

## LXXX.—Contributions to the Chemistry of the Cerite Metals. III.

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*Introductory Remarks.*

In a paper published several years ago (*Chem. Soc. J.*, Trans., 1882, 68, and *in extenso*, *Monatsh. Chem.*, 1882, 1—60), I endeavoured to determine the position of the cerite metals in the periodic system of elements, and arranged them in the order—

La <sup>iii</sup> .	Ce <sup>iv</sup> .	Di <sup>iii-v</sup> .
139	141·6	146·6

A little later (*Monatsh. Chem.*, 1882, 486, and Trans., 1883, 278), I succeeded in proving that the didymium from cerite is a *mixture*, and that the atomic weight of the true didymium is at most Di = 145·4. For lanthanum I found at the same time the number La = 138·28. Working with a more abundant supply of the rare material, Cleve, whilst confirming my number for lanthanum, that is, 138·28 (*Bull. Soc. Chim.*, **39**, 151, 289), found didymium to be Di = 142·3—142·4. If, as has hitherto been the case, the number found for the atomic weight of cerium by Böhlig (*J. pr. Chem.* **120**, 222), namely, Ce = 141·6, be admitted to represent the truth, the order of the atomic weights of the said elements in the system would be as follows:—

La.	Ce.	Di.
138·2	141·6	142·3
<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">             { 3·4           </div> <div style="text-align: center;">             { 0·7           </div> </div>		
Difference....		

It must be admitted that the lanthanum and didymium preparations with which Cleve determined the atomic weights of these elements were pure and homogeneous, and, as the method used by him does not involve any apparent source of error, we are justified in regarding his numbers as very nearly representing the truth. It is, however, very evident that the difference between the atomic weights of lanthanum and cerium (3·4) is much larger than that between cerium and didymium (0·7), and the question therefore arose whether Böhlig's number (Ce = 141·6) is really the atomic weight of cerium, as is generally believed, especially as Wolf (*Sill. Amer. J.* [2], **46**, 53—62) has found the atomic weight of the *purest* cerium to be Ce = 137,

a much lower number than Böhlig's. The object of the present investigation is to answer this question.

### *Historical Review.*

Since 1816, the atomic weight of cerium has been determined by many chemists, but the numbers found, especially those which seem to be the most trustworthy, differ more widely from each other than might be expected. The following is a short review of the determinations made. For details I must refer partly to the original papers, partly to the works recently published by G. F. Becker (*Constants of Nature*, Part IV, Washington, 1880); F. W. Clarke (*Constants of Nature*, Part V, Washington, 1882); Lothar Meyer and Seubert (*Die Atomgewichte der Elemente*, Leipzig, 1883); and by Ostwald (*Lehrbuch der Allgemeinen Chemie*, Leipzig, 1884). My comments on the individual determinations form a special chapter of the present paper.

I should state that I call the oxide  $\text{Ce}_2\text{O}_3$  and its salts *cerous*, and the oxide  $\text{CeO}_2$  *ceric* and *not* cerium peroxide, as is done by some chemists, as the latter name must be reserved for the oxide  $\text{CeO}_3$ , recently investigated by L. de Boisbaudran (*Compt. rend.*, **100**, 605), and Cleve (*Bull. Soc. Chim.*, **43**, 53). The numbers below refer to  $\text{O} = 16$ .

The number to be deduced from Hisinger's (*Schweig.*, **17**, 424; *Pogg. Ann.*, **8**, 186) experiments, made in 1814–16, is  $\text{Ce} = 137.9$ . The method is not given, and his cerium was contaminated with lanthanum and didymium, the existence of the last two elements not being known at that time.

Berlinger's (*Annalen*, **42**, 134) cerium salts were also rose-coloured. The numbers obtained by him were  $\text{Ce} = 142.3$  from the relation of ceric oxide to silver chloride;  $\text{Ce} = 142.3$  from that of ceric oxide to barium sulphate; and  $\text{Ce} = 141.6$  from the combustion of cerous formate.

Rammelsberg's (*Pogg. Ann.*, **55**, 65) analysis of anhydrous cerous sulphate, made in 1842, gives  $\text{Ce} = 134.3$ .

Hermann (*J. pr. Chem.*, **30**, 184) in 1843, determined the relation of anhydrous cerous sulphate to barium sulphate. His numbers give  $\text{Ce} = 139.4$ .

From Marignac's (*Ann. Chim. Phys.* [3], **27**, 209; *Arch. Sci. Ph. Nat.* [1], **8**, 273) volumetric analysis of cerous sulphate solutions by means of barium chloride, it follows that  $\text{Ce} = 141.8$ ; whilst the relation of anhydrous cerous sulphate to barium sulphate,  $\text{Ce}$  is 141.6. Later on (*Ann. Chim. Phys.* [3], **38**, 148), the same chemist gave the preference to the number  $\text{Ce} = 137.7$ , but without giving any experimental evidence.

Jegel, in 1858 (*Annalen*, **105**, 45), deduced the number  $Ce = 138.1$ , from the combustion of cerous oxalate. An analysis of the sulphate gave  $Ce = 137.8$ . In both cases, the ceric oxide was analysed iodometrically.

Lothar Meyer and Seubert calculate, instead of the above numbers,  $Ce = 137.4$  and  $138.3$ .

A combustion of the oxalate, made by Rammelsberg (*Pogg. Ann.*, **108**, 44) in 1859, gave  $Ce = 138.1$ .

All the above determinations were made with cerium preparations containing larger or smaller quantities of foreign earths, for the ceric oxide obtained was more or less brown coloured. In 1867, an extended investigation of the subject was undertaken by C. Wolf (*loc. cit.*) in Bunsen's laboratory, but unfortunately, it remained unfinished in consequence of his premature death, and has, up to the present, never been again taken up. The following details from Wolf's diary, published after his death by Genth, may be given here, as being important in relation to the present question.

