

ART. VIII.—*On the Equivalent of Cerium*; by the late Dr.
CHARLES WOLF, of Cincinnati, Ohio.

At the suggestion of Professor Bunsen in Heidelberg, the father of the late Dr. Charles Wolf of Cincinnati, Ohio, placed in my hands, papers and preparations relating to an investigation, which his son had made, while in the laboratory of Prof. Bunsen, and requested me to collate the same and prepare them for publication. This task I cheerfully accepted, the more, that I deemed the death of this young and promising chemist a real loss to the cause of science.

I here give a translation of Dr. Wolf's investigation on the equivalent of cerium, which Bunsen pronounces very valuable. I have examined all the data with the greatest care and gone over a great many of his analyses and calculations. The paper was about complete, when it came into my hands, all but a few of the last pages, which were in the shape of notes, but these were sufficiently copious to enable me to finish it, with the aid of some analyses, which I found among his papers.

I could not find the description of the crystalline form of his salts, to which he refers, nor is there the least evidence that any measurements have ever been made. This investigation may be of value to chemists laboring in the same field, as it designates the probable existence of *another* foreign substance in the "cerite-oxyds," and we must deeply regret that its author was not spared long enough to conclude his researches on the nature of this oxyd, which so considerably increases the equivalent of cerium.

Let us hope that the hints and suggestions thrown out by

Dr. Wolf may not be lost, but that they may induce some investigator to advance or conclude this highly interesting subject.

F. A. GENTH.

Philadelphia, April 26th, 1868.

Since the discovery of the peculiar oxyds contained in the cerite by Berzelius & Hisinger* and Mosander† they have been the subject of numerous researches. Their occurrence together with their very similar chemical properties presented very great difficulties in their separation and indeed the mixture of the three oxyds was for a long time looked upon as the oxyd of *one metal only*, which was called *cerium*. Notwithstanding the many investigations made on this subject, the methods for the separation and purification of the three cerite-oxyds are very imperfect.

The oxyd of cerium, which in its properties differs most from the oxyd of didymium and from lanthana, and which is the most common, is more readily obtained in a state of perfect purity than either of the two others.

The following investigation was made for the purpose of preparing salts of cerium of *absolute* purity, so as to determine from them the equivalent of the metal. The material used was Swedish cerite.

The method adopted for the preparation of the oxyds was substantially that recommended by Bunsen,‡ with some slight alterations, as will be seen from the following description.

The finely pulverized mineral, mixed in a porcelain dish with oil of vitriol to the consistency of a stiff paste, was put into a hessian crucible and exposed to a dull red heat. The excess of sulphuric acid was driven off and the ash-grey mass finely pulverized and gradually added to a large dish full of ice-water and ice. It was then agitated until the water had become saturated, when it was allowed to settle. The saturated solution was afterward poured off and the residue washed until the liquid became tasteless and gave no further precipitate with oxalic acid.

After having been concentrated by evaporation this solution was precipitated by sulphydric acid and filtered. The excess of sulphydric acid was driven off by heat, the liquid was then oxydized by chlorine, after which the excess of the latter was also expelled by heat. It was then strongly acidulated by chlorhydric acid, heated up to boiling and precipitated by a boiling solution of oxalic acid, while being constantly stirred. The precipitate of crystalline oxalates, which settled easily, was

* Berzelius & Hisinger, Gehlen's Journ. der Chemie, ii, 397.

† Mosander, Journ. für pract. Chemie, xxx, 1843; Pogg. Ann., clvi, 1843; Edin. & Dubl. Phil. Mag., Oct. 1843.

‡ Bunsen, Annalen der Chem. & Pharm., cv, 1858.

decanted and washed with boiling water. The mother-liquor still contained a large portion of the rare oxyds, but these were very much mixed with other bases.

The dried oxalates were then placed into a porcelain dish and decomposed by heat over an open fire, care being taken to stir them constantly. Should this precaution be neglected they might cake together, in which case a portion of the salt would remain undecomposed. Concentrated nitric acid was now poured upon the cinnamon-brown powder and the mixture was heated until the oxyds were dissolved.

The deep red violet solution was freed as much as possible from the excess of nitric acid by evaporation, and while still warm it was poured in a boiling mixture of water and sulphuric acid, containing 2 c. c. of sulphuric acid per liter of water.

The red violet color at once disappeared, and while a great evolution of gas took place, a dirty yellow precipitate of basic ceroso-ceric sulphate was formed. The mixture was allowed to boil up two or three times; it was then removed from the fire, when the precipitate settled rapidly.

