XXIV. *On the composition of chloride of barium. By Dr.* Edward Turner, *Professor of Chemistry in the University of London. Communicated by Dr.* Dionysius Lardner, *Fellow of the Royal Society.*

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In taking a review of the present state of chemistry;—of the numerous compounds that have been discovered within a very limited period, and of which many have as yet been but partially or imperfectly examined;—of the results, often discordant, which analysts have obtained;—and of the opposite theoretic views which are prevalent,—it is difficult to avoid suspecting the propriety of opinions that have been thought to rest on the sure basis of correct observation, or doubting the accuracy of analyses conducted by chemists of the highest reputation. The era of brilliant discovery in chemistry appears to have terminated for the present. The time is arrived for reviewing our stock of information, and submitting the principal facts and fundamental doctrines of the science to the severest scrutiny. The activity of chemists should now, I conceive, be especially employed, not so much in searching for new compounds or new elements, as in examining those already discovered; in ascertaining with the greatest possible care the exact ratio in which the elements of compounds are united; in correcting the erroneous statements to which inaccurate observation has given rise; and exposing the fallacy of opinions which partial experience or false facts have produced. Considerable as is the labour and difficulty of such researches, they will eventually prove of great importance to chemical science by supplying correct materials for reasoning; and will sometimes, even in the most familiar parts of analytical chemistry, lead to the detection of errors that had escaped notice, and which vitiate many analyses previously regarded without suspicion. An instance of this kind I shall have occasion to notice in the present communication.

The foregoing reflections have been more immediately elicited by circumstances connected with Dr. Thomson's "First Principles of Chemistry." The celebrated author of that work has attempted to ascertain the equivalents of all elementary substances; and as the result of his labours, has inferred the truth of an ingenious conjecture, suggested some years ago by Dr. Prout, that the weights of the atoms of bodies are simple multiples of the atomic weight of hydrogen. (Annals of Philosophy, vol. vi. p. 321.) This hypothesis is of so much importance if true, and may give rise to so much error if false, that its accuracy cannot too soon be put to the test of a minute experimental inquiry. The only chemists who to my knowledge have objected on experimental grounds to Dr. Thomson's support of this hypothesis, are Dr. Ure and Berzelius; but unfortunately both these gentlemen have written on the subject with such acrimony, and assumed a tone so unusual in scientific controversy, as in a great degree to have destroyed that confidence which their well-founded reputation for sagacity and skill would otherwise inspire. The uncertainty in which this question is still involved, has induced me to investigate it; and the essay which the Royal Society do me the honour to hear this evening, may be viewed as the commencement of a series of essays designed for the elucidation of the same subject. As I shall have occasion on individual points to differ repeatedly from Dr. Thomson, I embrace this opportunity to declare, that in considering his statements with the freedom required for eliciting truth, I bear towards him no other personal feelings than those of kindness for civility received at his hands, and of respect for a man who has devoted his life zealously and successfully to the promotion of science.

The object of the present essay is to determine the composition of chloride of barium. The frequent employment of this compound in chemical experiments renders an exact knowledge of its constitution peculiarly important; and it has been used so extensively by Dr. Thomson as a medium of analysis, that an examination of it will afford an excellent criterion of the accuracy of his researches. Dr. Thomson has employed chloride of barium in ascertaining the equivalent of sulphuric acid, and of not less than thirteen metals and their protoxides; so that if his examination of this substance is inexact, the error will probably affect a large portion of his treatise. Dr. Thomson has been led by his observations to adopt 36 as the equivalent of chlorine, 70 as that of barium, and 78 as that of baryta. The equivalent of chloride of barium is therefore 106; and on mixing this quantity of the chloride with 88 parts of sulphate of potash, each being previously dissolved in separate portions of distilled water, he finds that the clear liquid left after the insoluble sulphate of baryta has completely subsided, is not rendered turbid either by muriate of baryta or sulphate of soda. It is hence inferred, that by double decomposition the whole of the baryta has united with all the sulphuric acid, and that all the potash and muriatic acid are contained in solution in the form of muriate of potash. The resulting sulphate of baryta, after being collected and heated to redness, weighed exactly 118 parts; while the muriate of potash, when collected and duly heated, yielded 76 parts of chloride of potassium. It follows from this experiment that 40 is the equivalent of sulphuric acid, and 48 of potash; and on mixing with one equivalent of chloride of barium such a quantity of any soluble sulphate as should produce a similar interchange of elements, the constitution of that salt would be exactly determined.

