TABLE I

Run	A	B	C
Duration, hr.	1.0 ± 0.2	12.0 ± 0.2	76.0 ± 0.5
Temp. range, °C.	25 ± 2	21 ± 2	20–215
Hydrogen chloride partial pressure, mm.	87 ± 1	198 ± 2	123–213
Aluminum chloride partial pressure, mm.	0	0	0–162
Initial specific activ. of HCl gas, counts/min. mole	508 ± 15	508 ± 15	521 ± 8
Final specific activ. of HCl gas, counts/min. mole	500 ± 15	505 ± 7	86 ± 4
Decrease in sp. activ. of HCl gas, %	<exptl. error	<exptl. error	84 ± 4

plete exchange. This fact points to the possible existence of $HAlCl_4$ but it does not prove its existence, since there are other conceivable paths for exchange.

Taken as a whole, the findings of this research present the following picture in regard to compound-formation in the system studied. At lower temperatures there is absolutely no evidence of chemical reaction. This follows from the absence of pressure plateaus concerning phase equilibria measurements and no decrease in specific activity of the gas during exchange runs at room temperature. But at higher temperatures, creating the all-vapor system and allowing for a slight dissociation of the gaseous aluminum chloride dimer, the extent of interaction is so small that it is questionable. This follows from the small departure from ideality observed during *P–V–T* investigation and the complete exchange observed for the only exchange run involving elevated temperatures.

Acknowledgments.—Courtesies have been extended by Dr. A. B. Burg, Dr. K. J. Mysels, Dr. A. W. Adamson and especially the Filtrol Corporation. Valuable contribution has been made by the late Kenneth P. Warren, who constructed the high temperature oven, and Mr. J. K. Fogo.

VERNON, CALIF. RECEIVED AUGUST 24, 1950

[CONTRIBUTION FROM THE SCHOOL OF CHEMICAL ENGINEERING, GEORGIA INSTITUTE OF TECHNOLOGY]

The Heat Content, Specific Heat and Entropy of La_2O_3, Pr_6O_{11} and Nd_2O_3 Between 30 and 900°[1,2]

BY J. O. BLOMEKE[3] AND W. T. ZIEGLER

The heat contents of La_2O_3, Pr_6O_{11} and Nd_2O_3 have been measured from 30 to 900° using a copper aneroid calorimeter. Equations expressing the heat content, heat capacity and entropy of each of the rare earth oxides have been derived from the observed heat contents. As a means of testing the operational characteristics of the calorimeter, the heat content of a standard sample of α-Al_2O_3 was measured and found to compare favorably with values reported by other investigators.

Introduction

The rare earth elements and their compounds are a group of substances for which relatively few heat capacity data are available. This is due, in large measure, to the difficulty involved in separating them from one another in sufficiently pure form to warrant such measurements. Until recently, rare earth separations were most often carried out by the laborious process of fractional crystallization. The crystallization procedure has today been largely superseded by a more rapid, less arduous technique employing ion-exchange resins to effect these separations.[4]

This paper describes high-temperature heat content measurements made on samples of Pr_6O_{11} and Nd_2O_3 purified by means of the ion-exchange method and on a sample of La_2O_3 which was purchased commercially.

The calorimeter used for these measurements was calibrated electrically. Its operational characteristics were checked by measuring the heat content of α-Al_2O_3. The observed heat content for Al_2O_3 is compared with previous measurements from the literature.

Apparatus.—The calorimeter used for these measurements was patterned after one described by Southard.[5] This type of calorimeter consists of two main parts: a furnace in which the sample whose heat capacity is to be measured is brought to a constant temperature, and a calibrated copper block into which the sample is then dropped. From the temperature rise of the block and certain corrections characteristic of the particular arrangement used, the change in heat content of the substance can be obtained.

The winding of the present furnace was made of Nichrome V resistance wire. This winding limited the calorimeter to measurements below 1000°.

The capsule containing the sample was a 2.1 cm. × 2.1 cm. cylinder made of 0.2 mm. 90% platinum–10% rhodium alloy. The capsule had a tubular neck. Closure was made by sealing on a cap with fused gold.

