of an increasing fraction of nonmagnetic Ce^{4+} brought on by thermal contraction.

The effective moment for Yb (Table I) is 0.52 μ_B, much smaller than the value for Yb^{3+} (4.5 μ_B). This moment can be formally regarded as due to a mixture of 34% Yb^{3+} and 66% Yb^{2+} ions.

Behavior in the Region of Magnetic Ordering.—Two aspects of this phase of the work merit comment—the lack of ordering in YbN and CeN and the magnitude of the moment in NdN. As regards the former, the interactions in lanthanide systems are proportional to the de Gennes[22] function $(g - 1)^2J(J + 1)$. Since the ordering temperatures parallel the magnitude of the interactions, the expected Néel or Curie temperatures for CeN and YbN can be estimated from the known ordering temperature of another LnN, *e.g.*, GdN. They are both calculated to be less than 1°K, which accounts for the nonobservance of ordering in these materials in the present work.

The low moment measured for NdN is ascribed to the quenching effect of the crystal field. At 2°K the Nd^{3+} ions are in the doublet ground state. Using the reasoning outlined above the Penney–Schlapp a parameter can be evaluated for ferromagnetic NdN using 2.15 μ_B, the measured moment. a is calculated to be 2.34×10^{-16} erg or 1.17 cm^{-1}. Thus the first excited level is at 76°K and the over-all splitting is 234°K. These are in the same range as the values observed for PrSb and PrBi–59 and 52°K, respectively, for the energy of the first excited level and 226 and 201°K, respectively, for the over-all splitting.

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The Preparation and Some Properties of $Nd_2O_2C_2$[1]

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The results of hydrolysis experiments, X-ray powder diffraction data, and some thermodynamic properties of a phase in the neodymium–oxygen–carbon system of the approximate composition $Nd_2O_2C_2$ are reported.

Introduction

The reported presence of oxygen in uranium dicarbide preparations[3] and reports of a U(O,C) phase[4] establish the existence of ternary carbon–oxygen–metal phases. Since the dicarbide of uranium is structurally similar to those reported for lanthanide elements, such ternary phases are to be expected among the lanthanides. Recently, the probable existence of the phases Y_2C_2O and Sc_2C_2O has been reported.[5,6] This work was undertaken to examine the Nd–O–C system. The preparation and some properties of a ternary phase, $Nd_2O_2C_7$, are reported below.

Experimental Section

Preparation.—Two different preparatory procedures were followed. In the first of these, weighed quantities of calcined 99.9% pure neodymium sesquioxide (Michigan Chemical Co., St. Louis, Mich.) and either Acheson grade No. 38 graphite powder (Fisher Scientific Co.) or crushed spectrographic rods were ground together in the ratio of 1 mole of the sesquioxide to between 3 and 7 moles of graphite. The mixture was pressed into cylindrical pellets 0.6 cm in diameter and 1.4 cm in height at a pressure of about 2500 psi. Two pellets were centered into a previously outgassed graphite reaction crucible which was machined with a snugly fitting lid through which an 0.8-mm diameter hole had been drilled. This hole permitted the escape of gases and provided a line of sight for measurement of the cavity temperature. The crucible assembly sat on a 19 mm high graphite stand, of diameter equal to that of the crucible, supported by three 2.5-mm diameter tungsten or graphite legs. The inductively heated crucible assembly sat on a boron nitride support. A water-cooled Vycor heating tube equipped with an optical window at its top surrounded the crucible and its charge and permitted a pressure of approximately 10^{-5} torr to be attained in the tube. Temperatures were measured with a Leeds and Northrup disappearing-filament type of optical pyrometer calibrated at the National Bureau of Standards. All temperatures have been corrected for optical window (and prism) absorption errors. Since reaction did not proceed below 1350°, the reactants were outgassed by heating the loaded crucible at 1000° until the system exhibited a constant pressure, as measured with a stainless steel absolute-pressure type of Wallace and Tiernan factory-calibrated manometer (Model FA-145). Heating was then suspended and the system was reevacuated. Subsequently, the temperature of the system was elevated quickly to the desired operating temperature where it was maintained for 3.5–5 hr. After the product had cooled, it was removed and examined by X-ray powder diffraction to check for the presence of neodymium sesquioxide. If any was observed, it was removed by reheating the pellets and pumping off some of the carbon monoxide produced as a result of reaction. Usually two such pump-offs were required for a 3-g sample. Each time, the pellet was removed from the crucible and placed quickly into a glove box filled with dried helium.