Ceric nitrate prepared from the crude oxides, was decomposed by pouring its aqueous solution into boiling water containing some sulphuric acid, and the precipitate of basic nitrate and sulphate, N, was converted into cerous sulphate. This was recrystallised at least ten times. Wolf heated the sulphate over a small flame in a double platinum crucible, in order to determine the amount of water of crystallisation (by loss of weight), and from the aqueous solution of the anhydrous sulphate thus obtained the oxalate was precipitated by a boiling concentrated solution of oxalic acid. This, by careful ignition, was converted into ceric oxide. In the filtrate, the sulphuric acid was determined as barium sulphate. The excess of oxygen in  $CeO_2$  ( $Ce_2O_4$ ) over  $Ce_2O_3$  was determined iodometrically. From these four data ( $H_2O$ ,  $CeO_2$ ,  $Ce_2O_3$ , and  $SO_3$ ) the composition of the anhydrous cerous sulphate was first calculated, and from this the equivalent of cerium.

As the ceric oxide obtained in the first series of determinations had a brownish colour, part of the precipitate N was purified by dissolving and precipitating with boiling water; and in this way the precipitate  $N_a$  was obtained. The sulphate obtained from it gave a much paler ceric oxide.

The precipitates  $N_\beta$ ,  $N_\gamma$ , and  $N_\delta$  were obtained by Wolf in the same way, and the colour of the oxide was in each case paler than in the preceding. Wolf calls the oxide from  $N_\gamma$  *almost white*, and that from  $N_\delta$  *white*.

It is a very remarkable circumstance that, after every purification, as the oxide became more nearly white, the equivalent of cerium was found to decrease.

In Wolf's original paper the following numbers are calculated for the equivalent of cerium:—

I.	II.	IV.	V.
46·187	45·760	45·699	45·664

This multiplied by 3 would represent the atomic weight as—

I.	II.	IV.	V.
138·561	137·280	137·097	136·992

If, according to Clarke, the atomic weight be calculated from the relation of  $\text{Ce}_2(\text{SO}_4)_3$  to  $2\text{CeO}_2$ , as involving the least experimental error, the following numbers will be obtained (for O = 16, S = 32·06):—

I.	II.	IV.	V.
Ce = 139·64	138·27	138·04	138·00

From these experiments Wolf concluded that the remarkable diminution of the atomic weight of cerium could not be due to the elimination of didymium only, but that the first portions may have contained a foreign substance.

Wing (*Sill. Amer. J.* [2], 49, 358), in 1870, repeated Wolf's experiments and process of purification, without, however, going further, and his purest material gave Ce = 137·85. From Wolf's and Wing's experiments Clarke calculates as a mean Ce = 138·039.

Bührig's (*loc. cit.*) experiments made in 1875, with a material free from didymium, in which large quantities of cerous oxalate were analysed by combustion in a current of oxygen, gave a remarkably high number, namely Ce = 141·523 (Clarke). His ceric oxide varied from yellow to salmon colour. Later on I shall return to the objections which he raised against the analysis of cerous sulphate.

While my present investigation, which has occupied me for some time past, was in progress, H. Robinson (*Proc. Roy. Soc.*, 37, 150) published his paper on the same subject. The purification of his cerium salts was effected by Gibbs's method. The cerium solution, free from didymium, finally obtained, was precipitated with oxalic acid, and the air-dried oxalate was converted into the chloride by heating it in a current of hydrogen chloride. The cerous chloride, free from water and hydrogen chloride, was analysed volumetrically with a silver solution, according to Stas' method. As a mean of the results of seven experiments (reduced to a vacuum), Robinson found—

$$\text{Ce} = 140·2593 \text{ (O = 16) or } \text{Ce} = 139·9035 \text{ (H = 1).}$$

This number, as I shall show later on, is to be considered exact, for

in the method used by Robinson, all possible experimental errors are reduced to a minimum; but I have nevertheless continued my experiments for several reasons. Firstly, the method I have used is different from that adopted by Robinson, and our experiments therefore mutually control each other. Secondly, Wolf's experiments challenge investigation as regards the *homogeneous* character of the material, and as Robinson did not touch this question, it was all the more necessary for me to devote my attention to it. Experience has shown, especially in the case of the rare earth metals, that the atomic weights, determined even by the most trustworthy methods, may differ by *several units* from the truth, if the material used consisted of a *mixture* of earths. The history of scandium, yttrium, didymium, and erbium may be quoted as examples.

### *Method of Investigation.*

In the operations of dissolving, evaporating, and boiling, only such vessels were used as had been treated for some time beforehand with acids.

The acids, viz., hydrochloric, nitric, and sulphuric, were distilled shortly before use from a platinum retort, and kept in well-stopped bottles of Bohemian glass. A platinum tube, 60 cm. in length, 2.5 cm. wide, and weighing 600 grams, was used as a condenser, and for this I am much indebted to the Royal Society for a grant from the Government Grant Fund. Distilled water was once redistilled by means of the same arrangement, and absolute alcohol was similarly treated, the first and last portions of the distillate being rejected. The filter-paper used was kept in contact with warm hydrochloric acid for some time, and then well washed. In weighing, a fine balance, made by Verbeeck and Peckholdt, of Dresden, was used. In order to prevent the very sensible effect of radiant heat during weighing, the balance was covered on all sides with thick flannel, so that only the scale could be seen. To make the scale more visible, light was reflected upon it from the sides by mirrors, and at night the light of distant gas flames was concentrated upon it by lenses. If the method of vibrations be used in weighing, and the observation of the "point of rest" be often repeated, the weight of a body weighing about 50 grams may be determined accurately within 0.00001 to 0.00003 gram. The platinum crucibles were weighed in small thin glass bottles, and a similar vessel with platinum was used as counterpoise. As the weight of substance used was generally about 2 grams, rarely 5 grams, only a few small weights were used: in this way the errors of weighing were reduced to a minimum. The following was the true weight of the pieces used:—

