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CONTRIBUTIONS TO THE CHEMISTRY OF CERIUM.[1]

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THE mineral cerite was first found in one of the iron mines of Bastnäs, in Westmanland, Sweden. Its peculiarity was noticed as early as 1751 by Cronstedt,[2] and in 1784 it was analyzed by d'Elhuyar,[3] in Bergmann's laboratory, and was considered by these two chemists to be a silicate of lime and iron. In 1803 the mineral was again examined by Berzelius and Hisinger, and by Klaproth, and nearly at the same time, but independently, they discovered in the mineral a new oxide. Berzelius and Hisinger named the earth *ceria*,[4] after the planet Ceres which had been discovered two years before by Piazzi. Klaproth called it *ochroiterde*,[5] from its brownish-yellow color. Fortunately the former name was adopted, for the latter name would have been a misnomer, since pure cerium dioxide, as we now know it, has a pale-yellow color.

From that time to the present, cerium and its compounds have frequently been the subject of investigation, but the work of the earlier chemists is not of direct importance, since the ceria upon which they worked was, as we now know, a mixture of various oxides, chief among them being those of cerium, lanthanum, and didymium.

In 1839, however, Mosander make known a discovery of the highest importance; namely, that ceria was not a simple oxide

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[1] Read at the Brooklyn Meeting, August 15, 1894.

[2] *Sv. Vet. Akad. Handl.*, *1751*, S. 227.

[3] *Sv. Vet. Akad. Handl.*, *1784*, S. 121.

[4] *Afhandl. i. Fysik*, *Kemi och Mineral.*, 1, 58.

[5] *A. Gehl.*, 2, 303; *Beiträge.* 4, 140.

but a mixture of at least two. The newly isolated earth he called *lanthana*, and this, in 1842, he split up into lanthana proper, and another oxide which he named *didymia*.[1]

Dating from the time of Mosander's discoveries, the results of the various investigations upon cerium acquire, of course, much greater value, but the chemistry of this element and the other rare earths has remained one of the most difficult problems in the field of inorganic chemistry, chiefly because of the great similarity in the chemical behavior of these different elements and the consequent difficulty of separating any one of them completely from the others. Naturally, then, in an experimental investigation of the compounds of cerium, the first problem to be solved is the preparation of pure ceria.

I. SEPARATION OF CERIA FROM THE OTHER EARTHS.

The ceria was extracted from allanite from Amelia County, Virginia, a large amount of this mineral having been most kindly sent to us by Professor W. G. Brown, of the Washington and Lee University.

Nineteen hundred and twenty-four grams of the finely powdered allanite was heated in large porcelain evaporators with concentrated hydrochloric acid until the supernatant liquid became dark brown. The syrupy liquid was allowed to cool and was then poured off, the residual mineral being again treated in the same manner until it became grayish-white, three treatments of about ten hours each usually sufficing. A portion of the residue was then moistened with concentrated sulphuric acid and heated until all of the acid was driven off. The white residue was thrown, in small portions at a time, into ice-water, and to the filtered solution, oxalic acid was added. No precipitate resulted showing that the treatment with hydrochloric acid had removed all of the rare earths.

The rare earth chlorides, mixed with those of iron, aluminum, calcium, etc., were then diluted and filtered. A portion of this filtrate was treated with hydrogen sulphide for twenty-four hours, the solution being kept at 70°, but no precipitate appeared. The hydrogen sulphide was then expelled by boiling, the sulphur was filtered off, and the filtrate was added to

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[1] *Förh. Skand. Naturf. Stockholm*, *1842*, 357; *Phil. Mag.*, 28, 241; *Pogg. Ann.*, 56, 503; *J. prakt. Chem.*, 30, 276.

the original solution. This was oxidized by nitric acid and a concentrated solution of oxalic acid was then added in excess. The pinkish-white precipitate of the rare earth oxalates was allowed to settle, and the oxalates were then washed by decantation with hot water until the supernatant liquid was colorless. They were then digested in large evaporators with one per cent. hydrochloric acid until all iron had been removed and were then dried and ignited in a muffle furnace. The reddish-brown oxides resulting weighed 410 grams, a yield of over twenty-one per cent.