The temperature of the capsule in the furnace was determined with a single-junction platinum, platinum–10% rhodium thermocouple, the junction of which was located just above but out of contact with the capsule. The thermocouple had recently been calibrated by the National Bureau of Standards. All e.m.f. measurements were made with a Leeds and Northrup Type K-2 potentiometer. Corrections to the observed e.m.f. readings of this thermocouple were applied on the basis of experiments carried out in which a second such thermocouple, placed inside an empty capsule suspended in the furnace, was compared with the measuring thermocouple at a number of furnace temperatures between

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[1] From a dissertation submitted by J. O. Blomeke to the Graduate Division of the Georgia Institute of Technology in partial fulfillment of the requirements for the Ph.D. degree (1950).

[2] Presented before the Physical and Inorganic Section of the Southwide Chemical Conference, Atlanta, Georgia, Oct. 16–18, 1950.

[3] Oak Ridge National Laboratory, Oak Ridge, Tennessee.

[4] Symposium: "The Separation of Rare Earth, Fission Product and Other Metal Ions and Anions by Adsorption on Ion-Exchange Resins," THIS JOURNAL, **69**, 2769 (1947).

[5] J. C. Southard, THIS JOURNAL, **63**, 3142 (1941).

100 and 900°. It is believed that, after applying the appropriate correction, the true temperature of the capsule in the furnace was known to 1°.

The calorimeter proper was a gold-plated, cylindrical copper block, 4 inches in diameter by 7.5 inches high, supported by three bakelite cones in a gold-plated brass case. The case was immersed in a water-bath maintained at 30.00 ± 0.02°. The temperature of the block was determined with a 100-ohm copper resistance thermometer wound on the outside of the block and covering about half its lateral surface. The resistance of this thermometer was measured with a Leeds and Northrup Model G-2 Mueller Bridge which had recently been calibrated by the National Bureau of Standards. The block thermometer was calibrated experimentally over the range 0 to 40° and had a temperature coefficient of resistance of about 0.4 ohm per degree at 35°.

The block was calibrated electrically in defined calories (1 calorie = 4.1833 int. joules) required to raise the resistance of the copper thermometer one ohm. The energy input during calibration was measured with a Leeds and Northrup Type K-2 potentiometer. The e.m.f. of the potentiometer standard cell was checked daily during the experiments by comparison with two standard cells recently calibrated by the National Bureau of Standards and used only for reference. The time of electrical input (approximately 600 sec. in each calibration run) was measured with a 110-volt, 60-cycle timer whose performance had been checked to within 0.03% by comparison with signals broadcast by National Bureau of Standards radio station WWV. The indicated time of heating was corrected for deviations in the current frequency from 60 cycles during each calibration. The mean deviation for a set of 19 determinations of the block thermometer calibration energy relationship was 0.08%.

The thermal leakage modulus, *K*, was a variable for this calorimeter, being dependent on the difference in temperature between the block and case, or thermal head. The value of *K* varied from 0.0010 min.$^{-1}$ for thermal heads near zero to 0.0028 min.$^{-1}$ for a thermal head of 10°. This variation in *K* was taken into account when computing the heat loss correction for each heat content determination.

The heat contents above 30° of the samples at each temperature were found by subtracting from the apparent heat content of the full capsule that of the empty capsule as determined from a drop made with the empty capsule at the same temperature. This calculation involved the usual assumption[5] that the loss of heat from the full capsule is the same as for the empty during the short time required for it to fall from the furnace to the calorimeter.

Materials. La_2O_3.—The La_2O_3 used in this work was obtained from Adam Hilger, Ltd., London, England, and was stated by them to be at least 99.7% pure. It was a finely divided powder. Neodymium was the only significant impurity reported by the vendor to have been found by spectrographic analysis.

Pr_6O_{11} and Nd_2O_3.—The Pr_6O_{11} and Nd_2O_3 were samples which had been prepared previously in the Georgia Tech Low Temperature Laboratory from impure concentrates purchased from the Lindsay Light and Chemical Company.

