Summary

X-Ray data are reported for natural vaccenic acid, synthetic vaccenic acid and elaidic acid.

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[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STATE UNIVERSITY OF IOWA, IOWA CITY, IOWA]

On the Existence of the Higher Oxides of Neodymium[1]

BY ALEXANDER I. POPOV AND GEO. GLOCKLER

A literature survey showed that the question of the existence of the higher oxides of neodymium still remains unsettled. Earlier workers with the rare earth elements often claimed to have obtained NdO_2 and Nd_2O_5 either by heating the sesquioxide in air[2] or by heating the oxalate in oxygen.[3,4] Mark[5] claimed to have obtained excess of combined oxygen in a didymium–cerium mixture, which he attributed to the formation of neodymium "superoxide." Waegner[3] and Popovici[6] both claimed to have obtained Nd_2O_5 by fusion of the oxalate or the trifluoride with ammonium nitrate.

On the other hand Marsh[7] in 1946 repeated the work of Mark and failed to obtain any evidence for the formation of the higher oxides of neodymium. He also postulated that Waegner's and Brauner's results were due to the unusual stability of the basic neodymium oxide NdO(OH). This compound was first prepared by Joye and Garnier[8] in 1912 and seems to have the same reflection spectrum as Waegner's "superoxide." Pagel and Brinton[9] in 1929 attempted to oxidize the sesquioxide of neodymium by heating it to 350° with oxygen under 215-lb. pressure but found no evidence of oxidation.

Experimental Results

In an attempt to clarify this question the work of the earlier investigators was repeated. It was found that heating the sesquioxide in a current of oxygen at temperatures varying between 500 and 1000° did not result in any oxidation of the compound.

It was next decided to try the combustion of neodymium oxalate in a current of oxygen. The oxalate was obtained by precipitation of an acidified neodymium nitrate solution with oxalic acid and drying the precipitate at 120°. Weighed portions of the oxalate, in a porcelain boat, were introduced into an electrical combustion furnace. Dried commercial oxygen was passed while the furnace was progressively brought to the desired temperature. The period of heating was varied from one to two and a half hours. The resulting oxide was cooled in a current of dry nitrogen, weighed and dissolved in an acid potassium iodide solution. Liberated iodine was titrated with a standard sodium thiosulfate solution and the percentage of "active" oxygen calculated.

Seven experiments were made at 550, 700 and 950°. The average amount of "active" oxygen found in the product was 0.1%. No significant variation of this figure with temperature was observed. The active oxygen percentage in NdO_2 should be 4.54. The small amount of "active" oxygen found is probably due to traces of praseodymium, because the present sample of neodymium oxide was faintly grayish in color in comparison with a small sample of very pure neodymium oxide which originated in Professor Rolla's laboratory in Florence and which was at our disposal.

Neodymium oxalate which was heated to 550° was reintroduced into the combustion tube after being weighed and was heated again to 1000°. A tared drying tube was attached to the system and again a current of dry oxygen was passed. After heating the sample for one hour the boat was withdrawn and the weight of the drying tube redetermined. A blank was also run and gave negative results within the limits of experimental error (Table I).

TABLE I

DEHYDRATION OF BASIC NEODYMIUM OXIDE

	Sample, g.	Water obtained, mg.	Water calcd., mg.
Expt. 1	0.2412	13.0	12.2
Expt. 2	.2099	10.7	10.6
Expt. 3	.3714	19.0	18.9

It thus seems that the supposition of Marsh is correct and that by heating hydrated neodymium oxalate to 550° the basic oxide of the element is formed, which subsequently decomposes in the neighborhood of 1000° to the sesquioxide and water.

The fusion of neodymium oxalate, sesquioxide or the trifluoride with ammonium nitrate also failed to give any higher oxides.

As the fusion of praseodymium oxide with sodium chlorate yields praseodymium dioxide,[10]

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[1] From a thesis presented by Alexander I. Popov to the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] F. R. M. Hitchcock, THIS JOURNAL, **17**, 483 (1895).

[3] A. Waegner, *Z. anorg. allgem. Chem.*, **42**, 118 (1904).

[4] B. Brauner, *Coll. Czechoslov. Chem. Commun.*, **5**, 279 (1932).

[5] R. Mark, *Ber.*, **35**, 2370 (1902).

[6] J. Popovici, *ibid.*, **41**, 634 (1908).

[7] J. K. Marsh, *J. Chem. Soc.*, 20 (1946).

[8] P. Joye and C. Garnier, *Compt. rend.*, **154**, 510 (1912).

[9] H. A. Pagel and Paul H. Brinton, THIS JOURNAL, **51**, 42 (1929).

