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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[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

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)

(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).

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detail by Kelley, Naylor and Shomate.[6] The conventional thermochemical calorie[7] (1 cal. = 4.1833 int. joules) is used throughout, and the ice-point is taken as 273.16°K. The calorimeter contained 102.01 g. and 252.02 g. *in vacuo* of magnesium and calcium fluorides, respectively.

All the experimental results are listed in Table I and shown graphically in Fig. 1.

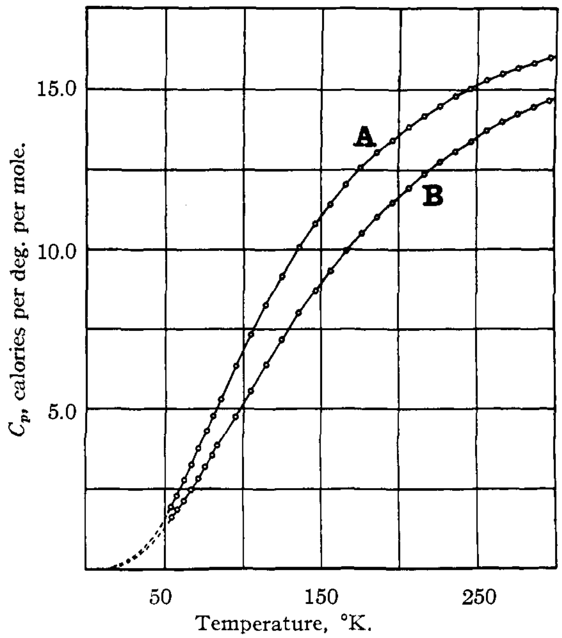

Fig. 1.—Heat capacities: A, CaF_2; B, MgF_2.

Also in Table I are extrapolated values of the heat capacity of each fluoride at 298.16°K. The molecular weights in Table I are taken from the 1947 table of international atomic weights.[8]

The heat capacity results are believed accurate on the average to within ±0.3% in the absolute sense and have a precision error under 0.1%. The early heat capacity measurements of Eucken and Schwers[3] on calcium fluoride from 17 to 86°K. have considerably less precision than the present work. In the overlapping temperature range, 53 to 86°K., their results run progressively higher than present values by amounts ranging from zero to 3%. At lower temperatures their values are below any reasonable extrapolation of the present results.

Entropies

The measured heat capacities were plotted against log T and the entropy increments between 51.00 and 298.16°K. (measured portion, Table II) were calculated by numerical integration. The entropy increments between 0 and 51.00°K. (extrapolated portion Table II) were obtained from the following combinations of Debye and Einstein functions fitted to all of the heat capacity results,[5] the average deviation between function sums and measurements being shown in parentheses.

$$MgF_2:\quad D\left(\frac{326}{T}\right) + 2E\left(\frac{553}{T}\right) \quad (1.0\%)$$

$$CaF_2:\quad D\left(\frac{308}{T}\right) + 2E\left(\frac{435}{T}\right) \quad (1.3\%)$$

Table II

Molal Entropies, Cal./Deg.

	MgF_2	CaF_2
0–51.00°K. (extrap.)	0.54	0.64
51.00–298.16°K. (meas.)	13.14	15.82
$S^\circ_{298.16}$	13.68 ± 0.07	16.46 ± 0.08

The extrapolated entropy values, 0.54 for magnesium fluoride and 0.64 for calcium fluoride, constitute less than 4% of their entropies at 298.16°K. as given in Table II. The previously accepted entropy value,[5] 16.4 ± 0.4 at 298.1°K., for calcium fluoride has not been changed materially by the present work but its uncertainty has been reduced sharply in magnitude.

Summary

The heat capacities of magnesium fluoride and calcium fluoride have been measured throughout the temperature range 52 to 298°K.

Their entropies at 298.16°K. have been calculated to be 13.68 ± 0.07 and 16.46 ± 0.08 cal./deg./mole, respectively.

Berkeley, California Received August 3, 1949

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(8) G. P. Baxter, M. Guichard and R. Whytlaw-Gray, This Journal, **69**, 731 (1947).