These oxides, in the form of rather fine powders, were prepared by the ignition of the pure oxalates in a muffle furnace for at least eight hours at 850°. It has been rather definitely established that the stable form of praseodymium oxide obtained under these conditions has the formula Pr_6O_{11}.[6] The purifications had been performed using the ion-exchange properties of the synthetic resin Dowex-50 and 5% citric acid solutions in much the same manner as described by Harris and Tompkins.[7]

Spectrographic analyses made using the copper spark method[8] revealed the probable presence of less than 0.2% La_2O_3 in the Pr_6O_{11} and Nd_2O_3. No spectrographic evidence for the presence of Sm, Nd, Pr and Ce as impurities was found. However, control experiments indicated that these elements could not be detected as impurities in amounts less than several tenths of 1%, because of interference between the principal lines of these elements and the principal rare earth constituent. However, from a careful consideration of the particular ion exchange purifications used for these samples, it is believed that both oxides were at least 99.5% pure, the major impurities in the Pr_6O_{11} being La, Nd, Ce and Ca and in the Nd_2O_3, Sm and Pr.

After a capsule had been filled with a given rare earth oxide it was heated overnight in a muffle furnace at 850° to decompose any hydroxide or carbonate which might have formed and then sealed under helium.

Al_2O_3.—A sample of α-Al_2O_3 (corundum) was obtained from the National Bureau of Standards. This sample was made available under a program set up to supply calorimetric standards to aid in the comparison of calorimeters.[9] The sample was in the form of particles, 2–4 mm. in diameter, and it is believed that this Al_2O_3 contained less than 0.03% total impurities.

Results

The sample of Al_2O_3 used in these measurements was presumably identical with one used by Ginnings and Corruccini[10] who reported the heat content over the range 0 to 900° with an accuracy of 0.2%.

TABLE I

THE HEAT CONTENT OF Al_2O_3 AT TEMPERATURES ABOVE 30°

FORMULA WT. = 101.94

T, °K.	$H_T - H_{303.2}$, cal./mole	Deviation from Eq. (1), %
383.7	1689	0.41
473.9	3820	.63
574.1	6410	.00
699.9	9843	− .35
852.2	14,150	− .28
997.0	18,350	.00
1099.2	21,420	.00
1171.9	23,610	.13

The observed values of the heat content of Al_2O_3 in calories per gram mole above 303.2°K. (30°C.) are given in Table I. These values are means of from 2 to 4 determinations made at each of the indicated temperatures. The weight of the sample used was 13.821 g., *in vacuo*. The precision of the calorimeter was 0.1% to 0.2% except in the neighborhood of 383°K. where it was about 0.4%. The following heat content equation was derived to fit the experimental data using the value of 19.15 cal./g.-mole/deg. given by Ginnings and Corruccini for the heat capacity of Al_2O_3 at 303.2°K. and the observed heat contents at 574.1 and 1099.2° K.

$$H_T - H_{303.2} = 26.12T + 0.002194T^2 + 762{,}900/T - 10{,}637 \quad (1)$$

The deviation of Eq. (1) from experimental data is shown in Table I.

Figure 1 is a plot of the results shown in Table I together with the Al_2O_3 measurements of Ginnings and Corruccini, Shomate and Naylor,[11] and Egan, Wakefield and Elmore,[12] all corrected to a common base temperature of 303.2°K. In Fig. 1, the mean heat capacities between 303.2°K. and *T*, °K. are plotted against the terminal temperature, *T*. It can be seen from Fig. 1 that the results of this investigation tend to be higher than those of Ginnings and Corruccini at temperatures below 700°K. while they are lower at temperatures above 700°K.

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[6] J. D. McCullough, THIS JOURNAL, **72**, 1386 (1950).

[7] D. H. Harris and E. R. Tompkins, *ibid.*, **69**, 2792 (1947).

[8] M. Fred, N. H. Nachtrieb and F. S. Tomkins, *J. Optical Soc. Am.*, **37**, 279 (1949).

[9] *Chem. Eng. News*, **27**, 2772 (1949).

[10] D. C. Ginnings and R. J. Corruccini, *J. Research Natl. Bur. Standards*, **38**, 593 (1947).

[11] C. H. Shomate and B. F. Naylor, THIS JOURNAL, **67**, 72 (1945).