Should the quantity of sulphuric acid and water have been insufficient, a portion of the nitric acid solution remains undecomposed and the supernatant liquid is yellow; this is also the case when the sulphuric acid water is too concentrated, because then a portion of the precipitate is dissolved by the excess of the acid. If the right proportions have been used, the supernatant liquid will have an amethystine color from the presence of didymium; in it neither boiling nor the addition of water or a few drops of sulphuric acid will give a precipitate. A few preliminary experiments will determine the requisite quantities of water and sulphuric acid.

The basic precipitate was washed by decantation, at first with boiling water containing per liter 1 c. c. of sulphuric acid, then with boiling distilled water. The precipitate settles easily. It is well to preserve the first wash-waters, since a portion of the precipitate dissolves in them even to the extent of one third. The last portion of the filtrate resulting from the washings with pure water need not be saved, as they contain traces only of the precipitate.

This basic sulphate, although sometimes prepared by a different process, has been used by most chemists as a starting point for the preparation of pure salts of cerium, and the sulphate obtained from it has served for the determination of its equivalent.

The washed basic salt, obtained by the method above mentioned, I divided into two equal parts; with the one I repeated the experiments made by previous observers, while the other

supplied me with the material for some new experiments, which I shall detail in due season. The first part was dissolved by the addition of a few drops of sulphuric acid and slightly heated, the yellowish-red solution reduced by sulphurous acid and evaporated to dryness. The dry salt, heated in a platinum crucible, was freed from its excess of sulphuric acid and water; the cerous sulphate therefrom resulting was dissolved in cold water, filtered and very slowly evaporated over a water bath. The slower the evaporation the better will the crystals be.

When but little of the mother-liquor remained, this was poured off, the salt washed twice with boiling water, and the purified salt dried over a water bath.

Upon being tested with the spectroscope, the mother-liquor showed the whole absorption spectrum of didymium, with the same distinctness as a moderately concentrated solution of didymium would do.

A solution of the purified crystals gave such lines as in the didymium spectrum are usually marked by their intensity. A small portion of the mother-liquor precipitated by oxalic acid gave on ignition of the oxalate an oxyd of a brown color, while the ceroso-ceric oxyd obtained by a similar process from the sulphate had already a brick-red color. For the purpose of further purification the whole mass of the sulphate was recrystallized five times in the manner above stated and the mother-liquor always separated from the crystals, then the salt was separated by fractional crystallization into five equal portions, as follows:

| | |
|-------------------------------|-----------------------|
| The mass of the crystals into | A_1 ; A_2 ; A_3 |
| A_1 “ | B_1 ; B_2 |
| B_1 “ | C_1 ; C_2 |

Of these salts B_2 , C_1 and C_2 were analyzed.

The following method was in general adopted: About 1.5 grams of the salt, which had previously been dried over chlorid of calcium, was weighed in a tared platinum crucible; this was transferred into a larger platinum crucible, in the bottom of which was a thick platinum spire, upon which the smaller crucible rested, fully surrounded by air. The large crucible covered by a mica plate was then very carefully heated during three hours, high over a small gas flame, and weighed. These weighings were repeated, the crucible remaining at the same height over the flame, while the heat was gradually increased, until finally a point was reached, when, notwithstanding a considerable increase in the temperature, the weight of the crucible remained invariable. From five to eight weighings generally sufficed to give the amount of water.

The anhydrous salt was then dissolved in a large quantity of water, the solution heated and precipitated by a concentrated boiling solution of oxalic acid. The filtrate should always be tested by ammonia and should not give a precipitate, if the proportions of oxalic acid are correct.

The greatest precautions are necessary in the ignition of the oxalate, because the resulting ceroso-ceric oxyd is in such an exceedingly finely divided condition that the slightest shaking will occasion a loss, unless the crucible be covered by a well fitting lid.

The resulting ceroso-ceric oxyd was always analyzed and the amount of cerous oxyd corresponding with it determined according to Bunsen's volumetric method by iodid of potassium and chlorhydric acid from the amount of liberated iodine.

- 1.—1.4542 grs. of B_2 gave 0.19419 grs. water and 0.76305 grs. ceroso-ceric oxyd, corresponding with 0.72443 grs. cerous oxyd; 0.70325 grs. of ceroso-ceric oxyd gave 0.66766 grs. of cerous oxyd.
- 2.—1.4104 grs. of C_1 gave 0.1898 grs. water and 0.7377 grs. of ceroso-ceric oxyd, giving 0.70217 grs. of cerous oxyd.
- 3.—1.35027 grs. of C_2 gave 0.1820 grs. water and 0.70665 grs. of ceroso-ceric oxyd, corresponding with 0.67261 grs. cerous oxyd; 0.6916 grs. ceroso-ceric oxyd gave 0.65829 grs. cerous oxyd.

