolved in dilute muriatic acid, in the same platina crucible, previously weighed; and then sulphuric acid was added in sufficient quantity. Sulphate of lime was precipitated; and the vessel was exposed to a heat, at first gentle, to evaporate the liquor; and then, by degrees, raised to a temperature which could expel every thing but the combined sulphuric acid, and leave the sulphate of lime completely calcined. The crucible with the salt was then weighed, and the augmentation was 76. It appears to me, that, if we admit (and I see no reason that we should not admit it) that calcined lime and calcined sulphate of lime are wholly exempt from water, it must be clear that the 76 additional weight were sulphuric acid; and that the sulphuric acid must in this state, more than in any other, approach nearer to what may be termed absolutely real acid. One hundred parts of calcined sulphate of lime contain, therefore,

Lime	-	57
Sulphuric acid	-	43
		<hr/>
		100

By the former experiments (those made upon sulphur converted into acid, and then united to barytes,) we had the quantity of sulphur contained in sulphate of barytes. By the latter (those made by directly combining lime with sulphuric acid) we had the proportion of real acid contained in calcined sulphate of lime. Consequently, by knowing the ratio that sulphate of barytes bears to sulphate of lime, with regard to the acid in each, we shall arrive at the knowledge of the quantity of sulphur contained in real sulphuric acid. For this purpose, I attempted to dissolve, in water, 100 parts of sulphate of lime. But finding in this method of proceeding a considerable inconvenience arising from the great quantity of liquor necessary to effect the solution of that salt, I had recourse to the following expedient:—Upon 100 grains of calcined sulphate of lime, I poured some oxalic acid, which attracts the basis with an affinity superior to that exercised by sulphuric acid. Oxalate of lime was here formed; but oxalate of lime is soluble in a very small excess of any acid. A little muriatic acid operated a complete solution; and thus a great quantity of sulphate of lime required but little water to dissolve it. Into this liquor, muriate of barytes was poured, and suffered to remain some time, gently heated. By these means any oxalate of barytes that might have been formed, was retained in solution by the original

excess of acid; and the entire quantity of sulphate of barytes was deposited. Of the exactness of all these methods, which I used as the instruments by which I ascertained these results, I convinced myself by various preliminary experiments. After the usual filtration, washing and drying at the gentle heat of a sand-bath, I obtained in one experiment 185, in another 183, and, lastly, in another 180. This difference does not exceed the limits of what all persons conversant in analytic chemistry will allow to experiments of this nature. We may therefore take 183 as the mean proportion; consequently we shall say, that 183 of sulphate of barytes contain the same quantity of sulphuric acid as 100 of sulphate of lime; and $183 : 43 :: 100 : 23.5$. Therefore 23.5 is the proportion of acid in 100 of sulphate of barytes. But we have before seen that 14.5 of sulphur, acidified by nitric acid, form that portion of sulphuric acid contained in 100 of sulphate of barytes, viz. 23.5. We must now say, that $23.5 : 14.5 :: 100 : 61.5$, and the fourth term will be the proportion of sulphur = 61.5, which combined with 38.5 of oxygen will form 100 of real sulphuric acid.

In neither of the proportions, whether it be of the acid contained in the salt, or of the combustible basis contained in the acid, do I agree with the two chemists whom I have quoted. This justly excited some doubts in my mind, and led me to repeat my experiments. Nor should I yet be thoroughly satisfied, if I could not, upon other grounds than by supposing inaccuracy in them, account for the apparent differences. We must ever expect to see the errors of our predecessors corrected by men much inferior in abilities, but who, by possessing more certain means, supply the want of genius and invention. At the time in which the experiments were made that determined the proportion of 33 per cent. of sulphuric acid in sulphate of barytes, it was not known that we had never obtained any barytes pure; and that a considerable portion of carbonic acid resisted the action of every degree of heat that had been applied to carbonate of barytes. The fact was, I believe, first observed by Pelletier, but the method of avoiding the inconvenience was pointed out by Vauquelin. He decomposes nitrate of barytes by fire, and a moderate degree of heat is sufficient to expel all the acid and the water. The chemists I have mentioned performed synthetical experiments by combining, directly or indirectly, sulphuric acid, and such barytes as they imagined to be pure. The constant similarity of their results is sufficient to prove the accuracy of their operations; but, working upon an impure substance, they must have been contented with a similarity of error.