[12] E. P. Egan, Jr., Z. T. Wakefield and K. L. Elmore, *ibid.*, **72**, 2418 (1950).

The average deviation is 0.35%. Recent measurements of the NBS standard Al_2O_3 made at the Bureau of Standards[13] are in agreement with these measurements to within 0.2% at all temperatures below 700°K. but are as much as 0.5% higher at temperatures above 700°K. The average deviation from the new Bureau of Standards measurements is 0.25%. No satisfactory explanation for this difference at the higher temperatures has been devised. It is suspected that the difficulty may arise from a difference in the convective heat losses of the full and empty capsule.

The results of Shomate and Naylor and Egan, *et al.*, all lie within 1% of the present investigation.

The heat contents found for La_2O_3, Pr_6O_{11} and Nd_2O_3 are presented in Table II. The weights, *in vacuo*, of these samples were 8.489, 11.072 and 12.879 g., respectively. No phase transitions or other sharp changes in the heat capacities of these three oxides were indicated over the range of temperature studied. On the other hand, as will be discussed later, the rather large difference between the heat contents of La_2O_3 and Nd_2O_3 at higher temperatures does suggest the presence of an electronic transition within the Nd^{+++} ion.

TABLE II

HEAT CONTENTS ABOVE 30°

T, °K.	$H_T - H_{303.2}$, cal./mole	Deviation from Eq., %
	La_2O_3 (formula wt. 325.84)	
383.7	2193	0.46
473.9	4742	.00
574.1	7643	.42
699.9	11,450	.00
852.2	16,150	− .19
997.0	20,660	.00
1099.2	23,910	.00
1171.9	26,290	− .19
	Pr_6O_{11} (formula wt. 1021.52)	
383.7	7751	0.00
473.9	17,010	− .65
574.1	27,480	.00
699.9	41,270	.00
852.2	58,520	.21
997.0	76,040	− .33
1099.2	88,250	.00
1171.9	96,960	.33
	Nd_2O_3 (formula wt. 336.54)	
383.7	2206	0.09
473.9	4837	.00
574.1	7873	.20
699.9	11,870	.00
852.2	16,820	.24
997.0	21,770	− .05
1099.2	25,300	.00
1171.9	27,810	.18

Heat content equations were derived to fit the data using the observed values of the heat content at three temperatures. The deviations of these equations from the data are noted in Table II.

$$La_2O_3(s):\ H_T - H_{303.2} = 28.86T + 0.001538T^2 + 327{,}500/T - 9971 \quad (2)$$

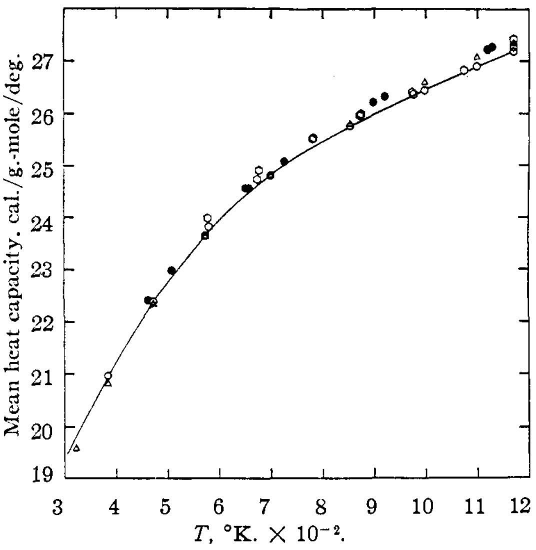

Fig. 1.—Mean heat capacity of Al_2O_3: O, this investigation; △, Ginnings and Corruccini; ●, Shomate and Naylor; ◇, Egan, *et al.*

$$Pr_6O_{11}(s):\ H_T - H_{303.2} = 95.29T + 0.01309T^2 + 930{,}900/T - 33{,}166 \quad (3)$$

$$Nd_2O_3(s):\ H_T - H_{303.2} = 28.99T + 0.002880T^2 + 415{,}900/T - 10{,}427 \quad (4)$$

Equation (2) was derived using the observed values for the heat content of La_2O_3 at 473.9°, 699.9° and 1099.2°K.