According to these results the anhydrous sulphate contains as follows :

| | B_2 | C_1 | C_2 | Mean. |
|---|---------------|---------------|---------------|---------------|
| Cerous oxyd, | 57.494 | 57.526 | 57.574 | 57.531 |
| Sulphuric acid, | 42.506 | 42.474 | 42.426 | 42.469 |
| | <hr/> 100.000 | <hr/> 100.000 | <hr/> 100.000 | <hr/> 100.000 |
| B_2 would give for the equivalent of cerium | | | | 46.104 |
| C_1 " " " | | | | 46.176 |
| C_2 " " " | | | | 46.281 |

giving as the mean result=46.187.

The anhydrous sulphate consists according to these numbers of one equivalent of base for one of acid.

The composition of the crystals is as follows :

| | B_2 | C_1 | C_2 | Mean. | Calculated. |
|-----------------|---------------|---------------|---------------|---------------|---------------|
| Cerous oxyd, | 49.816 | 49.785 | 49.813 | 49.805 | 49.628 |
| Sulphuric acid, | 36.830 | 36.758 | 36.708 | 36.765 | 36.634 |
| Water, | 13.354 | 13.457 | 13.479 | 13.430 | 13.738 |
| | <hr/> 100.000 | <hr/> 100.000 | <hr/> 100.000 | <hr/> 100.000 | <hr/> 100.000 |

These results agree with the calculated analysis, which corresponds to the formula: $3(CeO, SO_3) + 5HO$.

The equivalent 46·187 has been used for these calculations. The salt, which gave these results was crystallized in small crystals, elongated in one direction, the crystallographic description of which I shall subsequently give.

Let us compare this equivalent with the results which were previously obtained by other observers.

Beringer* made in Wöhler's laboratory four determinations of the equivalent of cerium. His salts were all prepared from the residue, remaining after the extraction of the mixed cerite-oxyds by dilute nitric acid. They were all rose-colored.

| | | |
|---|--------|--------|
| From the pale rose-colored cerous sulphate he obtained the number:----- | 577·24 | 46·179 |
| From the like colored cerous chlorid, ---- | 576·97 | 46·158 |
| By the conversion of the sulphid into oxyd, | 576·69 | 46·127 |
| From the cerous formate,----- | 576·00 | 46·080 |
| Mean,----- | 576·73 | 46·138 |

Hermann† found the number 575·00=46·00 by an analysis of the cerous sulphate prepared from the basic sulphate. In this case likewise the mixed oxyds were first extracted by nitric acid.

Marignac‡ used for his determinations the cerous sulphate, which was prepared from the basic sulphate, purified by several re-crystallizations. The basic sulphate was prepared from the mixed oxyds, remaining after having been extracted by nitric acid. The residue was dissolved in sulphuric acid, and the basic salt precipitated by dilution with water. Marignac adopts the number 46·00 as the equivalent of cerium.

Under the guidance of Bunsen,§ Jegel made several experiments. The mixed oxalates were ignited with *magnesia alba*, then dissolved in boiling nitric acid and the solution evaporated to crystallization. The solution of these crystals in water, when poured in boiling water, containing sulphuric acid, produced the basic ceric sulphate, from which the neutral cerous salt was obtained, which gave :

| | | | | |
|--------|--------|--------|--------|--------|
| 576·3 | 575·25 | 575·65 | Mean { | 575·73 |
| 46·104 | 46·020 | 46·050 | | 46·058 |

Rammelsberg|| obtained by the analysis of the cerous oxalate the number 575·90=46·072.

* Beringer, *Annalen der Chemie & Pharm.*, xlii, 1842.

† Hermann, *Journ. für Pract. Chemie*, xxx, 1843.

‡ Marignac, *Ann. de Chimie et Phys.*, III, xxxviii, 148; *Ann. der Chem. und Pharm.*, lxxviii, 1848.

§ Bunsen, *Annalen der Chem. & Pharm.*, cv, 1858.

|| Rammelsberg, *Poggendorf's Ann.*, cviii, 1859.

