2. With increasing total salt concentration, at a fixed (equivalent) salt-concentration ratio, (*a*) the value of C_c decreases very rapidly up to about 0.8 N, after which it decreases more and more slowly until it reaches a limit at 1.6 N; (*b*) the ion fraction of the sodium increases with increasing salt concentration up to about 1.6 N, where it reaches a limit value of 0.95 $Na^+ : 0.05\ Sr^{++}$.

3. With equivalent mixtures at a total concentration of 0.2 N, the value of C_c increases with increase of temperature between 15° and 30°. The heat of the reaction

$$2NaHg_n + SrCl_2 = SrHg_m + 2NaCl + (2n - m)Hg,$$

as determined from the van't Hoff equation, using values of C_c at 15°, 20°, 25° and 30°, is about + 4000 Cal.

4. In solutions of fixed concentration, the ion fractions of the two metals vary in the direction of, but not in proportion to, the mol-fractional variation of the salts in the solutions. The fact that the ion fractions are not proportional to the mol fractions in such solutions of strong electrolytes has been used as an argument that the mass law does not hold in the case of these solutions. In this investigation, however, the use of the mass law has led to the very conclusion that has been used against it.

5. The change in the degree of association of the metals ($Me + xHg \rightleftarrows MeHg_x$) with the dilution of the amalgams with mercury is much more rapid in the case of the strontium amalgam than in the case of the sodium amalgam.

URBANA, ILL.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE NATIONAL CARBON COMPANY.]

THE DECOMPOSITION OF CEROUS OXALATE IN A REDUCING OR INERT ATMOSPHERE AND A NEW PROPERTY OF THE HIGHER OXIDES OF CERIUM.

BY WALLACE S. CHASE.

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General.

In the course of certain investigations in this laboratory some cerous oxide was desired and its preparation was attempted by decomposing cerous oxalate in an atmosphere of hydrogen. While this experiment was unsuccessful from the standpoint of Ce_2O_3 yield, its results were of enough interest to prompt an investigation of the decomposition of this oxalate in the absence of oxygen. The present paper constitutes a brief description of the work done and its results.

An extended review of the literature showed that Mosander[1] claimed

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[1] *J. prakt. Chem.*, 30, 276 (1843).

to have obtained cerous oxide along with some carbide by decomposing the oxalate in hydrogen.

Buhrig[1] repeated Mosander's work and obtained what he regarded as a mixture of CeO_2, Ce_2O_3 and carbon, but no carbide.

Delafontaine[2] also duplicated Mosander's experiments, obtaining a grey-black powder that took fire on heating in air and which contained a substance that he considered a carbide of the formula CeC_3.

Finally Sterba[3] decomposed cerous oxalate under diminished pressure and came to the same conclusions as did Buhrig both as to composition of the residue and the presence of carbide. He describes the residue as a black amorphous powder, non-pyrophoric, three analyses of which gave 1.25, 1.35 and 1.47% carbon, respectively. Neither of these investigators actually proved the presence of cerous oxide in any decomposition residue, but all agree that that substance is not obtained in a pure state. Their work, somewhat meagre in detail, was all that could be found on the preparation of cerous oxide by decomposition of the oxalate.

Apparently Burger[4] was the first to succeed in preparing fairly pure cerous oxide. Inasmuch as the method he used was reduction of ceric oxide by metallic calcium, the only information of value obtained from his results was that relating to the physical and chemical properties of Ce_2O_3. He describes this substance as a yellowish green powder that takes fire on being heated in air to approximately 200°.

Experimental.

The cerous oxalate used in this work had been carefully purified, especially from the other cerium earths, and was extremely pure material.

A Hoskins carbon combustion furnace was used for decomposing the oxalate; the temperature was determined with a Pt-PtRh thermocouple in conjunction with an accurate millivoltmeter.

The usual precautions were observed to insure the purity and dryness of the hydrogen and nitrogen gases.

Experiment showed that approximately 550° was the lowest temperature at which the carbonate resulting from the decomposition of cerous oxalate, was completely decomposed, and all the residues were therefore prepared at that temperature.

Physical and Chemical Properties of Residue.