The oxides were dissolved in concentrated nitric acid. To facilitate solution sulphurous acid was added to one portion and oxalic acid to another, but with no perceptible benefit in either case. There were obtained four liters of an almost syrupy solution which showed the didymium absorption bands very strongly.

Many different methods for separating the ceria from the accompanying earths have been proposed but none of them seem to yield cerium which is completely free from lanthanum and didymium unless the method proposed be many times repeated. Mosander,[1] the earliest worker upon this problem, obtained a mixture of didymia and lanthana free from ceria by precipitating the mixed chlorides with potassium or sodium hydroxide and passing chlorine through the suspended hydroxides. Cerous hydroxide is oxidized to the insoluble ceric hydroxide while the hydroxides of lanthanum and didymium are changed to chlorides and dissolve. Jolin[2] found that the treatment must be made seven times before the ceria is completely free from didymia and lanthana. Popp[3] added sodium acetate to the solution of the chlorides and ran in chlorine, the cerium being precipitated. Later instead of passing in chlorine gas he added sodium hypochlorite and boiled. Gibbs[4] boiled the mixed earths with nitric acid (1:2) having first added considerable lead dioxide. Zschiesche[5] heated the rare earth sulphates with red lead and nitric acid. In each of the last two methods ceric oxide is formed. Winkler[6] separated ceria and didymia from lanthana by adding

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[1] *Phil. Mag.*, **28**, 241.

[2] *Bihang till K. Sv. Vet. Akad. Handl.*, **2**, 14; *Bull. Soc. Chim.*, [2] **21**, 533.

[3] *Ann.*, **131**, 359; *J. B.*, *1864*, 195 and 702.

[4] *Sill. Amer. Jour.*, [2] **37**, 332.

[5] *J. prakt. Chem.*, **107**, 65.

[6] *J. prakt. Chem.*, **95**, 410.

mercurous oxide to the solution of the chlorides and then potassium permanganate until the solution is colored by the latter. Ceria and didymia are precipitated. Welsbach[1] precipitates the ceria by fractional crystallization as cerium ammonium nitrate. Bunsen first[2] proposed to ignite the oxides with magnesia, to dissolve out the ceria as cerium magnesium nitrate and then pour the solution of the latter into a large amount of very dilute nitric acid, whereby ceric oxide is precipitated. Later[3] he abandoned this method and proposed instead the method which has been most employed for preparing pure ceria. A solution of impure cerium sulphate is poured into boiling water containing one part of nitric acid to the thousand, and basic cerium sulphate is thrown down. This procedure must be repeated several times and is also very wasteful because the yield is small, so that it can be used with advantage only on material that is already nearly pure. Brauner[4] increased the yield by dissolving finally in nitric acid instead of in sulphuric acid, driving off the excess of acid and precipitating with boiling water containing nitric acid. Debray[5] fused the nitrates of the earths with from eight to ten times their weight of potassium nitrate at a temperature between 300° and 350°. The nitrate of cerium is decomposed leaving the oxide which is insoluble in water. The other nitrates are undecomposed and are soluble in water. Many repetitions were necessary to free the ceria from the other earths. Pattinson and Clark[6] heated the mixed chromates to 110° when cerium chromate decomposes to ceric oxide, the other chromates remaining unchanged.

For the separation of the ceria from the other earths in the allanite solution obtained as stated above, the authors first employed the Mosander-Jolin method which so eminent an investigator as Cleve has pronounced to be the best. The nitrate solution of the earths was diluted, potassium hydroxide was added in excess and well-washed chlorine gas was run into the solution for from four to five days. The white precipitate of

[1] *Monatsh. f. chem.*, 4, 630.

[2] *Ann.*, 105, 40.

[3] *Pogg. Ann.*, 155, 375.

[4] *Monatsh. f. chem.*, 6, 792.