This leading experiment, from which Dr. THOMSON deduces the composition of chloride of barium as well as the atomic weight of baryta, is maintained by BERZELIUS to be inexact. He prepared chloride of barium and sulphate of potash with the greatest possible care; and on mixing them in the proportion mentioned by Dr. THOMSON, he found that a considerable quantity of the former, about 2.25 per cent of the amount employed, remained free in the residual liquid. (Lehrbuch der Chemie, vol. iii. p. 106.) In an answer to this objection, published in the Philosophical Magazine and Annals of Philosophy for last March, Dr. THOMSON has maintained the accuracy of his original experiment, stating that it had recently been repeated by six of his practical pupils, and in no case did the residual liquid contain a trace either of sulphuric acid or baryta. I regret that my observations have forced me to a conclusion precisely opposite. I have made the experiment in question repeatedly, with the greatest care, and with perfectly pure materials, and in every instance the result coincided with that obtained by BERZELIUS. The sulphate of potash which I used was prepared by repeated crystallization from the crystals of that salt as sold by the druggists, and was so pure that I could not detect in it a trace of foreign matter. The chloride of barium was formed by the action of pure muriatic acid on native carbonate of baryta. The resulting solution was rendered alkaline with pure baryta, in order to precipitate any oxide of iron or manganese which might be present; and the crystals subsequently obtained by evaporation were reduced to powder, boiled in successive portions of alcohol, and fused. The fused chloride was redissolved in distilled water, and again obtained in crystals. This salt dissolved without residue or turbidity in water, and the solution was not affected by pure ammonia; it was not discoloured by sulphuretted hydrogen, hydrosulphuret of ammonia, or chloride of lime; when precipitated by an excess of sulphate of potash, the soluble parts were not rendered turbid by an alkaline carbonate or oxalate of potash; and when thrown down by pure sulphuric acid, evaporated, and ignited, the dry mass did not yield a trace of any soluble sulphate to water. Both compounds were heated to redness before being employed; and the chloride of barium, which if perfectly anhydrous, attracts moisture freely from the atmosphere, was always placed while hot in a weighed bottle secured by a tight cork, and its weight ascertained when cold. This precaution is not necessary with sulphate of potash.

I have thought it right to enter into these details, not only that chemists may judge of the accuracy of my experiments by the care with which they were conducted, but because the error committed by Dr. THOMSON appears referable to the neglect of some of these precautions. This opinion seems the more probable, since Dr. THOMSON is uncertain whether in his original experiments he did not employ the muriate of baryta of commerce, and if so he doubtless must have operated with an impure substance. But independently of any inaccuracy arising from this source, I shall now endeavour to prove that his method involves an error which precludes an exact result even with the purest materials. When solutions of muriate of baryta and sulphate of potash are mixed together, a small portion of the latter invariably escapes decomposition, and falls tenaciously adhering to the sulphate of baryta. I was led to this fact by observing, that when a known quantity of chloride of barium is precipitated by sulphate of potash, the resulting sulphate of baryta always weighed more than when the precipitation was made with pure sulphuric acid. The appearance of the salts after exposure to a red heat, was likewise different; the impure sulphate being harder, more brittle, and less opaque than the pure sulphate. The former reduced to powder and boiled with water, yielded a solution which precipitated barytic salts freely, and afforded certain evidence of the presence of potash with muriate of platinum.

The presence of sulphate of potash was at first naturally ascribed to imperfect edulcoration; but as it was still found, even after the precipitate had been washed with unusual care, I was led to examine the subject minutely. A solution of sulphate of potash was mixed with a large excess of muriate of baryta; the insoluble sulphate was edulcorated until the washings ceased to contain a trace of baryta, and was then collected on a filter, and ignited. On boiling it in powder with water, sulphate of potash was dissolved. The experiment was varied by mixing the solutions at a boiling temperature, and continuing the ebullition for some minutes; but the result was the same as before. On edulcorating the precipitate with boiling water, sulphate of potash begins to make its appearance in the washings as soon as the excess of muriate of baryta has been removed; but neither by this means, nor by boiling the recent precipitate for hours in successive portions of distilled water, have I succeeded in removing all the sulphate of potash. The adhesion of this salt ensues even in a dilute solution; and it is not prevented by the presence of other salts, such as nitre, and nitrate or muriate of ammonia, nor by free muriatic acid. The quantity of adhering sulphate of potash is variable, depending apparently as well on the relative quantity of the two salts, and the strength of the solution, as on the manner and extent of edulcoration. I have known it to increase the weight of the sulphate of baryta by one per cent.