2 = 2·00006	0·5 = 0·49978	0·05 = 0·04996
1 = 0·99996	0·2 = 0·19992	0·02 = 0·02012
1' = 0·99996	0·1 = 0·10001	0·01 = 0·01010
1'' = 1·00005	0·1' = 0·10001	0·01' = 0·01012
		rider = 0·01002

The weighings were reduced to a vacuum. In the balance case was placed a Klinkerfues' hygrometer with a thermometer. As a rule, this indicated about 35 per cent. of humidity. The thermometer stood almost always at 18°, and the mean height of the barometer was 742 mm.; as the deviations were such as to affect the results much less than is done by the unavoidable experimental errors, the mean weight of 1 c.c. of air could be taken as 0·001187 gram. Under these circumstances, the loss of weight in air of the substances weighed is as follows:—

$$\text{CeO}_2 \text{ (sp. gr. = 6·7)} = 0·000172 \text{ gram.}$$

$$\text{Ce}_2(\text{SO}_4)_3 \text{ (sp. gr. = 3·9)} = 0·000303 \text{ gram.}$$

In order to obtain pure cerium preparations, I proceeded as follows:—From 2600 grams of cerite, 1380 grams of crude oxides were obtained by the method described in a former paper. After dissolving the oxides in moderately concentrated nitric acid and removing the excess of acid by evaporation, the remaining *syrup* was dissolved in a little water. On pouring this into a large quantity of *pure* boiling water, almost the whole of the cerium present (about half of the weight of the crude oxides) was precipitated as basic ceric nitrate. This could be easily and quickly washed on a Bunsen funnel with boiling water containing a little nitric acid. I shall call this first precipitate N.

For further purification, instead of using sulphuric acid, as is generally done, nitric acid was employed. This has the great advantage over the old method, that the excess of acid can be very easily removed by evaporation from the solution. If the solution of the resulting ceric nitrate, which is now *crystalline*, be again poured into boiling water, the filtrate will contain, besides the impurities which we wish to remove, *much less* cerium in solution than when sulphuric acid is used. This almost neutral ceric nitrate dissolves easily in a *very large* quantity of water, without undergoing decomposition.

This method, especially the removal of the excess of acid by evaporation, enabled me to carry the purification much further than Wolf was able to do. In using nitric acid, the quantity of cerium is diminished far less rapidly by each precipitation than is the case with sulphuric acid. Whilst Wolf could repeat the process of precipitation only five times, I could obtain, by repeating this tedious process with

a *part* of the first precipitate only, the following series of precipitates (N) and corresponding filtrates (F), the last being kept separate :—

N	N <sub>1</sub>	N <sub>2</sub>	N <sub>3</sub>	N <sub>4</sub>	N <sub>5</sub>	N <sub>6</sub>	N <sub>7</sub>	N <sub>8</sub>	N <sub>9</sub>	N <sub>10</sub>	N <sub>11</sub>
F	F <sub>1</sub>	F <sub>2</sub>	F <sub>3</sub>	F <sub>4</sub>	F <sub>5</sub>	F <sub>6</sub>	F <sub>7</sub>	F <sub>8</sub>	F <sub>9</sub>	F <sub>10</sub>	F <sub>11</sub> .

Now the question arose which cerium compounds were to be used for the atomic weight determination. After long deliberation, I chose the anhydrous cerous sulphate, as—with the exception of cerous chloride, which H. Robinson had succeeded in preparing only after my experiments were in progress—cerium does not form any other compound of definite composition suitable for the purpose. Bührig rejected cerous sulphate—firstly, because the salt retains free sulphuric acid from the mother-liquor so energetically that it cannot be freed from it even by repeated crystallisations; secondly, because he could not obtain the anhydrous sulphate, the salt retaining traces of water at a moderate heat, and undergoing partial decomposition when heated to incipient redness; and thirdly, he remarks, that on precipitating the solution of the sulphate with barium chloride and afterwards with oxalic acid, the barium sulphate thrown down contains cerium; whilst the cerium oxalate, on the other hand, contains barium, but he does not consider that, if the analysis is to be made by precipitation at all, the process may be executed in the inverse order, without fear of committing the above errors.

The first source of error was avoided in the following way:—Cerous sulphate, prepared by dissolving basic ceric nitrate in dilute sulphuric acid and sulphurous acid, and evaporating the solution in a platinum basin, was heated for some time in a magnesia bath, in order to expel the greater part of the excess of sulphuric acid. The product was then dissolved in a small quantity of ice-cold water, the heavy metals (platinum, &c.) precipitated by hydrogen sulphide, and the excess of the latter expelled first by the use of a water-pump, then by means of a current of air. In this way a solution was obtained, from which, on adding three times its volume of absolute alcohol, the whole of the cerium was thrown down in the form of a fine crystalline powder of the salt  $\text{Ce}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O}$ . After washing the salt with absolute alcohol, dehydrating at a gentle heat, and again precipitating with alcohol, a completely *neutral* cerous sulphate was obtained. Although free from any excess of sulphuric acid, the salt is not pure, even if it be thrown down from most carefully prepared purified alcohol, it retains traces of foreign organic matter, probably betaine, and consequently turns yellow or brownish on subsequently heating. It dissolves in water, also with a peculiar feeble empyreumatic odour. To purify it, the salt must therefore be once more dissolved in cold water, and after filtering, the solution contained in a beaker is plunged



quickly into boiling water, so as to heat it to 100°. If the hot super-saturated solution be now stirred with a glass rod, the salt present is instantly precipitated as a fine crystalline powder of the composition  $\text{Ce}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O}$ . This is collected with the aid of the pump on a platinum cone, and can be at once placed in a bottle, for it dries in a few instants when put on a smooth filter-paper.