[5] *Compt. rend.*, 96, 828.

[6] *Chem. News*, 16, 259.

the hydroxides soon changed to a dirty violet and became light yellow soon after the action of the chlorine began. The ceric oxide was washed by decantation until the wash-water gave no precipitate with ammonium hydroxide, this washing occupying nearly a week as the precipitate settles very slowly. The precipitate was then dissolved in hydrochloric acid and the treatment with chlorine was repeated. After seven complete treatments the concentrated solution of cerium chloride showed no absorption bands when a layer ten cm. thick was examined with a Krüss spectroscope. The solution was then nearly neutralized with ammonium hydroxide and hydrogen sulphide was run in for twenty-four hours, the solution being warmed to 70°. A very slight precipitate of copper sulphide resulted. This was filtered off, the hydrogen sulphide was expelled by boiling and the separated sulphur was removed by filtration. To the filtrate was added a concentrated solution of pure oxalic acid, a snow-white precipitate of the oxalates of the rare earths resulting. This precipitate was treated with a hot solution of hydrochloric acid (two per cent.) until the washing liquid failed to give a reaction for iron when tested with potassium sulphocyanate and ether. The oxalate was then dried and ignited in porcelain crucibles over the blast-lamp. The resulting oxide was of a pale yellow color resembling in tint very light chamois leather.

In the meantime the method of separation proposed by Debray was tried upon another portion of the rare earths. It was found that the melting point of the mixture of rare earth nitrates and potassium nitrate was usually about 325°. (The melting point of potassium nitrate is stated to be 339°.) Upon treating the fused mass with water it was found that the insoluble residue contained, even after two fusions, appreciable amounts of didymium. Since cerium nitrate begins to decompose at 200° and didymium nitrate at about 300°, the cause of the presence of didymium in the insoluble cerium oxide is evidently to be ascribed to the high melting point of the nitrate mixture employed by Debray. If then the melting point of the mixture could be lowered the probable result would be that less of the didymium nitrate would be decomposed and it seemed reasonable to expect that, by sufficiently depressing the melting point, cerium oxide completely free from didymium might be obtained by a single fusion. With this end in view the potassium nitrate was replaced by sodium nitrate, the melting point of the latter, 316°, being somewhat lower than that of the potassium nitrate. But even with this salt more than two fusions were necessary to free the cerium from didymium.

Carnelley and Thomson[1] have shown that while potassium nitrate melts at 339° and sodium nitrate at 316°, a mixture of these two salts in molecular proportion melts at 231°. Consequently, this mixture was next tried with the rare earth nitrates, the details of the method being as follows:

The oxalates of the rare earths, after being freed from iron, as above described, are placed in porcelain evaporating dishes, the oxalates being covered by funnels of such size that when inverted they fit inside the edge of the evaporating dish. Concentrated nitric acid is now poured over the oxalates. Action begins at once in the cold, but it can be greatly hastened by warming on a water-bath. After the nitrogen oxides cease to come off, and the liquid has become clear, the solution, which should be so concentrated as to be syurpy in consistency, is poured while still hot into large porcelain crucibles half-filled with the well-ground mixture of potassium and sodium nitrates. About enough of the solution to completely cover the dry nitrates is poured in and the whole is thoroughly mixed by stirring.

For heating the crucibles a double air-bath was used. Both of the air-baths and the two covers were lined within and without with asbestos board. Through the two covers, openings were made through which thermometers could be introduced at various points within the inner bath. The crucibles were placed in circular openings cut in a piece of asbestos board, this board resting on pipe clay rods in the inner air-baths. The asbestos board was also pierced with many smaller openings to allow free circulation of air. The air-bath was heated by two Bunsen burners, the height of the flame being kept constant by means of "precision" gas-cocks.