The foregoing observations, unless I am much deceived, will fully justify the statement, that Dr. THOMSON's method of analyzing chloride of barium is radically defective. For if chloride of barium and sulphate of potash be mixed in the proportion to make a perfect interchange, some of the former will remain in the liquid, proportional to the quantity of the latter which escapes decomposition; whereas the absence both of sulphuric acid and baryta from the liquid can only occur, when the quantity of chloride of barium is insufficient for effecting complete double decomposition with the sulphate of potash. So that when the proportions appear to be right, they are certainly wrong; and they may be right, when they appear to be wrong. It is obvious, too, that Dr. THOMSON's analysis of sulphate of potash by means of chloride of barium, is not more satisfactory than his analysis of chloride of barium by sulphate of potash. The equivalent of potash, deduced from that analysis, cannot be relied on; and his proof of 40 being the exact equivalent of sulphuric acid is also liable to objection. But the error upon which Dr. THOMSON has so unhappily fallen, has been also committed by other chemists. Every analysis of sulphate of potash, or of salts containing this alkali and sulphuric acid, must be regarded with suspicion. Thus the analysis of common alum by Dr. THOMSON and BERZELIUS can scarcely be quite exact; and the analysis of potash-minerals, in which baryta has been separated by sulphuric acid, may also be suspected of slight inaccuracy.

The process by which I have endeavoured to analyze chloride of barium consists of two parts. In the first, a given quantity of the chloride was dissolved in water, and the baryta thrown down as sulphate by sulphuric acid. In the second, a similar solution was precipitated by nitrate of silver, and the chlorine inferred from the quantity of fused hornsilver which was produced. The quantity of chloride of barium employed in each experiment varied from 30 to 40 or 45 grains. The sulphuric acid had of course been purified by distillation, and left no residue when evaporated on platinum.

The process by sulphuric acid was varied: one while the solution and precipitate were evaporated to dryness in a platinum capsule; and at another, the insoluble sulphate was collected on a double filter. Both methods were frequently repeated, and the sulphate of baryta was always dried by exposure to a red heat. The quantity of sulphate of baryta obtained by the first method from 100 parts of the chloride ranged from 112.17 to 112.2, being more frequently the latter than the former; and 112.19 may be adopted as a mean of the most successful experiments. The quantity obtained by filtration fell rather short of this, varying in the best experiments from 112.08 to 112.12. The difference is referable to a trace of sulphate of baryta being retained by the acid solution, in which it may really be detected by evaporation. The first series of experiments may therefore be considered the more accurate, and it may be inferred that 100 parts of pure chloride of barium are capable of yielding 112.19 parts of sulphate of baryta. This result agrees very closely with that stated by BERZELIUS in the last edition of his System of Chemistry, who in one experiment got 112.17, and in another 112.18, of sulphate from 100 parts of chloride of barium. According to Dr. THOMSON, 100 parts of the chloride yield only 111.32 parts of sulphate of baryta. It is proper to state, in reference to the foregoing experiments, that traces of chloride of barium are apt to adhere to the sulphate of baryta; but this source of error is easily avoided by decanting the supernatant fluid after subsidence, and stirring the precipitate with hot water acidulated with sulphuric acid.

In order to determine the chlorine of chloride of barium by means of silver, it was desirable to ascertain the composition of hornsilver. For this purpose some fine silver containing only traces of gold and copper was dissolved in nitric acid, precipitated by sea-salt, digested in dilute nitro-muriatic acid, and washed. The dry chloride was then reduced by means of carbonate of potash in the usual manner, and after throwing a few fragments of nitre upon the fused metal, it was granulated and then boiled repeatedly in distilled water. In the silver thus prepared I could not detect potash, gold, copper, or any other impurity; whereas it is difficult in employing common silver, to purify it completely by one operation.