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[1] Presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

[2] Abstracted in part from the Master's Thesis of G. L. Buchel, submitted to the College of Natural Science of Michigan State University.

[3] C. B. Alcock, H. A. Eick, E. G. Rauh, and R. J. Thorn in "Nuclear Metallurgy," Vol. X, J. T. Waber, P. Chiotti, and W. N. Miner, Ed., Edwards Bros., Ann Arbor, Mich., 1964, p 257.

[4] R. F. Stoops and J. V. Hamme, *J. Am. Ceram. Soc.*, **47**, 59 (1964).

[5] G. V. Samsonov, T. Ya. Kosolapova, M. D. Lyutaya, and G. N. Makarenko, *Redkozem. Elementy Akad. Nauk SSSR, Inst. Geokhim. Analit. Khim.*, 8 (1963).

[6] T. Ya. Kosolapova and G. N. Makarenko, *Redkie i Redkozem. Elementy v Tekhn. Akad. Nauk Ukr. SSR, Inst. Probl. Materialoved.*, 94 (1964); *Chem. Abstr.*, **62**, 8561*c* (1965).

The second procedure utilized the arc-melting technique. Samples were mixed according to the stoichiometries indicated in eq 1–3 and were arc melted under a 1-atm pressure of carbon

$$\mathrm{Nd(s) + Nd_2O_3(s) + 3C(s) \longrightarrow {}^3/_2Nd_2O_2C_2(s)} \qquad (1)$$

$$\mathrm{Nd_2O_3(s) + 3C(s) \longrightarrow Nd_2O_2C_2(s) + CO(g)} \qquad (2)$$

$$\mathrm{Nd_2O_3(s) + NdC_2(s) + C(s) \longrightarrow {}^3/_2Nd_2O_2C_2(s)} \qquad (3)$$

monoxide using a carbon probe as cathode and a water-cooled copper hearth as anode. The phase has also been prepared by melting the metal with the arc in a CO atmosphere. When sesquioxide and graphite were being arc melted, excess carbon monoxide was pumped off slowly so that the pressure did not exceed 1 atm. The samples were transferred to a glove box, crushed, and examined visually for homogeneity. Inhomogeneous samples were remelted.

Equilibrium Pressure Studies.—The equilibrium carbon monoxide pressure was determined in two different assemblies. The first was that described above for the preparatory studies. In this system, a sesquioxide–graphite mixture was heated for 1 hr at 1200° in a pressure equal to or less than 10^{-5} torr. The system was then valved from the diffusion pump and the temperature was elevated to a preselected value. This temperature was maintained until the pressure, as observed on the manometer, remained constant to within the precision of the gauge (48 hr at lower temperatures; 30 min for higher temperatures). The temperature was first elevated sequentially to a maximum value which was chosen for the experiment and which was dictated also by the pressure at which gauge fluctuations became severe (discussed later) and then lowered to check for reproducibility. To check for the establishment of equilibrium, carbon monoxide was pumped off occasionally at a constant temperature. The return of the pressure to within ±0.5 torr of the initial value was interpreted to indicate equilibrium. After the series had been completed, the sample was examined by X-ray powder diffraction to determine the phases present. A composition–temperature ternary phase diagram was not constructed.

The second system consisted of a 100-mm Pyrex pipe into which a water-cooled current concentrator was fitted. This assembly eliminated both heating and cooling problems encountered previously. To ensure uniform temperature, the cell charged with approximately 2 g of a pulverized arc melted NdOC–sesquioxide mixture sat inside an inductively heated larger cell. A common lid connected these cells. Temperatures were measured by sighting through a window (and prism) into the orifice. During some experiments, the temperature was monitored continuously with a Latronics Corp. two-color pyrometer to check for temperature variation. Because of its large volume (*ca.* 2 l.), this system was pressurized with Matheson CP grade carbon monoxide to either slightly above or slightly below the expected equilibrium value. With the cell at a constant temperature, the final value at which the pressure stabilized was noted. Subsequently, carbon monoxide was pumped off (or added) so that the pressure was 3–40 torr below (or above) the value noted previously. If this pressure stabilized within ±0.2 torr of the initial value, equilibrium was considered established. Absolute pressures of less than 40 torr were checked with a mercury U-shaped manometer, the column height difference of which was determined with a Gaertner Scientific Co. Model M-908 cathetometer.