After the crucibles have been placed in position the temperature is brought up slowly, too rapid heating being liable to cause

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[1] *J. Chem. Soc.*, **53**, 782.

the mass in the crucibles to swell and run over the edge. The two covers are placed in position, and a thermometer is inserted through the center opening to such a distance that its bulb is on a level with the bottoms of the crucibles. The heat is gradually increased until the thermometer shows a temperature of 300° in the inner bath. The mixture melts at a little below 230°, and decomposition of the cerium nitrate begins almost immediately. As the temperature rises the brown fumes come off copiously, the evolution gradually lessening as the heating continues. If, after removing the covers, it is seen that the evolution of gas from the fusion has entirely ceased, then the decomposition possible at the temperature employed is complete. This usually takes from four to five hours after the temperature has risen to 300°. It was found that the cerium nitrate is not entirely decomposed even when the temperature has been kept at 350° for some time, and also that if the temperature rises above 320° the cerium oxide will contain some didymium. After the evolution of nitrogen oxides ceases, the bath is allowed to cool rapidly since by so doing the solid mass can usually be removed by inverting the crucible and tapping the edge gently. If it cannot be removed in this way it can usually be loosened by throwing a jet of hot water around the upper edge. The removal of the mass in a solid block is of advantage since the condition of the decomposition may be judged by the color of the oxide which has collected at the bottom. If it is bright yellow or nearly white the ceria is probably pure, but if brownish in color then some of the didymium nitrate also has been decomposed.

The solid mass is now treated with hot water which dissolves all but the oxides. These are allowed to settle and the supernatant liquid is decanted off through a filter. More hot water containing from four to five per cent. of nitric acid is poured over the oxides and the liquid is brought to boiling and poured while hot through the filter. This is repeated six times and finally the oxides are washed with hot water alone, the washing being continued until the wash-water gives no precipitate with ammonia.

The oxides are dissolved by heating them with concentrated sulphuric acid until fumes of sulphur trioxide begin to escape, allowing the mass to cool and then treating it with a large amount of water. More rapid solution can, however, be effected by throwing a jet of water upon the hot sulphates and stirring the mass constantly. There is some tendency to spatter, but solution is obtained in much less time and with much less water than in the first procedure. A concentrated solution of cerium sulphate thus obtained showed no didymium absorption bands in a layer thirty cm. thick.

To test the separation quantitatively, weighed amounts of pure cerium and didymium oxalates were mixed, the mixture was dissolved in nitric acid as above described and the mass was fused with the mixed alkali nitrates. The soluble portion from the first fusion was evaporated down and again fused with the alkaline nitrates, and this solution and fusion was repeated in all four times. The temperature during each fusion was about 300° The insoluble cerium oxide resulting from the fusions was in each case free from didymium, and of the total cerium taken more than sixty-three per cent. was obtained completely free from didymium by the four fusions.

Another sample of the mixed nitrates was fused at about 350°. The layer of cerium oxide which collected at the bottom of the fused mass showed a brown coloration at the edges, and the insoluble residue after being carefully washed and dissolved in sulphuric acid gave the didymium bands clearly. The filtrate tested by the hydrogen peroxide method mentioned below showed some cerium still present with the didymium.

From the foregoing it will be seen that while the method is not quantitative it is nevertheless quite rapid and the yield is comparatively high. Its chief merit lies in the fact that the cerium oxide resulting from each single fusion is free from didymium, an advantage which does not seem to be possessed by the other separation methods with which the authors are acquainted.

II. QUALITATIVE TESTS FOR CERIUM.

Early in the work the necessity arose for testing various solutions and residues for the presence of traces of cerium, and a comparison of the different methods which have been proposed was made to ascertain which test was most distinctive and delicate.

Until 1864, when Gibbs[1] proposed his lead dioxide test for ceria, no satisfactory method for the qualitative detection of this earth was known. In 1882, Hartley[2] proposed a more delicate and also a more easily applied test, using ammonium acetate and hydrogen peroxide. In 1885, Lecoq de Boisbaudran,[3] and also Cleve,[4] observed that hydrogen peroxide gave to solutions of cerium salts, to which an excess of ammonium hydroxide had been added, a precipitate of the same color as that yielded by Hartley's reagents; namely, an orange-red. Sonnenschein,[5] in 1870, had proposed the use of ceria as a test for strychnia, and Plugge[6], in 1891, has reversed this, using strychnia as a test for ceria. Finally, Gibbs[7], in 1894, has proposed to substitute bismuth tetroxide for lead dioxide in his test.