The residue obtained by the decomposition at 550° of cerous oxalate in a hydrogen or nitrogen atmosphere, is a very dark blue-black amorphous powder; it is unstable, even at ordinary temperature, if drawn directly into the air from a *hydrogen* atmosphere when it will invariably take fire

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[1] *J. prakt. Chem.*, **12**, 215 (1875).

[2] *Arch. sci. phys. nat.*, **22**, 38 (1901).

[3] *Ann. chim. phys.*, [8] **2**, 193 (1904).

[4] *Ber.*, **40**, 1652 (1907).

and burn vigorously, forming CeO_2. This phenomenon is not observed when the material is drawn from *nitrogen* into the air, and therefore, as might be expected, its instability in the first case was found to be due to absorbed hydrogen. If oxidation of the adsorbed gas occurs slowly, as, for example, by mixing small quantities of air into the hydrogen stream in which the residue is being cooled, on withdrawing the latter into the air it is quite stable.

The adsorption of hydrogen by the residue will be dealt with further on.

Qualitatively, the residue either from a hydrogen or nitrogen atmosphere gives the same tests, showing ceric oxide, a lower oxide or oxides and free carbon, to be present. On being heated to between 400 and 500° in air the residue takes fire, glowing quite vigorously and forming CeO_2. It, however, is quite stable at lower temperatures, though at about 200° a slow oxidation of the carbon begins to take place, so that if a sample is held at that temperature for several hours a gradual lightening in color is detected. The carbon present is in such a finely divided state that its combustion results on heating the residue to the higher temperature above mentioned.

The stability of the residue towards heat, and its color, indicated the absence of cerous oxide, according to Burger's work. This generally is in agreement with the analytical results which show that very little, certainly not over 1% of cerous oxide, could be present, considering the oxygen content of the material and the relative amount of soluble and insoluble oxide. There is no doubt, however, that not even a trace of cerous oxide is present, for in addition to Burger's work that of Newberry and Pringe[1] demonstrates the difficulty of preparing that substance owing to its great reducing power.

Analyses and Composition of the Residue.

Careful analyses of various samples of the residue prepared in hydrogen, gave the following results:

TABLE I.

Partial Analyses of Residue.

Sample.	1.	2.	3.
Total Ce	76.71%	77.02%	76.82%
Observed oxygen content[2]	16.56%	16.68%	16.55%
Calc. oxygen content for Ce as CeO_2	17.50%	17.57%	17.53%
Calc. oxygen content for Ce as Ce_4O_7	15.32%	15.38%	15.34%

These data show that the cerium is present as a mixture of the two oxides in the proportion shown in the following table, which gives three complete analyses of different samples of the residue.

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[1] *Proc. Roy. Soc. London,* **92A**, 276 (1916).

[2] Determined by solution in sulfuric acid and ferrous ammonium sulfate and titration of the excess of ferrous iron with potassium permanganate.

TABLE II.

Approximate Composition of Residue.

Sample.	1.	2.	3.	Mean.
CeO_2	53.59%	56.15%	52.13%	53.96%
Ce_4O_7	39.68%	37.55%	41.24%	39.49%
Carbon (average of six determinations)				2.64%
Adsorbed air (average of twenty determinations)				3.43%
			Total,	99.52%

The oxide values given above were calculated from the oxygen content found by analysis, and are about what was expected from qualitative tests, which indicated that the amount of oxide soluble in hydrochloric acid was not very much less than that which was insoluble, the ceric oxide.

Carbon was determined by the usual combustion method, and the average of six results, 2.64%, was taken as correct. The possible significance of this value will be discussed further on.

The approximate adsorbed air content of the residue was carefully determined with many samples. Briefly, it was found that losses of from 4.71 to 5.70% were sustained by the residue on igniting in platinum at a temperature of approximately 1200°. At this temperature practically a constant weight is obtained, little further loss occurring at higher temperatures.