Originally I had intended to convert the hydrated sulphate by strong calcination into ceric oxide, and to calculate the atomic weight from the relation of the oxide to the hydrated salt, a method which has been used by Nilson and Pettersson (*Ber.*, **13**, 1441 and 1453) in determining the atomic weights of beryllium and scandium. Unfortunately all cerous sulphates either alter on exposure to the air, or, if they are stable, they seem to include the mother-liquor in small cavities, a property of salts first noticed by Sorby. On heating the neutral solution of the sulphate to 40—50°, Marignac's (*loc. cit.*) hydrate,  $\text{Ce}_2(\text{SO}_4)_3 + 9\text{H}_2\text{O}$ , was never obtained, but instead of this, white turbid crystals of the salt with  $8\text{H}_2\text{O}$  always separated out. By spontaneous evaporation in the air at the ordinary temperature, the same salt was obtained in beautiful clear and glistening crystals instead of the salt  $\text{Ce}_2(\text{SO}_4)_3 + 12\text{H}_2\text{O}$ . At 100°, the salt with  $6\text{H}_2\text{O}$  alone is separated, but it quickly alters in the air. It is possible that the hydrates with  $5\text{H}_2\text{O}$ ,  $9\text{H}_2\text{O}$ , and  $12\text{H}_2\text{O}$ , which I could not obtain from neutral solutions, crystallise only when free sulphuric acid is present.

For these reasons, I was unable to prepare a cerous sulphate with a definite (theoretical) amount of water of crystallisation which could be used for the atomic weight determination. In only two out of twenty cases in which the water was exactly determined was the theoretical amount of water found, viz., in the clear crystals,  $\text{Ce}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O}$ , obtained on spontaneous evaporation at the ordinary temperature.

As I had to give up the above plan, I tried to prepare the anhydrous sulphate. It is impossible to obtain it by simply heating the hydrated salt in the air, for at a low temperature the water is not entirely given off, and at about 500° the salt may lose a trace of sulphuric acid, or it absorbs some oxygen and becomes heavier and slightly yellow-coloured by passing partly into ceric salt. But, on following Baubigny's (*Compt. rend.*, **97**, 854) example, I found that, at the temperature of boiling sulphur, cerous sulphate entirely loses its water without being decomposed or otherwise altered.

Hitherto it has not been very easy to operate with boiling sulphur, and yet I wanted an arrangement that would allow me to heat the salts for many weeks at 440° without special difficulty. After many trials I succeeded in devising an apparatus for this purpose. A very



thin glass beaker, 18 cm. long and 7 cm. in diameter, is covered with a sheet of thick cardboard, having in its middle a round opening 4 cm. in diameter. To prevent this cardboard from burning, it is soaked repeatedly with alum, soluble glass, or sodium tungstate. Through the opening in the cardboard is passed a test-tube of thin glass, 20 cm. long and 4 cm. wide, the bottom of the tube being 4 cm. above the bottom of the beaker. The beaker is kept suspended in a wire triangle, and its bottom rests on a piece of thin wire gauze. The beaker is first placed on a sand-bath, and about 50 grams of sulphur are fused in it. Then it is placed on the gauze and heated with 2 or 3 Bunsen's burners, so that the sulphur boils. In this way the whole of the beaker becomes filled with the vapour of boiling sulphur, which condenses on the sides, and flows down again. In order to prevent the upper portion of the beaker from being too strongly heated, the cardboard from carbonising, and the sulphur-vapour from escaping, it is surrounded with a shorter open glass cylinder (a broad beaker with the bottom cut off) about 12 cm. high and 11 cm. wide, covered at the top by a plate of thin sheet copper (15 cm. square), having in its middle an opening of 7 cm., through which the thin long beaker (the sulphur-bath) passes, so that only its lower two-thirds are heated to the boiling point of sulphur, whilst the upper third, being freely exposed to the air, is prevented from becoming too strongly heated. With such an arrangement, the vapour of boiling sulphur reaches to two-thirds of the height of the bath, and the lower part of the test-tube is surrounded by it.

When the cerous sulphate is to be dehydrated, it is placed on a small platinum crucible, and this is suspended by a loop of long thin platinum wire, the upper end of which is bent over the upper edge of the test-tube, in order to prevent the crucible from falling into the boiling sulphur, if the test-tube should crack. (Once, before I made this arrangement, the tube cracked, but, although the crucible was plunged for a quarter of an hour in boiling sulphur, it was not altered in appearance or weight after being washed with potash solution.) The sulphur is then heated slowly to its boiling point, and after a while the platinum crucible is surrounded by sulphur-vapour far above its upper edge. Whilst the greater part of the water of crystallisation of the sulphate is escaping, the test-tube is kept open until a cold beaker held over no longer shows signs of dew. During the operation, the crucible is covered with a lid having the ear cut off, so that there is but very little space between the crucible and the side of the test-tube. When water-vapour ceases to escape, the test-tube is covered with a porcelain crucible lid, and the bath is heated until the weight of the crucible *plus* sulphate is found to be constant. This is easily effected if after one hour's heating the salt be stirred with a

thick platinum wire and heated for another hour. When the operation is finished, the sulphur which has cooled down so that it no longer takes fire in the air, but is still fused, is poured out into a porcelain basin, for if it is allowed to remain in the beaker it would certainly crack either as the sulphur cools or on fusing it again.

When these precautions are observed, the same quantity of sulphur may be kept boiling in this simple apparatus for half a year or longer, from morning to night, without fear of anything happening to it.