Hartley appears to have been the only observer previous to Plugge to test the delicacy of the reactions proposed. He found that if a quantity of a cerium salt, equivalent to one mgm. of the element, were dissolved in 100 cc. of water, the addition of ammonium acetate and hydrogen peroxide gave a distinctly brown or orange-red precipitate which could be filtered off, dried, ignited, and weighed. "Hence, we can separate one part of cerium from 100,000 parts of liquid."

To test the delicacy of these various reactions one-half gram of ceric oxide was dissolved, as sulphate, in a liter of water. Each cubic centimeter of this solution would contain one-half mgm. of ceric oxide. When one cc. of this solution was diluted to 100 cc., and five cc. of the diluted solution was boiled with excess of lead dioxide and nitric acid (1 : 2), a faint yellow tint was to be observed, but four cc. failed to yield a distinguishable color; that is, 0.025 mgm. can be detected in about seven or eight cc. The bismuth tetroxide detected 0.017 mgm. under the same conditions.

In testing Hartley's reaction, one cc. containing one-half mgm. was diluted to 100 cc., each cubic centimeter then containing

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[1] *Am. J. Sci.*, [2] 37, 352.

[2] *J. Chem. Soc.*, 41, 202.

[3] *Compt. rend.*, 100, 605.

[4] *Bull. Soc. chim.*, [2] 43. 57.

[5] *Ber. d. chem. Ges.*, 3, 631.

[6] *Arch. d. Pharm.*, 229, 558.

[7] *Am. Chem. J.*, 15, 546.

0.005 mgm. of ceria. When two cc. of this solution was diluted so much that with the solution of ammonium acetate and hydrogen peroxide it formed about four cc., a yellow color was visible, especially on looking downward into the test-tube held above a white surface; 0.01 mgm. of ceric oxide, or rather the cerium salt equivalent to this, can, therefore, be detected. Ammonium hydroxide and hydrogen peroxide gave as distinct a color with one cc., that is, Boisbaudran's test is twice as delicate as Hartley's.

Next, Plugge's strychnia test was tried and proven to be as delicate as he claims. The strychnia solution is prepared by dissolving one part of strychnia in one thousand parts of sulphuric acid. The solution suspected of containing ceria, or a few cubic centimeters of it, is rendered alkaline by sodium hydroxide, evaporated to dryness, and a drop of the strychnia solution is added. One-tenth of a milligram of ceria gives a distinct blue or violet color changing to red. One-hundredth of a milligram gives a faint blue tinge which rapidly fades. If oxalic acid be present it must be decomposed or the test fails. Boisbaudran's test is then the most delicate of any yet proposed.

Finally, known amounts of lanthana and didymia (mixed) and ceria in solution were mixed and Boisbaudran's test applied. A distinct coloration of the hydroxides was produced when 0.01 mgm. of ceria was mixed with 0.1 gram of lanthana and didymia in about 100 cc. of solution.

To apply the test in the presence of a large excess of other rare earths, very dilute ammonium hydroxide solution should be employed and this added drop by drop until the first permanent hydroxide remains after shaking. The hydrogen peroxide is then to be added—only a couple of drops are needed—and the mixture well shaken. By this means the weakly basic ceria is precipitated almost alone and the orange-red color cannot be disguised.