Three causes may exist which are capable of accounting for any variation, whether in *plus* or in *minus*, that might have appeared in the experiments, by which Lavoisier determined the quantity of sulphuric acid obtained by the combustion of sulphur in oxygen gas.

1st, A part of the sulphur may be volatilized during combustion.

2d, All the sulphur may not be converted into sulphuric acid, but part may remain in the state of sulphureous acid.

3d, In rectifying, some acid may come over along with the water; or, *vice versa*, some water remain with the acid. These considerations will excuse me for having proposed a doubt, where the authority of so great a man exists against the experiments which I have related.

The method which I had used to ascertain the quantity of sulphur in an ore had been practised by Tassaert (*Annales de Chimie*, No. 82: Analysis of Cobalt from Tunaberg); but he calculated according to the proportions of Lavoisier and of Fourcroy. In another paper by Thenard, (*Annales de Chimie*, No. 96,) he states the proportions of sulphuric acid, obtained by treating sulphur with nitric acid, to be

Sulphur	-	-	55.56
Oxygen	-	-	44.44
			<hr/>
			100.00

but in the extract given by Guyton in that number of the *Annales de Chimie*, the mode of operation is not described. Calcined fulphate of barytes is estimated in the same paper to contain

Barytes	-	-	74.82
Sulphuric acid	-	-	25.18
			<hr/>
			100.00

which proportions are as near to what I had found as can be expected; for fulphate of barytes does not contain more than 3 per cent. of water of crystallization, and they must be deducted from the quintal.

Having determined with accuracy the proportion of acid in any insoluble fulphate, it is easy to proceed to the determination of that contained in any other fulphate. The domestic art, or analytic chemistry, in general, cannot however expect to derive such advantages from the knowledge of soluble salts, as of those which, from their insolubility, may be used with accuracy, in delicate experiments, to determine the proportions of the constituent parts of bodies.

But if with this mode of operating we compare the quantities of real acid, said (in those excellent tables with which Mr. Kirwan has enriched the science) to be contained in sulphuric acid of different specific gravities, each will serve as a proof of the validity of the other; and perhaps demonstrate, that sulphuric acid, without the intervention of water, may enjoy liquidity at the temperature and pressure which act upon our globe.

XIX. *Experiments on Platina.* By L. PROUST.

[Continued from p. 55.]

XIII. *Of the Crystallization of Solutions of Platina.*

THE small yellow, red, and sand like grains which are deposited at the bottom of the united solutions, and which sometimes assume the octaedral form, are generally taken for muriate of platina. The quantity of these crystals, which is always very small, does not increase by concentration; which, however, ought to be the case, if these crystals were really muriate of platina. No more of them appear in solutions from which they have been once separated; and their separation is even complete a long time before the moment when the real muriate of platina begins to crystallize.

These crystals are a double salt, composed of muriate of platina and potash, as will be seen hereafter: they are formed from the small quantity of potash which, by the inadvertency of the workmen, remains in the neck of the retorts, when preparing nitric acid, and from that also which is carried over in the distillation itself; for nitre is always found, after the rectification of aquafortis, at the bottom of the retorts. The greater part of those who have operated on platina having in general employed the acids sold in the shops, we need not be surprised that they should have found crystalline deposits of the kind here alluded to, and that none of them are ever seen in solutions made on purpose with acids well purified.

If some of these crystals be heated in a glass tube closed at one end, their nature may be soon distinguished; because the muriatic acid, charged with the oxygen of the metal, is volatilized in gas; while the platina, reduced to the metallic state, and mixed with the muriate of potash, remains at the bottom of the tube.

Lewis, in my opinion, is the only person who has accurately observed the crystallization of platina. The solution

was