1. Of this silver 28.407 grains were dissolved in pure nitric, and precipitated by pure muriatic acid, both of which had been prepared with the greatest care. The whole mass was evaporated to dryness, and yielded 37.737 grains of fused chloride of silver.

2. In a second similar experiment 41.917 grains of silver yielded 55.678 grains of hornsilver.

3. In a third, 40.006 grains of silver yielded 53.143 of hornsilver.

According to the first and third experiments 100 parts of silver correspond to 132.84, and according to the second to 132.83 parts of hornsilver.

4. In a fourth experiment, 30.922 grains of silver were dissolved in nitric acid, and precipitated by muriate of baryta in excess. The precipitate after being carefully washed and collected on a double filter, yielded 41.07 grains of fused chloride; and hence the silver and chloride are in the ratio of 100 to 132.82.

5. In a fifth experiment, 42.255 grains of silver were dissolved as usual, precipitated by an excess of muriatic acid, and collected on a double filter. The fused chloride amounted to 56.09 grains, giving the proportion of 100 to 132.74. When the silver is thus precipitated by free muriatic acid, and the chloride collected on a filter, the result is constantly below that obtained by the other

methods, owing to a trace of the chloride being dissolved by the strong acid solution.

It may be inferred, as a mean of the four first experiments, that 100 parts of silver correspond to 132.83 parts of chloride of silver. The proportion stated by Berzelius is 100 to 132.75; and it is estimated at 100 to 132.72 by Dr. Thomson. All these results, therefore, are closely correspondent.

From one of the experiments (No. 4.) just mentioned, it is manifest that the precipitation of chloride of barium by nitrate of silver does not involve any appreciable source of error. To be quite certain, however, as to this fact, chloride of barium was mixed with nitrate of silver in excess, and the precipitate carefully washed. It was then boiled in distilled water, and the fluid examined for silver and baryta; but not a trace of either could be detected. It dissolved completely in ammonia, and the addition of sulphuric acid did not cause the slightest turbidity.

In five analyses made by precipitating chloride of barium by an excess of nitrate of silver, I obtained the following proportions.

	Chloride of Barium.	Chloride of Silver.
Exp. 1.	100 yielded	137.45
2.	100	137.54
3.	100	137.70
4.	100	137.62
5.	100	137.64

Though all these analyses were made with great care, the last two were the most successful, as being less influenced by errors of manipulation than the others. Instead, therefore, of taking the mean of the five, which is 100 to 137.61, I adopt the mean of the two last experiments, which is 100 to 137.63. In one of these the precipitate was washed with distilled water only, and in the other with water acidulated with nitric acid. Berzelius in his experiments on this subject found that 100 parts of chloride of barium corresponded to 138.06 in one experiment, and 138.08 in another. This is the only material difference between us which I have yet had occasion to notice. It induced me to reconsider every part of my experiments; but as I am unable to detect the slightest inaccuracy in the two analyses from which my result was derived, I cannot hesitate to adopt it. I conclude, accordingly, that 100 parts of chloride of barium correspond to 137.63 parts of chloride of silver; and as, consistently with the preceding researches, this quantity of hornsilver contains 34.016 parts of chlorine, it follows that chloride of barium consists of

Barium	65.984
Chlorine	34.016
	100.000

Its constitution according to Dr. THOMSON and BERZELIUS is shown by the following numbers:

	THOMSON.	BERZELIUS.
Barium	66.037	65.926
Chlorine	33.963	34.074
	100.000	100.000

It is impracticable, from the composition of chloride of barium as above stated, to make any satisfactory inference relative to the real equivalent of barium, because the real equivalent of chlorine is not yet clearly ascertained. By Dr. THOMSON it is estimated at 36, and by BERZELIUS at 35.43; and on calculating the equivalent of barium according to both estimates, the following result will be obtained.

Barium	69.832	68.726
Chlorine	36.000	35.430
	105.832	104.156

Hence if 36 is the equivalent of chlorine, that of barium will be 69.832, or very near 70 as stated by Dr. THOMSON; but if the calculation be continued, still taking the results of my experiments as its basis, the equivalent of sulphuric acid will turn out to be 40.901 instead of 40. From these considerations it appears evident that at least one of the equivalent numbers concerned in the calculation must be incorrect. I abstain, however, from offering any further opinion on this point at present, as it will form the subject of another communication.