III. CEROUS CHLORIDE.

The ceric oxide, prepared according to the directions given in the first section, was purified from any thoria present, by boiling the oxalate (prepared from the sulphate) with a concentrated solution of ammonium oxalate. Any thorium oxalate dissolved, was poured off and a similar solution poured over the residual cerous oxalate. The whole was then bottled and allowed to stand for some months with occasional shaking. The mixture was then brought to boiling and the liquid again poured off, the residual oxalate being washed with a similar solution. This washed oxalate was then dissolved in nitric acid, care being taken to ensure full decomposition and it was then almost neutralized with ammonium hydroxide. Potassium hydronitride was then added[1] so long as it continued to throw down a precipitate. This was filtered off leaving a solution of cerium nitrate containing only potassium and ammonium salts with possibly traces of calcium. This solution was precipitated with ammonium hydroxide and washed by decantation until a liter of the wash-water left no residue on evaporation. The ceric hydroxide was then tested for calcium, potassium, etc., with the spectroscope and proved to be free from all foreign material. This pure hydroxide has been employed to prepare salts of cerium.

As this work has been in reality only preliminary to an extended study of cerium, many of the already known salts were prepared in order to become familiar with their characteristics, but of these there is no need to speak at length.

A salt, which may probably be rightly claimed to be a new compound, was prepared while endeavoring to obtain cerium tetrachloride. This latter should be capable of existence if cerium is properly placed in the periodic system. Every other element in group IV of that system forms such a chloride not even excepting lead.[2] Among other attempts made, one was as follows: A concentrated solution of cerous chloride, obtained by dissolving ceric chloride in hydrochloric acid and evaporating was placed in a wash-bottle surrounded by a freezing mixture (snow and salt) and dry chlorine gas run in. This was rapidly absorbed, and after a short time a white crystalline mass settled out. This was placed on a porous porcelain plate to remove the greater part of the liquid, and then the following experiments were tried with different portions.

An attempt was at first made to dry it to constant weight over

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[1] Dennis and Kortright, *Am. Chem. J.*, 16, 79.

[2] *Monatsh f. Chem.*, 14, 505.

dry caustic potash in vacuo. A large, but irregular, loss of weight occurred and the crystals evidently effloresced. On exposing it to the open air again it gained in weight till almost as heavy as at first.

An attempt to dry it over calcium chloride gave a similar result. A portion was then dried in air, dust being excluded.

	Grams.
Weight of sample taken	2.9824
" " " after 72 hours	2.9801
" " " " 118 "	2.9790
" " " " 142 "	2.9786
" " " " 166 "	2.9786

The chloride therefore assumes a constant weight in air.

In analyzing this air-dried chloride the cerium was first precipitated from the aqueous solution of the salt by ammonium hydroxide. The precipitate was so gelatinous that it was difficult to wash it free from chlorides and the oxide obtained by ignition of the precipitate was not of a pure yellow color. The percentages of cerium obtained in two analyses were 38.01 and 38.19.

In two other samples the cerium was thrown down by ammonium hydroxide and hydrogen peroxide was added. The orange-colored hydroxide thus formed was not as gelatinous as that formed with ammonia alone, and was much more easily washed, but on ignition of the precipitate the resulting ceric oxide was of a pale pink color. This color may have been due to the presence of a small amount of a higher oxide, for the results—38.01 and 37.93 per cent. cerium—while not agreeing as well as could be wished, were too high (see analysis below). The chlorine was determined by precipitation as silver chloride and the water by the method suggested by Kraut.[1]

	Calculated for $CeCl_3 7H_2O$.	Found.
Ce	37.63	37.97
Cl	28.54	28.58
H_2O	33.83	33.88

The above analysis showed that the compound formed by passing chlorine into a cold saturated solution of cerous chloride was merely a finely crystalline form of cerous chloride and not a

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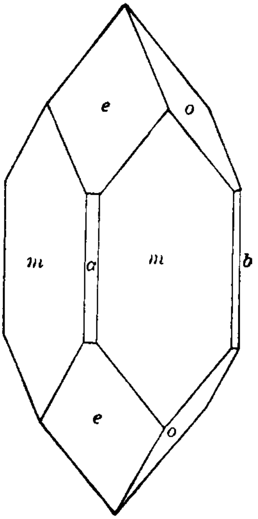
[1] *Ztschr. anal. Chem.*, 2, 242.