Assuming a carbon and Ce_4O_7 content of 2.64 and 40%, respectively, the adsorbed air value is derived as follows:

Average loss on ignition	5.07%
Average carbon content	2.64%
Apparent air adsorption	2.43%
Gain in wt. due to oxidation of Ce_4O_7 to CeO_2	1.00%
Actual air adsorption	3.43%

The expulsion of absorbed air from the residue was found to be directly proportional to temperature. It was possible to burn off the carbon at as low a temperature as 350°, using oxygen and heating in the combustion furnace; under these conditions the *apparent* air adsorption is practically nil, or, in other words, the loss in weight of the residue approximates its carbon content. If, however, the residual CeO_2 is heated at gradually increasing temperatures, a progressive loss is sustained, until finally at 1200° the total loss approximates the average loss on ignition value.

This adsorption explains the property exhibited by the "rare earth" oxides of commerce in that their density is proportional, in a very marked degree, to the ignition temperature.

The Carbon Value.

An explanation of the presence of carbon cannot be given at present with certainty, but it is hoped to make a further investigation of the question.

Inasmuch as cerous oxalate decomposes to carbonate without the liberation of carbon, the latter is obviously produced by the breaking down of the carbonate. It was found that if pure cerous fluoride is fused with sodium carbonate as in the ordinary analytical procedure, a mixture of CeO_2 and the blue oxide Ce_4O_7 is obtained. This furnished positive visual evidence of the formation of the intermediate oxide Ce_4O_7 on the decomposition of cerous carbonate, $Ce_2(CO_3)_3$, in the absence of oxygen, and showed that oxidation of the Ce_4O_7 by the liberated carbon dioxide is incomplete even when decomposition takes place at as high a temperature as that of the fusion, 900 to 1000° approximately. As might be expected, relatively much more Ce_4O_7 is formed at the lower temperature of the decomposition in hydrogen, 550°. Knowing by this experiment that Ce_4O_7 is produced under the above conditions, the foregoing calculations based on analyses of the residue became possible, as did also the formulations offered for consideration below.

Oxidation of the cerous oxide produced on the decomposition of the carbonate could take place in the several ways typified by the following reactions:

		Theoretical carbon content of residue corrected for adsorbed air.
1.	$2Ce_2O_3 + CO_2 = 4CeO_2 + C$	1.65%
2.	$Ce_2O_3 + CO_2 = 2CeO_2 + CO \longrightarrow C + O$	3.26%
3.	$2Ce_2O_3 + CO_2 = Ce_4O_7 + CO \longrightarrow C + O$	1.69%
4.	$4Ce_2O_3 + CO_2 = 2Ce_4O_7 + C$	0.85%

On the basis of the qualitative tests, which showed much lower oxide to be present, Reactions 2 and 3 appear the more probable considering the carbon value of 2.64% in the residue. (In those reactions the catalytic decomposition of carbon monoxide by the cerium oxides is assumed. Though this assumption is wholly theoretical its plausibility is possibly strengthened by Sterba's[1] work on the reduction of CeO_2 by CO, in which he found that the unacted upon ceric oxide was colored by separated carbon.)

Using these two reactions and calculating from the average carbon value found, the composition of the residue is found to be CeO_2 56.49, Ce_4O_7 37.44, C 2.64, adsorbed air 3.43%. It is noteworthy that these values approximate those calculated from the oxygen content of the residue. In other words, the composition of the residue is approximately the same whether calculated from the oxygen or carbon content. This would seem to indicate that Reactions 2 and 3 are the ones that take

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[1] *Loc. cit.*

place, as no other combination of the reactions will give both the same carbon value, and composition of the residue.

On the other hand, there is a possibility that the carbon value is of no significance as indicating the composition of the residue, and therefore that the above apparent relation is merely a coincidence. This is so because it was found that if the cerium group carbonates, *free from cerium*, are similarly decomposed, carbon is also produced, indicating catalytic decomposition of carbon dioxide. This action might occur also with cerium carbonate, though not necessarily so, for as an example of dissimilarity in behavior of cerium and the cerium earths, the fact that the oxalate decomposition residue of the former adsorbs hydrogen, while that of the other earths does not, may be cited.

It is obvious that further investigation is required to establish positively the significance of the carbon value.

The Adsorption of Hydrogen by the Residue.

Quantitative estimations of the amount of hydrogen adsorbed were made by heating the freshly prepared residue in pure oxygen and weighing the water formed. Two careful determinations gave results of 10.2 cc. and 11.7 cc. of hydrogen at 0° and 760 mm. per gram of residue. Assuming a density of 5 for the residue, this represents an adsorption of hydrogen by the residue of from 51 to 58.5 times its volume.