Equation (3) was derived using the observed values for the heat content of Pr_6O_{11} at 383.7°, 699.9° and 1099.2°K.

Equation (4) was derived using the observed values for the heat content of Nd_2O_3 at 473.9°, 699.9° and 1099.2°K.

Differentiation of the above heat content equations gave the following heat capacity relationships:

$$La_2O_3(s):\ C_p = 28.86 + 0.003076T - 327{,}500/T^2 \quad (5)$$

$$Pr_6O_{11}(s):\ C_p = 95.29 + 0.02618T - 930{,}900/T^2 \quad (6)$$

$$Nd_2O_3(s):\ C_p = 28.99 + 0.005760T - 415{,}900/T^2 \quad (7)$$

Using Eq. (5), (6) and (7) and the relationship

$$dS = (C_p/T)\,dT$$

the following equations were calculated expressing the entropy above 303.2°K:

$$La_2O_3(s):\ S_T - S_{303.2} = 66.46 \log T + 0.003076T + 163{,}800/T^2 - 167.6 \quad (8)$$

$$Pr_6O_{11}(s):\ S_T - S_{303.2} = 219.5 \log T + 0.02618T + 465{,}500/T^2 - 543.9 \quad (9)$$

$$Nd_2O_3(s):\ S_T - S_{303.2} = 66.76 \log T + 0.005760T + 208{,}000/T^2 - 169.7 \quad (10)$$

Discussion

The mean specific heat of La_2O_3 at 50° constitutes the only heat capacity data found in the literature for the three rare earth oxides studied. Using an ice calorimeter, Nilson and Pettersson[14] found the mean molecular heat capacity between 0 and 100° to be 24.42 cal./g.-mole/deg. The value of the mean heat capacity between 30 and 70° as calculated from Eq. (2) is 26.73 cal./g.

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[13] D. C. Ginnings, personal communication.

[14] L. F. Nilson and O. Pettersson, *Ber*, **13**, 1459 (1880).

mole/deg., or 8.6% higher than the value of Nilson and Pettersson. It is not possible to explain this deviation in the light of the little which is known of the experimental procedure and history of the sample used by Nilson and Pettersson.

Examination of the results reveals that the heat capacity of Nd_2O_3, while about equal to that of La_2O_3 at room temperature, lies well above that of La_2O_3 at higher temperatures. In view of the similarity in crystal structure and ionic character of these two oxides,[15] it seems likely that the contribution to the heat capacity arising from the lattice is probably very nearly the same for both oxides—that is, the Debye θ's for the two oxides are nearly equal. Furthermore, the contribution $(C_p - C_v)$ may be expected to be small and approximately equal throughout the temperature range under consideration. It seems reasonable, therefore, to assume that the difference between the heat capacities of Nd_2O_3 and La_2O_3 is to be ascribed to an electronic transition (or transitions) within the Nd^{+++} ion.

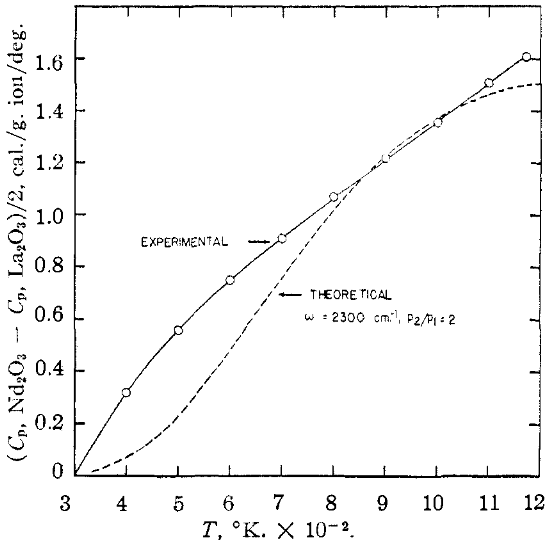

Fig. 2.—Difference in heat capacity of Nd_2O_3 and La_2O_3.