When hydrated cerous sulphate is heated in the above apparatus until the weight is constant, and then allowed to cool in a small desiccator containing phosphorus pentoxide, it is found to be perfectly anhydrous, without, however, undergoing the slightest decomposition; the water which escapes from it, and which can be collected on a cool beaker, being neutral and unaffected by barium chloride. If the anhydrous sulphate be heated to a higher temperature in a test-tube, no trace of water is given off, but a mixture of sulphur dioxide and trioxide escapes, so that the decomposition takes place in accordance with the equation  $\text{Ce}_2\text{O}_3 \cdot 3\text{SO}_3 = \text{Ce}_2\text{O}_4 + 2\text{SO}_3 + \text{SO}_2$ .

This behaviour affords evidence of the powerful reducing power of cerous oxide, and it will be easily understood that it cannot be prepared in the free state. For analysis, the anhydrous sulphate was carefully heated in a double platinum crucible over the flame of an ordinary burner, until sulphur trioxide fumes were no longer given off. In order to expel the last trace of sulphuric anhydride, I tried heating the salt to a white heat in a Fletcher's blast furnace with injector, but I had to relinquish this plan, as not only does the crucible lid become welded to the crucible, but the platinum seems to evaporate perceptibly at this high temperature; the *inner* of the two platinum crucibles which is not exposed to the direct flame, losing in a short time as much as 12 mgrms. If the injector is put in a vertical position, and the air blown in in such a way that the flame, which is generally 30 to 50 cm. long, is converted into a short, hissing, hardly visible one (the flame will be often blown out entirely before the necessary practice is obtained in regulating the air and gas supply), a temperature is obtained *in the free air* at which an ordinary pretty thick platinum wire fuses *instantly*. This is certainly the highest temperature obtainable from a mixture of gas and air without a furnace, and I think that this simple arrangement will prove useful to chemists. The cerous sulphate contained in a double platinum crucible loses every trace of its sulphur at this temperature in 10 to 15 minutes, and it will take weeks before the inner crucible loses 0.0001 gram in weight.

*Experiments with Mixtures.*

Before the above method of operating with boiling sulphur had been worked out, I tried to decide whether the above precipitate  $N_4$  could be split up into different fractions. For this purpose, one part of it was converted into the neutral sulphate, which was dissolved in water, and then fractionally precipitated with dilute ammonia. I will call the most basic portion remaining in solution A. The precipitate was dissolved in dilute sulphuric acid, and again precipitated. After four precipitations, the least basic portion B was obtained. On heating the hydrated neutral sulphate prepared from the portions A and B high over the flame in a double platinum crucible to constant weight, Wolf's "anhydrous" sulphate (it is really *not* anhydrous) was obtained, and this was converted into ceric oxide by strong calcination. The formulæ used for the atomic weight calculation will be given later on. The following results were obtained:—

Weight of $Ce_2(SO_4)_3$ .	Weight of $CeO_2$ .	Loss of weight.	Per cent. of $CeO_2$ .	"Atomic weight." Ce =
A. { 1·2750 1·3153	0·7717 0·7958	0·5033 0·5195	60·525 60·501	139·83 139·74 } Mean.. 139·78
B. { 1·71305 1·8702	1·03534 1·1308	0·67771 0·7394	60·440 60·404	139·53 139·46 } Mean.. 139·49

These numbers are not absolutely exact, as the water was not entirely expelled, but they may be considered relatively true, for they were determined by the same method. As the "atomic weight" was in one case  $Ce = 139·78$ , and in the other  $Ce = 139·49$ , the question remained open whether the material used was homogeneous.

This circumstance suggested an attempt to split up a portion of the precipitate  $N_3$ , which was less pure, but contained only traces of didymium. The basic ceric nitrate from this was converted into cerous sulphate, from which the excess of free acid was removed by alcohol. The aqueous solution of the sulphate was partially precipitated by adding to it strong alcohol, drop by drop, and in this way the portions A, B, C, D were obtained. These precipitated sulphates were dried between smooth blotting-paper, and then in a state of fine powder dehydrated in the sulphur-bath and analysed as before, with the following results:—

Weight of $\text{Ce}_2(\text{SO}_4)_3$ .	Weight of $\text{CeO}_2$ .	Loss of weight.	Per cent. of $\text{CeO}_2$ .	"Atomic weight."
A .... 1·3601	0·8241	0·5360	60·591	140·34
B .... 2·4780	1·5009	0·9771	60·568	140·18
C .... 2·3191	1·4041	0·9150	60·545	140·00
D .... 1·5179	0·9245	0·5934	60·906	142·65

The difference in the percentage of ceric oxide of the single fractions is far more striking than in the first case. The oxide obtained from fraction D had a peculiar flesh colour mixed with a pale orange, and it is very remarkable that it turned *grey* under the influence of light, whereas pure ceric oxide is white with a yellowish tint, and does not alter when exposed to light. The portions A, B, and C were far less orange than D. If we assume that the loss of weight on ignition is represented by the same equation as in the case of pure cerous sulphate, viz.,  $\text{Ce}_2\text{O}_3 \cdot 3\text{SO}_3 - (3\text{SO}_3 - \text{O}) = 2\text{CeO}_2$ , the "atomic weight" of the earth metal in the fraction D would be  $R = 142\cdot65$ .