Analysis.—Weighed samples of a pellet which had been pulverized in diamond or agate mortars were hydrolyzed in 1 *N* HCl, digested for 4 hr on a hot plate, and filtered to remove free carbon which was dried subsequently and weighed. The neodymium was precipitated as the oxalate and determined gravimetrically. A different sample was weighed into a quartz boat and burned in a stream of dry oxygen in a tube furnace. The carbon monoxide produced was oxidized to carbon dioxide by cupric oxide and collected in a tower filled with Ascarite. Bound carbon was assumed to be the difference between total carbon and free carbon. Since the determination of the percentage of oxygen depended upon the difference between two rather large numbers, one preparation which exhibited the interplanar *d* spacings of the oxycarbide phase only was analyzed directly for oxygen, nitrogen, and hydrogen by the vacuum-fusion technique in which tared samples wrapped in platinum foil were dropped into a graphite-saturated molten platinum bath. After the volume of the gases liberated by reaction of the weighed sample with the carbon had been determined, the gas mixture was analyzed quantitatively. In addition, samples of the gases liberated initially when the sesquioxide reacted with graphite and gas samples collected from the equilibrium pressure experiments were analyzed mass spectrometrically.

Hydrolysis Experiments.—A sample of the oxycarbide was hydrolyzed in 3 *N* HCl and the gases produced were swept slowly with helium into a U tube suspended in liquid nitrogen. Those gases which condensed were analyzed using an F & M Scientific Corp. flame-ionization gas chromatograph (Model 609) which had been standardized with ethane, ethene, and acetylene.

X-Ray Powder Diffraction and Infrared Analyses.—The oxycarbide phase was examined by X-ray powder diffraction with copper Kα radiation ($\lambda_{\alpha_{\mathrm{u}}}$ 1.5418 A) using 114.59-mm Debye–Scherrer powder cameras. An infrared spectrum was obtained on a Unicam SP 200 spectrometer using the KBr pellet technique.

Results

The vacuum-fusion analyses indicated that only oxygen was present in the sample—neither nitrogen nor hydrogen was found. Similarly, the gases liberated when the sesquioxide reacted with graphite were found by the mass spectrometer to consist of greater than 99% carbon monoxide, with 0.3% H_2, 0.1% N_2, and traces of other unidentified species.

The percentages determined from 20 analyses performed on seven different sesquioxide–graphite preparations are as follows: Nd, 82.9 ± 1.0; C, 6.3 ± 0.9; O, 10.8 ± 1.1 (difference), 8.43 ± 0.21 (fusion). This carbon content was considered a minimum value since the sample was always exposed briefly to air. These data are reasonably consistent with the composition NdOC, for which the calculated percentages are: 83.7% Nd, 7.0% C, and 9.3% O.

The temperature range in which this oxycarbide phase could be prepared in its purest form from Nd_2O_3–C compacts was determined by varying the temperature (and, consequently, the CO pressure) of various preparations and then comparing the X-ray powder diffraction photographs of the products. In the temperature range 1805–1815°, when some CO was pumped off, the oxycarbide phase could be produced free of other phases detectable by X-ray powder diffraction, with the pellet retaining its original shape. At 1865°, with some of the carbon monoxide being pumped off, the pellet started to melt. The hard, melted portion was fractured and found to be slightly yellow—a color characteristic of the dicarbide, whose presence was confirmed by X-ray powder diffraction photographs which indicated its presence in addition to the characteristic NdOC diffraction lines. At 2150°, the dicarbide phase was found in essentially pure form in a solidified melt located at the bottom of the crucible, the walls and bottom of which had several large cavities produced as a result of reaction between the molten oxycarbide and the graphite container. Above the dicarbide was a loose, cindery material which contained large quantities of Nd_2O_3.

The oxycarbide phase could be prepared only in the presence of a partial pressure of carbon monoxide. Attempts to prepare it by heating (either in an evacuated graphite container or in a helium atmosphere in the arc melter) an equimolar mixture of the sesquioxide, dicarbide, and graphite according to eq 1 were unsuccessful. Either the dicarbide or another oxide-carbide phase of a different stoichiometry was obtained. Since the melting point of NdC_2 is in excess of 2000°, the partial melting which was exhibited when the pellet was heated to 1865° seems to indicate eutectic formation and, hence, for this phase, a melting temperature (with decomposition to the dicarbide) in excess of 1875°. It is interesting to note that, even when pelletized mixtures were equilibrated below 1850°, regardless of the over-all composition in the cell, Nd_2O_3 was found on both the interior and exterior walls of the crucible.