Figure 2 is a plot of the difference in C_p of La_2O_3 and Nd_2O_3, expressed per gram ion of metal ion. The spectroscopic terms for the Nd^{+++} appear not to have been worked out. However, calculations show that this heat capacity difference may be approximated by assuming an electronic transition between two states having an energy separation of about 2300 cm.$^{-1}$, the degeneracies of the states having a ratio $p_2/p_1 = 2$. The calculations can be made to fit the difference curve somewhat better at lower temperatures if lower energy states such as have been shown to be present in $Nd_2(SO_4)_3 \cdot 8H_2O$[16] are taken into account.

Acknowledgment.—The authors wish to express their appreciation to Dr. W. M. Spicer for performing the spectrographic analyses; to Mr. J. T. Roberts, Jr., for aid in the electrical calibration; and to Mr. G. W. D. Cook for his help and suggestions relating to the construction of the calorimeter. One of us (J. O. B.) wishes to acknowledge the assistance provided by a Tennessee Eastman Corporation fellowship.

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[15] V. H. Bommer, *Z. anorg. allgem. Chem.*, **241**, 273 (1939).

[16] J. E. Ahlberg, E. R. Blanchard and W. O. Lundberg, *J. Chem. Phys.*, **5**, 552 (1937).

ATLANTA, GEORGIA RECEIVED APRIL 30, 1951

[CONTRIBUTION FROM THE NAVAL MEDICAL RESEARCH INSTITUTE AND THE MELLON INSTITUTE]

Calculation of Thermodynamic Functions of Adsorbed Molecules from Adsorption Isotherm Measurements: Nitrogen on Graphon[1,2]

BY TERRELL L. HILL, P. H. EMMETT AND L. G. JOYNER

If isotherm measurements are available at neighboring temperatures down to relatively low pressures, it is possible to calculate not only the conventional (isosteric) differential energy and entropy of adsorption but also the integral energy and entropy of adsorption. The latter quantities give the energy and entropy of the adsorbed molecules which are directly comparable with the usual statistical mechanical quantities.

In the present paper the distinction between differential and integral entropies is illustrated and emphasized using the Brunauer, Emmett and Teller theory. The complete set of thermodynamic functions is calculated and discussed for the system nitrogen on graphon, using the data of Joyner and Emmett. The effects of uncertainties in low-pressure measurements on these calculations are pointed out.

In physical adsorption of a gas on a solid it is probably an excellent approximation to assume that the adsorbed molecules do not alter the thermodynamic properties of the solid.[3] It is therefore of interest to attempt to interpret experimental data for systems of this type in terms of the thermodynamic functions of the adsorbed molecules treated as a one-component system in the potential field presented by the solid adsorbent. Thus, one is interested in the energy E_s, entropy S_s, etc., of the system of N_s adsorbed molecules on an adsorbent surface of area $\mathfrak{A}$. These are the thermodynamic functions implicit in statistical mechanical theories of adsorption.

A detailed discussion of the above thermodynamic system has been given in earlier papers.[4-6]

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[1] Some preliminary work on this subject was done by one of us (T. L. H.) while at the University of Rochester, Rochester, N. Y.

[2] Presented at an American Chemical Society Meeting, Boston, Mass., April, 1951; also in part at an A. A. A. S. Gordon Research Conference, New London, New Hampshire, June, 1948, and at the National Colloid Symposium, American Chemical Society, June, 1950.

[3] See, however, the recent paper by M. A. Cook, D. H. Pack and A. G. Oblad, *J. Chem. Phys.*, **19**, 367 (1951).

[4] T. L. Hill, *ibid.*, **17**, 520 (1949). Hereafter referred to as V.

[5] T. L. Hill, *ibid.*, **18**, 246 (1950). Hereafter referred to as IX (see also T. L. Hill, *ibid.*, **17**, 507 (1949)). Among other things, paper IX removes the above restriction to adsorbents which are unperturbed by adsorbed molecules and which have an "area"; but this generalization is probably not important here.[3] Paper IX shows that if adsorbent perturbations are present they are automatically included in thermodynamic calculations of the type carried out in this paper.

[6] T. L. Hill, *Trans. Faraday Soc.*, **47**, 376 (1951).