To facilitate comparison I will tabulate the different results:

| | O=100 | H=1 |
|-------------------|--------|--------|
| Beringer,----- | 576.73 | 46.138 |
| Hermann,----- | 575.00 | 46.000 |
| Marignac,----- | 575.00 | 46.000 |
| Bunsen,----- | 575.73 | 46.058 |
| Rammelsberg,----- | 575.90 | 46.072 |
| Wolf,----- | 577.33 | 46.187 |

The new number differs from all the others and is even higher than that obtained by Beringer with far less purified material ; all his salts were rose-colored, owing to the presence of didymium, my salts, on the contrary, were perfectly colorless, each had been re-crystallized at least ten times (always rejecting the mother-liquor).

Having used the very greatest care both in the preparation and in the analyses of the salt, it is difficult to account for this high result ; either the same analytical error has been committed in the three analyses, or there may be present *another* foreign substance besides didymium. The first supposition is contradicted by analyses, which have been made by exactly the same methods and which will be given hereafter, while the second I shall discuss presently.

A sample of salt, which had been re-crystallized twenty times, still distinctly showed the line D of the absorption spectrum of didymium, and it being evident that by crystallization *alone* no absolutely pure cerous sulphate can be prepared, it was therefore necessary to search for another method for its preparation. To ascertain the purity of the resulting product the cerous oxalate was used, and from the color of the oxyd produced by its ignition the state of purity was readily ascertained.

Mosander had already correctly stated that the brown color of the mixed oxyds was due to the presence of foreign substances ; he obtained the ceroso-ceric oxyd of a reddish white color ; Hermann had it of an isabel color. By a slight alteration in the mode of preparation, Bunsen obtained it of a yellowish white color. On my part I have made numerous experiments in order to produce it as white as possible.

For this purpose the previously mentioned second portion of the basic sulphate was used. Out of the numerous methods which I have tried, but *two* have given encouraging results.

The first was as follows : A small portion of the precipitate was dissolved by heating it with a few drops of sulphuric acid and this solution precipitated by pouring it into a large quantity of boiling water. After its conversion into oxalate the new precipitate gave a paler ceroso-ceric oxyd ; a repetition of

the same process still gave a better result, but the reduction in color was not very rapid and it would have required at least eight or ten precipitations to produce as pale an oxyd as that obtained by the following process; besides, another disadvantage, incident to these numerous washings, is the very large quantity of solution and the great loss of material, which are the consequences. Far better results were obtained by the use of nitric instead of sulphuric acid. The crude precipitate was dissolved in a small quantity of nitric acid, and the deep red solution treated as above, by which a far paler precipitate of basic salt was obtained. The resulting mother-liquor gave on evaporation the complete didymium spectrum and the color of the oxyds prepared from it was brown like that of the original mixed oxyds.

To save repetitions, I will call the crude basic salt N and the precipitate resulting from it $N\alpha$. $N\alpha$ was re-dissolved again in nitric acid and the solution treated as above; it gave a new $N\beta$, which was easily discernible from N and $N\alpha$ by its paler color and greater purity. It separated far more readily from the supernatant liquid than N and $N\alpha$ and was more easily washed out.

The mother-liquor from $N\beta$ examined with the spectroscope still indicated the presence of didymium, and $N\beta$ itself yielded a yellowish white ceroso-ceric oxyd, in which *traces* of didymium were still perceptible.

A portion of $N\beta$ was converted into sulphate and this was re-crystallized six times, the mother-liquor being always separated at each operation. The crystallizations were obtained by a very slow evaporation of the liquid, and I observed that the forms of the crystals had materially changed. As already stated, the still impure sulphate always gave thin slender crystals, while now, after repeated evaporations and crystallizations, no other but small octahedral forms were produced.

From this salt several new determinations of the equivalent were made.

The pulverized salt was dried over sulphuric acid and the analyses conducted as already described :

- β_1 . 1.4327 grs. gave 0.2733 grs. water and 0.69925 grs. of ceroso-ceric oxyd, corresponding with 0.66491 grs. cerous oxyd ;
- β_2 . 1.5056 grs. gave 0.2775 grs. water and 0.7405 grs. of ceroso-ceric oxyd, corresponding with 0.70413 grs. of cerous oxyd ; 0.8816 grs. of the ceroso-ceric oxyd from β_1 and β_2 gave 0.8383 grs. cerous oxyd.
- β_3 . 1.44045 grs. gave 0.2710 grs. water and 0.7052 grs. ceroso-ceric oxyd, corresponding with 0.67044 grs. cerous oxyd. 0.5102 grs. of the ceroso-ceric oxyd gave 0.48505 grs. cerous oxyd.