[10] W. Prandtl and K. Huttner, *Z. anorg. allgem. Chem.*, **149**, 235 (1925).

this method was tried for the oxidation of neodymium. Weighed portions of the sesquioxide were mixed intimately with about 20 times their weight of C. P. sodium chlorate and the mixture was fused for various lengths of time (thirty minutes to six hours and thirty minutes) at 250–300°. The melt was extracted with hot water, washed, dried and dissolved in acid potassium iodide solution. In all cases only traces of iodine were liberated.

Conclusions

The results obtained seem to indicate that the earlier reports of the existence of the higher oxides of neodymium were due to the use of impure compounds or to the mistaken identity of the basic oxide. It seems reasonable to conclude that the trivalent state of neodymium is the highest oxidation state of the element observed up to the present time.

Summary

1. A product claimed to be neodymium dioxide was identified as basic neodymium oxide NdO(OH).

2. The trivalent state of neodymium is the highest oxidation state observed so far.

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Heat Capacities at Low Temperatures and Entropies of Magnesium and Calcium Fluorides

BY S. S. TODD[1]

In an earlier paper[2] from this Laboratory, heat content and entropy-increment data were reported for magnesium and calcium fluorides, in the temperature range 298.16 to 1800°K. The present paper is a low-temperature calorimetric study of these compounds from 52 to 298°K. Throughout this temperature range, heat capacities of magnesium fluoride and calcium fluoride were obtained at regular intervals, and from the data their entropies were calculated. No previous similar data exist for magnesium fluoride. Eucken and Schwers[3] have investigated the heat capacity of calcium fluoride from 17 to 86°K. and Koref[4] has made two mean specific heat measurements at 136.4 and 236.5°K. However, from these data an entropy value[5] for calcium fluoride at 298.16°K. was derived which had an uncertainty of about 2.5%.

Materials

The magnesium fluoride used in these measurements was part of the material prepared for the heat content study of this substance by Naylor.[2] His method of preparation and analysis are repeated here. Baker C. P. Analyzed magnesium oxide, containing less than 0.3% Ca and 0.5% SO_4, was treated with hot 48% HF for sixteen hours and then dried at 400°. Analysis for magnesium by conversion to sulfate and weighing as magnesium sulfate gave 38.97% Mg (theoretical 39.02%).

The calcium fluoride sample was some large natural fluorite crystals, having a very faint purple color, which were coarsely ground in a diamond mortar and the iron removed with a magnet. Since Naylor[2] employed some of the same batch of fluorite, his analysis is given here. The ground fluorite when successively treated with hydrochloric and sulfuric acids and weighed as $CaSO_4$, gave 51.27% Ca (theoretical 51.33%).

Heat Capacities

The method and apparatus used in the heat capacity measurements have been described in

TABLE I

MOLAL HEAT CAPACITIES

T, °K.	C_p, cal./deg.	T, °K.	C_p, cal./deg.	T, °K.	C_p, cal./deg.
MgF_2 (mol. wt., 62.32)					
54.22	1.577	114.54	6.380	216.7	12.37
58.05	1.836	124.76	7.169	226.4	12.74
62.12	2.131	135.83	8.007	236.2	13.06
66.64	2.467	146.10	8.707	246.1	13.38
71.12	2.818	155.72	9.339	256.2	13.73
75.72	3.188	166.02	9.951	266.3	13.98
80.20	3.552	176.0	10.51	276.2	14.23
83.62	3.852	186.0	11.02	286.5	14.47
94.70	4.754	196.0	11.49	296.5	14.67
104.30	5.547	206.3	11.94	(298.16)	(14.72)
CaF_2 (mol. wt., 78.08)					
53.51	1.908	114.43	8.266	216.4	14.19
57.55	2.309	124.37	9.146	226.2	14.49
62.04	2.758	135.5	10.06	236.4	14.80
66.74	3.253	146.0	10.80	245.8	15.04
71.40	3.763	155.6	11.42	256.3	15.29
76.25	4.300	165.9	12.03	266.0	15.50
80.43	4.758	175.7	12.56	276.0	15.68
85.32	5.295	186.0	13.04	286.4	15.84
95.04	6.336	195.9	13.42	296.5	16.00
104.51	7.313	206.2	13.82	(298.16)	(16.02)

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[1] Chemist, Pacific Experiment Station, Bureau of Mines. Article not copyrighted.

[2] B. F. Naylor, THIS JOURNAL, **67**, 150 (1945).

[3] A. Eucken and F. Schwers, *Ber. deut. physik. Ges.*, **15**, 578 (1913).

[4] F. Koref, *Ann. physik*, **36**, 49 (1911).

[5] K. K. Kelley, U. S. Bur. Mines Bull. 434 (1941).