It will be seen from the numbers given hereafter, that the numbers found for A, B, and C represent very nearly the true atomic weight of cerium. The high percentage of oxide in fraction D cannot be due to the presence of didymium, because anhydrous sulphate of didymium contains only 58·09 per cent. of the oxide, and the peroxide would be completely decomposed at such a high temperature. Still, it might be due to the presence of thorium, its anhydrous sulphate containing 62·42 per cent. of the earth. In order to entirely exclude any thorium possibly present, the following process was used. The earths contained in the filtrates  $F_1$ ,  $F_2$ ,  $F_3$ , and  $F_4$  were precipitated with potassium hydroxide, and the precipitate, consisting chiefly of cerous hydroxide, was suspended in strong caustic potash solution, and treated for three days with chlorine, in order to remove the greater part of the lanthanum and didymium present. After thoroughly washing, the precipitated ceric hydroxide was dissolved in nitric oxide, and the excess of acid removed by evaporation, when a gelatinous mass of ceric nitrate was obtained. Its solution in cold water was poured into boiling water, and so the greater part of the purer cerium salt was thrown down as basic nitrate. From the filtrate containing impure cerium salt, the earths were thrown down with ammonia and converted into the sulphates. After dissolving in five parts of ice-cold water and separating the heavy metals with hydrogen sulphide, the solution was heated at 60—70° for some time. At this temperature most of the cerous sulphate separates out, and if any thorium be present, its sulphate will, according to Nilson's experiments (*Ber.*, 15, 2519), also crystallise out. The same holds

good as regards lanthanum sulphate. The last mother-liquor contains, besides cerium, some didymium. It was split up into two parts by adding strong alcohol, and the *last* precipitate (*i.e.*, the most soluble salt) was recrystallised from water and used for the atomic weight determination :—

$R_2O_3, 3SO_3$ .	$RO_2$ .	Loss of weight.	Per cent. of $RO_2$ .
1·8649	1·1459	0·7190	61·444
2·4310	1·5011	0·9299	61·135
0·7863	0·4829	0·3034	61·414
			Mean . . . 61·331

This strikingly high percentage of oxide, if calculated out in accordance with the above equation, would correspond with an "atomic weight" of  $R^{III-IV} = 145·72$ .

The material was not entirely free from didymium, and, although it was improbable, for the reasons stated, that its presence could render the percentage of the oxide higher, experiments were undertaken with cerous sulphate artificially contaminated with a little didymium salt, in order to decide the question. The following negative results were obtained :—

Sulphate.	Oxide.	Per cent. of oxide.
0·6941	0·4203	60·55
1·6320	0·9878	60·53

I could not yet decide the question as to whether the presence of one of the many rare earths, some of which have been but very little studied up to this time, makes the atomic weight of impure cerium higher, neither could I find out the reason of the high numbers obtained. In any case, it is seen from the above experiments, that under certain conditions "cerium" may consist of a *mixture*. The nature of this admixture must be ascertained by further experiments; but before this is done we must become acquainted with the properties of really pure cerium.

#### *Experiments with Pure Material.*

The object of the following series of experiments was to ascertain how far cerium has to be purified in order to furnish a truly homogeneous product. For the experiments, the following of the above-mentioned precipitates of basic nitrate and the corresponding filtrates were used :—

N <sub>5</sub>	N <sub>6</sub>	N <sub>7</sub>	N <sub>8</sub>	N <sub>9</sub>	N <sub>10</sub>	N <sub>11</sub>
F <sub>5</sub>	F <sub>6</sub>	F <sub>7</sub>	F <sub>8</sub>	F <sub>9</sub>	F <sub>10</sub>	F <sub>11</sub>

These were found to be entirely free from lanthanum and didymium.

It will be seen from an inspection of this series, and a consideration of the process of fractionation, that the cerium in the *filtrates* is far more strongly "fractionated" than the *precipitates*, especially as the quantity of earth in each filtrate is much smaller than that in the corresponding precipitate. For this reason the filtrates alone were used to determine the question of homogeneity, and, as no fundamental stoichiometric numbers were to be obtained, the following simple process was used for the preparation of cerous sulphate from them:—The filtrates, after adding to them some of the sulphuric acid, and later on some sulphurous acid, were evaporated to dryness in a platinum basin, and from the sulphates obtained in this way the excess of sulphuric acid was driven off by heating the residue in a magnesia-bath; it was then dissolved in water, and the sulphate thrown down by alcohol. After repeating this process, the anhydrous sulphate was dissolved in water, and the neutral sulphate separated out by heating the solution at 100°. The dehydration in the sulphur-bath and the analysis were carried on in the way described above. The results are given in uncorrected numbers:—

Filtrates.	Ce <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .	CeO <sub>2</sub> .	Per cent. of CeO <sub>2</sub> .
F <sub>5</sub> ..... {	2·3797 1·8258	1·4424 1·1073	60·614 60·648
F <sub>6</sub> + F <sub>7</sub> .....	2·2670	1·3749	60·649 (maximum).
The two together....	2·1869	1·3252	60·597 (minimum).
F <sub>8</sub> + F <sub>9</sub> .....	2·5807	1·5648	60·634
The two together....	2·0149	1·2216	60·627
F <sub>10</sub> + F <sub>11</sub> .....	1·6519	1·0013	60·615
The two together....	1·6193	0·9815	60·612
			Mean.... 60·624

The material used for these experiments, although containing no other earth metal but cerium, had been too much in contact with filter-paper, with glass and porcelain vessels in strongly acid solution, and with air, so that the numbers were neither corrected, nor were they used for the calculations of the atomic weight. But, as they are for all fractions exactly the same, showing neither a regular increase nor decrease, and differ from the mean number at the outside by  $\pm 0\cdot025$  of a unit in percentage, the conclusion must be drawn

that the cerium of the filtrates  $F_8$  to  $F_{11}$  is a perfectly homogeneous body.