ceric chloride. Inasmuch then as the formation of the compound was probably due not to the oxidizing action of the chlorine, but to its dehydrating power, it seemed reasonable to expect that dry hydrochloric acid gas would accomplish the same result. The hydrochloric acid gas was made by the action of concentrated sulphuric acid upon solid ammonium chloride, the apparatus of Norblad being used for this purpose. Upon passing the gas into a cold concentrated solution of cerous chloride, the same white finely crystalline compound separated as with the chlorine. This was dried in the air to constant weight and then analyzed. In determining the cerium, the orange-colored hydroxide was precipitated by ammonium hydroxide and hydrogen peroxide but, before filtering, the solution was heated just to boiling. The suspended hydroxide changed to a bright yellow color but it did not become gelatinous and was easily washed. On ignition it yielded a ceric oxide of the usual pale yellow color.

	Calculated for $CeCl_37H_2O$.	Found.	
Ce	37.63	37.70	37.71
Cl	28.54	28.41	28.45
H_2O	33.83	by diff. 33.89	33.84



The crystalline form of the chloride was kindly determined by Mr. A. S. Eakle, of the Geological Department of the University, who states that "the cerous chloride is orthorhombic in crystallization, and of the form shown in the figure.

The axial ratio $\check{a}:\bar{b}:c = 0.80834:1:1.44187$.

$a = \infty P \bar{\infty}$ (100)
$b = \infty P \check{\infty}$ (010)
$e = P \bar{\infty}$ (101)
$m = \infty P$ (110)
$o = P \check{\infty}$ (011)

Faces.	Angles measured.	Angles calculated.
$110 : 1\bar{1}0$	77° 54′	......
$110 : \bar{1}10$	102° 12′	102° 6′
101 : 011	49° 20′	......"

The above chloride seems to be distinct from that obtained by Jolin[1] and by Lange[2] for which the formula $2CeCl_3 15H_2O$ is generally given.[3] That chloride may be made by dissolving ceric hydroxide in hydrochloric acid and evaporating on the water-bath until the solution becomes quite viscous. This solution placed in a desiccator while hot solidifies on cooling to a crystalline mass of a yellow color. If these crystals be allowed to stand in the air, they lose their color and a glassy coating appears to form over the surface. The differences between the results obtained by Jolin and by Lange and the variation of each of their analyses from the calculated percentages made it seem desirable to repeat the analysis of chloride prepared by Jolin's method to see if better results could not be obtained. A sample of their chloride was therefore prepared by us and analyzed, but the results showed as great a variation from the theory as those already mentioned.

	Calculated for $2CeCl_3 15H_2O$.	Jolin.	Lange.	Magee.	Calculated for $CeCl_3 7H_2O$.
Ce	36.74	36.89	37.37	36.37	37.63
Cl.....	27.87	28.40	28.80	28.65	28.54
H_2O ...	35.39				33.83

IV. THE HYDROXIDES OF CERIUM.

The peculiar color changes of the hydroxides of cerium have often been noticed by chemists who have experimented with that element. When any one of the alkaline hydroxides is added to a solution of a cerous salt a white hydroxide is precipitated. This, so most authorities state, becomes slowly yellow on exposure to the air, more rapidly if chlorine or other oxidizing agents be present. Popp,[4] however, claims that he obtained a dirty violet hydroxide by leading chlorine into a solution of a cerium salt precipitated by an acetate. This he claimed to be a higher hydroxide than the yellow. He states that it gave on ignition a red oxide. Others have claimed that his violet hydroxide was a basic acetate. Rammelsberg[5] obtained a like-colored hydroxide by precipitating a hot solution of ceroso-ceric sulphate with caustic potash. Hermann[6] and Stapff[7] also obtained

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[1] *Bull. Soc. Chim.*, [2] **21**, 153.

[2] *J. prakt. Chem.*, **82**, 129.

[3] *Gmelin-Kraut*, *Dammer and others.*

[4] *Ann.*, **131**, 361.

[5] *Pogg. Ann.*, 108, 45.