The gas chromatograms indicated the condensed hydrolysis product of the oxycarbide was predominantly acetylene, with only traces of ethene and ethane. The relative peak heights (acetylene:ethene:ethane) were 945:8:5. Methane could not be collected in the liquid-nitrogen-cooled condensation flask because of the proximity of the boiling points of the two species.

In the presence of moisture—or even upon exposure to laboratory air—the oxycarbide hydrolyzes rapidly to the sesquioxide. It cannot be kept uncovered in a phosphorus pentoxide dried, helium-filled glove box for more than 1 day without considerable decomposition, but must be kept in a sealed container or under a moisture-free oil.

Table I lists the principal interplanar *d* values of this phase and their relative intensities obtained from two different preparations. Their precision is estimated to be ±0.01 A. A comparison of these values with those exhibited by the known lanthanide sesquioxide structure types—hexagonal, monoclinic, and cubic—indicates some similarity with the monoclinic B modification. Attempts to index these data using the samarium sesquioxide lattice parameters adjusted slightly to correct for the differences in the *d* values and the computer program PR-1 described by Werner[7] were unsuccessful. Although many of the lines could be indexed satisfactorily, a few remained outside the limit of error (±0.0005) allowed in the $\sin^2 \theta$ values obtained by averaging three readings of the same Debye–Scherrer film. Attempts to index the data on an orthorhombic or higher symmetry cell were even less successful. Weissenberg photographs taken of a poor-quality, single-crystal, isostructural LaOC phase indicate the symmetry is probably monoclinic. Thus, we conclude that this crystal structure is of monoclinic or lower symmetry and is probably a distorted M_2O_3 B-type structure. The infrared spectrum does not exhibit any absorption peaks in the carbonyl region, 2000 cm^{-1}.

TABLE I

$Nd_2O_2C_2$ X-RAY POWDER DIFFRACTION DATA

I	*d*, A	*I*	*d*, A	*I*	*d*, A
w	7.04	w	1.859	vvw	1.467
m	3.55	vvw	1.793	vvw	1.452
w, m	3.42	vvw	1.744	vw	1.425
vw	3.36	vw	1.701	w	1.342
vs	3.11	vvw	1.680	vvw	1.322
s	2.968	w	1.655	vvw	1.305
w	2.600	vw	1.623	vw	1.295
m	2.370	vvw	1.607	vw	1.282
m	1.989	vw	1.586	vvw	1.268
m	1.968	w	1.554	m	1.257
w	1.926	w	1.540		
vw	1.890	vw	1.496		

The pressure of carbon monoxide in equilibrium with the solid sesquioxide, graphite, and solid NdOC was measured over the temperature range 1400–1900°. The heat capacity of the oxide carbide phase was assumed to be that of the sesquioxide plus 7.5 cal/deg-mole, the latter figure being three-fourths of the difference between the extrapolated heat capacities[8] of CaO and CaC_2 at 1750°. Combining this datum with heat capacity values listed for Nd_2O_3,[9] C,[10] and CO,[11] ΔC_p was estimated to be −1.7 cal/deg-mole at 1750°. Using 1750° as a reference temperature and assuming ΔC_p to be constant over the temperature range of interest, the function Σ, defined as $\Sigma = R \ln p_{CO} - \Delta C_p(\ln T + 1750/T)$, was graphed against $10^4/T$ (see Figure 1). Series no. 1–3 were made in the first apparatus with a starting mixture of Nd_2O_3 and graphite, while series no. 4–8 were made in the second apparatus with starting mixtures of NdOC and sesquioxide, or only NdOC. A different series number indicates a different specimen. The arc-melted NdOC phase reacted rapidly with CO at temperatures slightly below 1400° and was observed to establish equilibrium up to temperatures at which surface fusion or sintering occurred. All mixtures for which equilibrium could not be confirmed were observed to be either fused or melted. Even though "X-ray powder diffraction pure" NdOC could be prepared from Nd_2O_3 and graphite, Nd_2O_3 could not be prepared by allowing the NdOC phase to react with CO. After a conversion to about 63% sesquioxide had occurred, the specimens failed to establish equilibrium, and further conversion became impossible. One sample which ceased equilibrating was removed from the cell, crushed, and inserted again. New data points were found to reproduce previous values to within the limits of error of the measurement. Data could not be collected above a temperature of 1850° with the NdOC phase as the predominant species since melting always occurred and ruined both the sample and the crucible. When

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(8) K. K. Kelley, U. S. Department of the Interior, Bureau of Mines, Bulletin 584, U. S. Government Printing Office, Washington, D. C., 1960.