Now it remained only to use the last of all the precipitates, viz.,  $N_{11}$ , containing the best purified cerium, for the definite atomic weight determination, and to ascertain whether, on comparing it with the filtrates mentioned above, it furnishes the same results. For the same purpose, in I and II (see table), part of the precipitate  $N_{10}$  was used. The remaining 21 determinations were made with a material obtained from different preparations, in order to meet the objection that only one kind of material had been used. For, in such a case, even if the results agreed, they might not be accurate. It is almost unnecessary to remark that the following series of determinations was made with the greatest possible care, and that they involve the correction both of weights and for displaced air. I did not exclude one single experiment which I made, not even numbers XIV and XXIII, although they may be considered a little too low, for the difference of weight to which these low numbers are due, falls within the allowed experimental errors.

Number of experiment.	Cerous sulphate.	Ceric oxide.	Loss by calcination.	Percentage of $CeO_2$ .	Atomic weight of cerium.
I..	2·16769	1·31296	0·85473	60·5695	140·183
II..	2·43030	1·47205	0·95825	60·5707	140·191
III..	2·07820	1·25860	0·81960	60·5620	140·128
IV..	2·21206	1·33989	0·87217	60·5721	140·201
V..	1·28448	0·77845	0·50603	60·6043	140·433 (max.)
VI..	1·95540	1·18436	0·77104	60·5687	140·176
VII..	2·46486	1·49290	0·97196	60·5673	140·167
VIII..	2·04181	1·23733	0·80448	60·5997	140·400
IX..	2·17714	1·31878	0·85836	60·5739	140·215
X..	2·09138	1·26654	0·82484	60·5600	140·114
XI..	2·21401	1·34139	0·87262	60·5863	140·304
XII..	2·44947	1·48367	0·96580	60·5711	140·194
XIII..	2·22977	1·35073	0·87904	60·5771	140·237
XIV..	2·73662	1·65699	1·07963	60·5488	140·033 (min.)
XV..	2·62614	1·59050	1·03564	60·5642	140·144
XVI..	1·67544	1·01470	0·66074	60·5632	140·137
XVII..	1·57655	0·95540	0·62115	60·6007	140·407
XVIII..	2·72882	1·65256	1·07626	60·5600	140·110
XIX..	2·10455	1·27476	0·82979	60·5716	140·198
XX..	2·10735	1·27698	0·83037	60·5965	140·377
XXI..	2·43557	1·47517	0·96040	60·5678	140·170
XXII..	3·01369	1·82524	1·18845	60·5649	140·150
XXIII..	4·97694	3·01372	1·96322	60·5537	140·068
Total....	53·77424	32·57367	21·20057	60·5747	140·2210

For the calculation of the atomic weight Lothar Meyer's and Seubert's example was followed, viz., the several amounts of sub-



stance weighed were added together, and the atomic weight calculated from the totals according to the following formula. (It has been proved mathematically by Ostwald, that such a method of calculation is correct.)

$$\text{Ce}_2(\text{SO}_4)_3 : 2\text{CeO}_2 = 53.77424 : 32.57367 \text{ grams,}$$

when if  $\text{Ce}_2(\text{SO}_4)_3 = 100$ ,  $\text{CeO}_2 = 60.5747$ .

Difference of  $\text{Ce}_2(\text{SO}_4)_3$  and  $\text{CeO}_2$  (loss of weight) = 21.20057 grams.

$$\frac{32.57367 \times (3\text{SO}_3 - \text{O})}{21.20057} = 2\text{CeO}_2, \quad \frac{2\text{CeO}_2 - 4\text{O}}{2} = \text{Ce}.$$

If we replace all by numbers and take for O = 16 and S = 32.06, we have  $(3\text{SO}_3 - \text{O}) = 224.18$ ; then we have—

$$\begin{aligned} \frac{32.57367 \times 224.18}{21.20057} &= \frac{344.4420}{64} \\ \frac{2\text{Ce} = 280.4420}{\text{Ce} = 140.2210}. \end{aligned}$$

If calculated with hydrogen numbers, O = 15.96 and S = 31.98, then—

$$\text{Ce} = 139.8707.$$

I have *not* calculated the atomic weight and its probable error by the method of least squares, because the following different numbers have been calculated by different chemists (for O = 16) as the atomic weight of sulphur on which such a calculation should be founded.

Stas .....	32.074
Ostwald .....	32.0626
Sebelien* .....	32.0608
L. Meyer and Seubert .....	32.0592
Clarke.....	32.058

The extreme difference of these numbers is = 0.016, and the calculation of the probable error would become uncertain.

It is, no doubt, a very good principle to determine the atomic weight of an element by several independent methods; unfortunately it was impossible in the above case from want of choice of suitable cerium compounds. I have tried to obviate this objection by making a greater number of determinations.

On the other hand, my number is severely controlled by the numbers

\* Sebelien, *Beiträge zur Geschichte der Atomgewichte*, Braunschweig, 1884, p. 155.

found by Robinson (*loc. cit.*) for both numbers, determined by widely different methods, are in as good an accordance as can be expected :—

	Robinson.	Brauner.
For O = 16	Ce = 140·2593	140·2210
For O = 15·96	Ce = 139·9035	139·8707.

If we compare the above series of determinations with that made for the purpose of investigating the homogeneous nature of cerium (from the filtrates  $F_5$  to  $F_{11}$ ), both series are seen to agree well, and from this the conclusion must be drawn that the pure cerium preparations used by me were *homogeneous*.

The simple method which I adopted for the purification of cerium preparations must be considered very good, as from 1380 grams of crude oxides, containing in all 690 grams of ceric oxide, I obtained 720 grams of *pure* nitrate, representing over 500 grams of ceric oxide.