These results give for the anhydrous sulphate:

| | β_1 | β_2 | β_3 | Mean. |
|-----------------------|-----------|-----------|-----------|---------|
| Cerous oxyd, ----- | 57·349 | 57·335 | 57·329 | 57·338 |
| Sulphuric acid, ----- | 42·651 | 42·665 | 42·671 | 42·662 |
| | <hr/> | <hr/> | <hr/> | <hr/> |
| Equivalent, | 100·000 | 100·000 | 100·000 | 100·000 |
| | 45·784 | 45·754 | 45·741 | 45·760 |

The hydrous sulphate has the composition:

| | β_1 | β_2 | β_3 | Mean. |
|-----------------------|-----------|-----------|-----------|---------|
| Cerous oxyd, ----- | 46·409 | 46·767 | 46·544 | 46·573 |
| Sulphuric acid, ----- | 34·515 | 34·802 | 34·642 | 34·653 |
| Water, ----- | 19·076 | 18·431 | 18·814 | 18·774 |
| | <hr/> | <hr/> | <hr/> | <hr/> |
| | 100·000 | 100·000 | 100·000 | 100·000 |

From these analyses it becomes evident that the composition of this hydrous sulphate differs from that previously described and that it can be expressed by the formula $2(\text{CeO}, \text{SO}_3) + 5\text{HO}$, which would give:

| | |
|-----------------------|--------|
| Cerous oxyd, ----- | 46·241 |
| Sulphuric acid, ----- | 34·406 |
| Water, ----- | 19·353 |

The equivalents resulting from these analyses differ very much from those previously obtained, but it is hardly possible that the separation of didymium *alone* can be the cause of the reduction from 46·187 to 45·760. Bunsen's and Rammelsberg's equivalents 46·058 and 46·072 were certainly made with cerium salts *free* or *almost free* from didymium. The salt which gave 45·760 still contained a trace of this metal.

From all these facts we are led to conclude that the reduction of the equivalent of cerium from 46· to 45·760 is *not* owing to the separation of didymium, but to that of *another foreign* substance.

The mother-liquor and wash-waters from $\text{N}\beta$ gave with ammonia a very minute precipitate.

Encouraged by the results obtained by this method of separation, I have continued in the same manner. A portion of $\text{N}\beta$ was dissolved in nitric acid, and this solution re-precipitated by boiling water. The new precipitate $\text{N}\gamma$ was *almost* white. In the mother-liquor the presence of didymium could hardly be detected by the line D, while in the precipitate itself *not a trace* was visible.

The sulphate prepared from $\text{N}\gamma$ again showed the habitus of the first sulphates and crystallized in slender crystals, which gave the same angles with no new modifications; analysis proved that their composition also was nearly the same. I found that—

1·4684 grs. gave 0·1880 grs. of water and 0·7717 grs. of ceroso-ceric oxyd, which gave 0·7338 grs. of ceroso-oxyd.

The sulphate contains therefore as follows :

| | The anhydrous: | The hydrous: |
|-----------------------|----------------|---------------|
| Cerous oxyd, ----- | 57·310 | 49·973 |
| Sulphuric acid, ----- | 42·690 | 37·224 |
| Water, ----- | ----- | 12·803 |
| | <hr/> 100·000 | <hr/> 100·000 |

The equivalent calculated from this analysis is again lower, being equal to 45·699.

Although the cerous sulphate from which the last determinations had been made was *entirely free* from didymium, still I thought that a repetition of the same mode of purification might lead to a still greater reduction of the equivalent, owing to the removal of the foreign substance above alluded to.

A portion of N γ was therefore treated as usual, and produced the basic salt N δ .

After washing it was perfectly white, though otherwise in appearance similar to N, N α , N β and N γ .

The oxyds obtained, both from the oxalate, prepared from the mother-liquor, and that from the basic salt, were white. In neither could the least trace of didymium be detected. The sulphate prepared from N δ after repeated and very careful recrystallizations, had the habitus of the first sulphates and gave on analysis the following results :

1·3756 grs. gave 0·1832 grs. water and 0·7186 grs. of ceroso-ceric oxyd, yielding 0·68318 grs. of cerous oxyd.

These results would give for :

| | The crystallized salt. | The anhydrous salt. |
|-----------------------|------------------------|---------------------|
| Cerous oxyd, ----- | 49·664 | 57·294 |
| Sulphuric acid, ----- | 37·018 | 42·706 |
| Water, ----- | 13·318 | ----- |
| | <hr/> 100·000 | <hr/> 100·000 |

The equivalent was again reduced by this operation, which now makes it equal to 45·664, which number must be considered as the equivalent of the purest cerium, which has as yet been prepared.

Further investigations will be needed to ascertain, whether a continued repetition of the same operation can reduce the equivalent of cerium to a still lower number.