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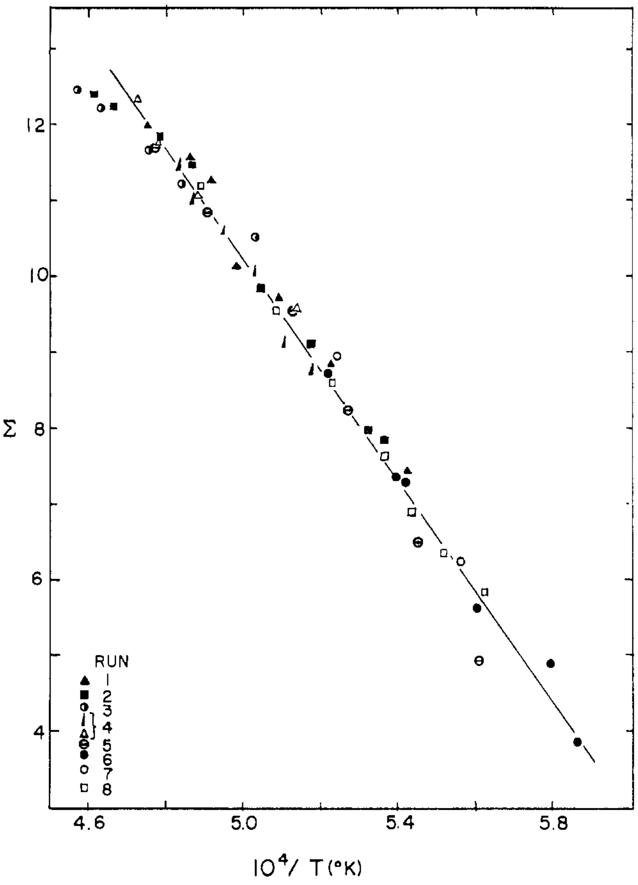

Figure 1.—Graph of Σ ($\Sigma = R \ln p_{CO} - \Delta C_p(\ln T + 1750/T)$) *vs.* $10^4/T$ for the reaction: $Nd_2O_3 + 3C \rightleftharpoons Nd_2O_2C_2 + CO(g)$.

the cell content was primarily sesquioxide (assembly 1), pressure data could be obtained up to temperatures in excess of 2000°. However, additional scatter in these higher temperature data and a break in the log p *vs.* $1/T$ curve at 1850° cause us to think that a different reaction is being studied. Thus, data collected above 1850° are not included in the calculations.

In this higher temperature region, the pressure as recorded on the gauge fluctuated rapidly and erratically about a mean value, the magnitude of the fluctuations increasing with increasing temperature. That these fluctuations were not related to the system being studied but only resulted from convection currents which circulated around the inductively heated crucible was proved by substituting helium for carbon monoxide. The linear least-squares equation which describes the data in the temperature region 1350–1850° is

$$\Sigma = \frac{-(72.7 \pm 1.3) \times 10^3}{T} + (46.60 \pm 0.68)$$

From this equation, the following thermodynamic data are calculated for reaction 2: $\Delta H°_{1750°K} = 72.72 \pm 1.3$ kcal/gfw; $\Delta S°_{1750°K} = 32.2 \pm 4.3$ eu. The standard deviation is reported for the enthalpy, while the entropy includes an estimated error of ±0.5 cal/deg-mole in the heat capacity. This enthalpy may be corrected to 298°K by making use of tabulated heat content and entropy data for the sesquioxide, graphite, and carbon monoxide and by estimating the heat content for the $Nd_2O_2C_2$ to equal that of the sesquioxide plus three-fourths of the difference between heat content values for CaC_2 and CaO. An entropy correction was estimated in a similar manner. From these calculations, $\Delta H°_{298}$ (second law) = 75.9 ± 3.0 kcal/gfw and $\Delta S°_{298} = 33.3 \pm 4.4$ eu. The errors are estimated.

To check this second-law heat, a third-law value was calculated from data compiled from references cited previously for Nd_2O_3, C, and CO and an estimated free energy function of $Nd_2O_2C_2$ (the assumed structural unit). The free energy function of $Nd_2O_2C_2$ was assumed to equal twice the sum of the free energy functions of the three components. The oxygen contribution was assigned a value of 2.2—the average of the free energy function difference between CaO and Ca[12] at various temperatures.