[6] *J. prakt. Chem.*, **30**, 189; **92**, 113.

[7] *J. prakt. Chem.*, **79**. 257,

peculiar hydroxides to which they attempted without much success to assign formulas. Later Lecoq de Boisbaudran,[1] by the addition of ammonium hydroxide and hydrogen peroxide to a solution of a cerous salt, obtained an orange-red precipitate, which was studied by Cleve,[2] who, as a result of his observations, considered it the hydroxide corresponding to an unknown CeO_3; namely $Ce(OH)_6$.

The following observations may throw some light upon the matter. A solution of mixed chlorides, containing lanthanum, didymium, and cerium was boiled and precipitated, while hot, with ammonium hydroxide. This was done in a large bottle which could be tightly corked. The mixed hydroxides were almost perfectly white, having possibly a faint pinkish tint. After the hydroxides had settled, the supernatant liquid was poured off and the bottle was refilled with thoroughly boiled distilled water. This was repeated until all foreign salts had been removed, the bottle being kept closely stoppered except while decanting and refilling. The hydroxides suffered no change of color upon standing for some days. Therefore, cerous hydroxide and the hydroxides of didymium and lanthanum when mixed are almost white. Didymium hydroxide by itself, however, or without much intermixture of white hydroxides, has a pinkish color. Finally air was blown through the suspended hydroxides. The color rapidly changed, at first to a dull purple and finally to a pale yellow.

Next a solution of cerous chloride was treated in the same manner. The hydroxide remained perfectly white while air was excluded, but, being exposed to air, it took on a dull purple color changing later to a bright yellow. Through another similar sample, air freed from carbon dioxide was passed; the same change in color resulted. Through yet another, pure carbon dioxide was passed. It remained white and did not change to purple even when, after some time, air was substituted for the carbon dioxide, the stability doubtless being due to the complete transformation of the hydroxide to the carbonate. Through yet another sample, air from which both oxygen and carbon dioxide were removed, that is, nitrogen, was passed. It remained white. Next a bottle was about one-

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[1] *Compt. rend.*, 100, 605.

[2] *Bull. Soc. Chim.*, [2] 43, 57.

sixth filled with cerous chloride and this was precipitated—white—with ammonium hydroxide, and the bottle was then filled with unboiled water and lightly stoppered. The precipitate changed in color quite rapidly to light purple which gradually became darker from above downward and finally the top began to change to yellow. After about four months the upper third had become yellow, that below it being still violet.

Both the white and the purple hydroxides when washed on filter paper, dried at a low temperature and then ignited, gave an olive-green oxide, which did not become yellow even when the highest heat of the blast-lamp was applied. On powdering it very finely it seemed more nearly yellow. The weights seemed to agree well, however, with that called for by ceric oxide. The yellow hydroxide when dried and ignited gave a pale yellow ceric oxide. When the yellowish-white oxide prepared by this method or by igniting the oxalate is again ignited over the blast-lamp, but in an atmosphere of hydrogen, it becomes olive-green without marked loss of weight. For example 0.1263 gram of yellow oxide ignited in hydrogen weighed 0.1261 gram; 0.1574 gram similarly treated gave 0.1570 gram. When again ignited in air or oxygen, the oxide became yellow and regained its original weight. Bunsen[1] obtained very similar results.

As mentioned in a previous section, the precipitate obtained by the united action of ammonium hydroxide and hydrogen peroxide, on being dried and ignited, gives a pink oxide which seems to weigh somewhat more than ceric oxide, CeO_2, should.

Another point, perhaps worthy of notice, was that when some of the purple hydroxide was dissolved in sulphuric acid and allowed to stand for a few days there separated out a crystalline sulphate which, on analysis, gave results too high for cerous and too low for ceric sulphate.

It is to be concluded, then, so far as the present observations go, that cerous hydroxide is white; that on exposure to oxidizing agents including atmospheric air it becomes first purple and then yellow, or, in other words, the purple hydroxide is an intermediate product.

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[1] *Ann.*, 105, 40.

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