#### *Discussion of Former Determinations of the Atomic Weight of Cerium.*

It will be almost unnecessary to discuss several of the above quoted determinations, for they were carried out with a material containing other cerite metals. This may be said of the experiments made by Hisinger in 1814–16, by Beringer in 1842, and by Rammelsberg in the same year. The method followed by Hermann (1843) and by Marignac (1848), viz., precipitation of the sulphuric acid in a solution of cerous sulphate with barium chloride, has been declared by Marignac himself to involve a considerable source of error, as the barium sulphate carries down some cerium with it. Besides, for the reasons given by Bührig, and quoted above, it is very improbable that the sulphate used by these and other authors (especially by Jegel) had a definite *normal* composition.

Jegel (in 1858) and Rammelsberg (in 1859) determined the atomic weight of cerium by the combustion of cerous oxalate. It has been shown by Nilson (*Ber.*, **15**, 2519) in his paper on the atomic weight of thorium, that the method of elementary analysis of an oxalate involves several errors which make it unsuitable for the exact determination of the atomic weight of an element.

I shall therefore not enter more fully into an analysis of the papers published up to 1860, but proceed to discuss the work done by Wolf. As regards, first of all, his observation that the atomic weight of cerium *diminishes* on further purification of the preparations, I think it may be regarded as *confirmed* by my own experiments. But this decrease ceases as soon as we get to the precipitate  $N_5$  (it would correspond to Wolf's  $N_6$  which, however, he never obtained). Wolf's ceric oxide was *white*. The same was the case with my *purest* ceric oxide, though I should prefer to call it the palest "*chamois*."

On the other hand, I cannot confirm the very low atomic weight found by Wolf. Firstly, Wolf did not prove that his sulphate had a definite normal composition. His hydrated salt, as can be concluded from my own experiments on this subject, most probably did not contain the theoretical amount of water of crystallisation, and according to Bührig it must have contained some free sulphuric acid, which can be got rid off only by the process quoted above. If these two sources of error are not taken into consideration, the atomic weight of cerium will be found *lower* than it really is. As regards the numbers calculated from the "anhydrous" sulphate, they cannot be regarded as exact, for cerous sulphate, heated high over a small flame in a double platinum crucible, retains a trace of water, as has been already pointed out by Bührig, and as may be seen from the following experiment.

3.0283 grams of crystallised cerous sulphate gave, on heating for two hours in a double platinum crucible at a temperature at which the bottom of the outer crucible was red hot for a short time (the temperature applied by Wolf was never so high), 2.3843 grams of "anhydrous" salt. On heating it in the sulphur-bath at  $440^{\circ}$ , it lost the last trace of its water, and its weight diminished by 0.0046 gram, namely to 2.3797 grams. As at a high temperature the sulphate yielded 1.4424 gram of  $\text{CeO}_2$ , the atomic weight, calculated from the first number, would be  $\text{Ce} = 139.65$  instead of  $\text{Ce} = 140.22$ .

Secondly, I found that, on precipitating a solution of cerous sulphate with boiling oxalic acid solution, a trace of cerium, the oxalate of which is partly soluble in the free sulphuric and oxalic acids, remains in solution even after long standing.

1.3506 gram of anhydrous sulphate, precipitated and ignited by Wolf's method, gave 0.8173 gram  $\text{CeO}_2 = 60.514$  per cent. Directly analysed, the same sulphate gave 60.60 per cent. of  $\text{CeO}_2$ . This error, although slight, gives a smaller atomic weight.

Thirdly, on precipitating the filtrate from the cerous oxalate with barium chloride, a little more barium sulphate is always obtained than corresponds with the sulphuric acid contained in it, for not only is the trace of cerium which remains in solution carried down with barium sulphate, but also some barium oxalate. This causes the atomic weight of cerium found to be lower.

From the above filtrate, after separation of cerous oxalate, 1.6831 gram of  $\text{BaSO}_4$ , corresponding with 0.5781 gram, or 42.803 per cent. of  $\text{SO}_3$ , was obtained (theory requires only 42.24 per cent). From the relation of 0.8173  $\text{CeO}_2$  : 0.5781  $\text{SO}_3$ , the atomic weight calculated is  $\text{Ce} = 137.78$  instead of  $\text{Ce} = 140.22$ .

If only one or all of these sources of error are left out of consideration, the atomic weight of cerium found will always be lower than the

true one. I think, therefore, that I have sufficiently explained the low numbers found by Wolf.

In striking contrast with Wolf's work is that done by Bührig, who found the high number  $Ce = 141.5$ . Bührig analysed large quantities of cerous oxalate by combustion (the details will be found in Clarke's recalculation), but he made the mistake of using a material resulting from one preparation only. I do not believe, however, that Bührig's oxalate contained an admixture of basic salt, as is sometimes stated.

Another cause of error in Bührig's work must be looked for in the fact, as Nilson has shown (*loc. cit.*), that the analysis of oxalates by combustion is subject to constant errors which make the atomic weight *higher*. For example, Cleve, by this method, found the atomic weight of thorium to be  $Th = 233.80$  to  $233.97$ , whereas Nilson's analysis of the sulphate gave  $Th = 232.40$ .

But, as Bührig used for combustion large quantities of oxalate—about 10 grams at once—the loss of carbonic anhydride and the *plus* of water cannot have been the only source of the difference between the number obtained and the true one. I am inclined to believe that the reason of Bührig's higher number was partly the same which caused me to find the "atomic weight" of the *impure* cerium to be  $R = 142.65$ , and even  $R = 145.72$ , for Bührig points out distinctly that his oxide was yellow. Further, as this oxide when strongly heated is converted with loss of weight into one which is of a pale salmon colour, the former may have contained some of the unstable peroxide, the admixture of which would cause the atomic weight found to be a little higher.

In conclusion, it may be pointed out that, in consequence of the present new determinations, the differences between the atomic weights of lanthanum, cerium, and didymium, elements following each other in the periodic system, harmonise far more than was previously the case. Thus we have,

La.	Ce.	Di.
138.2	140.2	142.3
Difference.... 2.0		2.1