The third-law data are independent of temperature (range 1706–2118°K), and their average value, together with its standard deviation, is 84.46 ± 0.63 kcal/gfw. When the errors associated in the estimation of the values for $Nd_2O_2C_2$ are considered, the agreement between the second- and third-law values is considered satisfactory. For further calculations, the second-law value was assumed to be correct. From these data, $\Delta G°_{298} = 66.0 \pm 3.3$ kcal/gfw. By combining these data with the heat and free energy of formation of $Nd_2O_3(s)$[13] and CO(g),[14] the heat and free energy of formation of $Nd_2O_2C_2(s)$ are calculated to be $\Delta H_f° = -329.8 \pm 3.0$ kcal/gfw and $\Delta G_f° = -309.9 \pm 3.9$ kcal/gfw at 298°K. The errors reported are the accumulated propagated errors resulting from arithmetic manipulation of a fixed value and its standard deviation.

That the pressures recorded were reasonably accurate was confirmed by studying reaction 4, which has been examined previously by both Heusler[15] and Piazza.[16]

$$UO_2(s) + 4C(s) = UC_2(s) + 2CO(g) \qquad (4)$$

For this reaction, we obtained $\Delta G° = 164{,}480 - 76.20T$, while Piazza obtained, over a 300° lower temperature range, $\Delta G° = 164{,}500 - 74.23T$. The data of Heusler and Piazza are essentially in agreement.

Discussion

The gas chromatographic examination of the condensed hydrolysis products indicated that greater than 99% of the gases collected was acetylene. Even though the absence of methane could not be established conclusively, hydrolysis studies of rare earth carbides[17] indicate that, when it is present, higher alkane and alkene homologs are found also since they

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[17] G. J. Palenik and J. G. Warf, *Inorg. Chem.*, **1**, 345 (1962).

result from reduction of the acetylene by the metal. Thus, the absence of these alkanes and alkenes implies not only that the neodymium is present in the +3 oxidation state, as the stoichiometry indicates, but also that the carbon must be present as C_2^{2-} units. Thus, the formula should be written as $Nd_2O_2C_2$ rather than NdOC.

Since C_2^{2-} is in many ways analogous to an oxide ion, it would not be too surprising if this phase results from the replacement of an oxide ion by an acetylide ion. The average carbon–carbon bond distance in the lanthanide dicarbides is 1.285 A[18] (but the anisotropic hole it creates in the lattice is much larger). The radius of an oxide ion in metal oxides is usually about 1.3 A; thus, the substitution of an acetylide unit for an oxide ion seems theoretically possible. The rapidity with which the hydrolysis reaction of carbides proceeds is considered by Bradley and Ferris[19] to be an indication of the ionic character of the metal–carbide bond. Thus, in $Nd_2O_2C_2$, the metal–acetylide bond must be very ionic, further supporting the substitution hypothesis proposed above. The anisotropic character of the acetylide ion would be expected to deform markedly the oxide structure.

The lack of stability of the $Nd_2O_2C_2$ phase in a carbon container at about 1850° and yet its formation in an arc melter at temperatures well in excess of 2000° indicate that the factor limiting the temperatures is eutectic formation with graphite. The severe attack of the graphite container during melting substantiates this postulated eutectic formation. Since the dicarbide is one of the decomposition products, either gaseous NdO or solid Nd_2O_3 or both must be produced. The presence of Nd_2O_3 on the exterior of the cell probably results from the transport of neodymium by way of gaseous NdO, whose existence is well known.[20] Since the gaseous NdO apparently reacts with graphite to form Nd_2O_3 and CO(g), a plausible, though speculative, *over-all* decomposition reaction is

$$7Nd_2O_2C_2(s) = 6NdC_2(s) + 4Nd_2O_3(s) + 2CO(g) \qquad (5)$$

As would be expected, the heat and free energy of formation of this phase are greater than the corresponding values of neodymium sesquioxide, and much less than those of a typical acetylenic carbide, CaC_2.[12]

The X-ray powder diffraction patterns indicate narrow composition limits for this neodymium oxycarbide phase since specimens in equilibrium with the dicarbide, graphite, and carbon monoxide had the same interplanar *d* spacings as those in equilibrium with the sesquioxide, graphite, and carbon monoxide.

This phase is not unique to neodymium but is a phase common to at least all the lighter lanthanide elements. Its distinctly different chemical properties make it an easier species to study than the uranium oxycarbide phases which are difficult to distinguish from the closely related monoxide and monocarbide.

Undoubtedly, other phases exist in these lanthanide–oxygen–carbon systems. Since the pressure of carbon monoxide is quite critical, one would expect that at different CO pressures, different species would be observed.

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