Experiment showed that the adsorbed hydrogen is removed by passing a stream of pure nitrogen over the residue heated to 550°; complete removal of the hydrogen is more or less difficult, varying periods of treatment in nitrogen being required, though from 2 to 4 hours usually suffices for a few grams of residue if same is loosely packed. In no case was the formation of NH_3 detected during the treatment in nitrogen, which corroborates what the slowness of the action indicates, namely, that the hydrogen is displaced mechanically. At ordinary temperatures, this displacement, if it occurs at all, is so extremely slow as to be negligible for practical purposes.

The combustion of the residue when drawn from a hydrogen atmosphere into the air, is due of course to the adsorbed hydrogen being so rapidly oxidized that sufficient heat is generated to cause oxidation of the Ce_4O_7 and finely divided carbon, resulting in ignition of the mixture.

Similarly, experiment showed that the combustion on exposure to air of the more or less pure Ce_4O_7 obtained by reduction of CeO_2 at about 950° C. with hydrogen, is due to the oxidation of adsorbed gas.

Several previous investigators, notably Rammelsberg,[1] Winkler,[2] Brauner[3] and Sterba,[4] each obtained a so-called pyrophoric substance by

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[1] *Ann. Physik.*, [1] 8, 41 (1803).

[2] *Ber.*, 24, 873 (1891).

[3] *Z. anorg. Chem.*, 34, 103 (1903).

[4] *Loc. cit.*

this reduction. Sterba attributed its spontaneous combustion to the formation of finely divided metallic cerium, which assumption the above results show is erroneous, however, as does also the work of Newberry and Pring previously mentioned.

Summary.

It has been shown that the decomposition of cerous oxalate, and resulting carbonate, in a hydrogen or nitrogen atmosphere, yields a bluish black mixture of CeO_2, Ce_4O_7 and carbon.

This residue when prepared in hydrogen will take fire if drawn directly from that atmosphere into the air, due to oxidation of adsorbed hydrogen; it is capable of adsorbing that gas to the extent of from 51 to 58.5 times its own volume under the conditions worked with.

Qualitatively the residue shows the same composition whether prepared in hydrogen or nitrogen.

Several analyses of residues prepared in hydrogen are given, the mean of which indicate a composition as follows: CeO_2 53.96, Ce_4O_7 39.49, C 2.64, absorbed air 3.43%, respectively.

CeO_2 and Ce_4O_7 have been shown to possess in marked degree the power of adsorbing gases.

CLEVELAND, OHIO.

A STUDY OF TANTALUM CHLORIDE WITH REFERENCE TO ITS USE IN THE DETERMINATION OF THE ATOMIC WEIGHT OF TANTALUM.

BY GEORGE W. SEARS.

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A consideration of the ratios that have been studied for the determination of the atomic weight of tantalum shows that they have almost universally involved the use of either tantalum chloride or tantalum oxide. In 1866 Magrignac[1] established the formula of tantalum oxide and studied a number of ratios only one of which did not involve either the chloride or the oxide. Since that time four ratios have been studied. Hinrichson and Sahlbom[2] in 1906 determined the ratio $2Ta : Ta_2O_5$ by direct ignition of the metal to the oxide. In 1910 Balke[3] converted the chloride into the oxide by hydrolysis and subsequent ignition with nitric acid, obtaining the ratio $2TaCl_5 : Ta_2O_5$. The same process was used by Chapin and Smith[4] in 1911 in the study of the ratio $2TaBr_5 : Ta_2O_5$. In 1915 Sears and Balke[5] published an investigation of the ratios $2TaCl_5 : Ta_2O_5$ and $TaCl_5 : 5Ag$ in which it was found that tantalum oxide obtained from the

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[1] Abegg's "Handb. der Anorg. Chem.," [3] 3, 839.

[2] *Ber.*, 39, 2600 (1906).

[3] THIS JOURNAL, 32, 1122 (1910).

[4] *Ibid.*, 33, 1497 (1911).

[5] *Ibid.*, 37, 833 (1915).