U-rich UN was cooled from the retrograde region, liquid U precipitated rapidly and only a portion was retained within UN grains. Similarly, when Th-rich ThN was quenched from temperatures 1870 to 2000°, liquid Th precipitated rapidly, but precipitation of solid Th was slower and it could be resolved optically only after the specimens were annealed at temperatures 1200 to 1450°. Therefore, in contrast to the experimental results obtained with the UN phase, quantitative microscopic data could be obtained foı the Th-rich ThN phase boundary. The microscopic and the congruent sublimation results are consistent as shown in Figure 1.

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# Ranges of Composition of the $Th_2N_2O$ and $ThO_2$ Phases Equilibrated with Different Nitrogen (Plus Oxygen) Atmospheres[1]

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**Abstract:** The $Th_3N_4$, $Th_2N_2O$, and $ThO_2$ phases were equilibrated with $N_2$ at different pressures and selected temperatures between 1600 and 2000°. An appreciable homogeneity range in the $Th_2N_2O$ and $ThO_2$ phases was revealed by microscopic examination of the cooled products. The compositions of all the phases and phase mixtures were found to be describable by the single formula $ThN_{4/3-(2z/3)}O_z$, where $z$ is the composition variable ranging in value from 0 to 2. Accordingly, the elements in these phases exhibit valences identical with those of the ions $Th^{4+}$, $N^{3-}$, and $O^{2-}$.

Measurements of the electrical conductivity of $ThO_2$[2] and emf measurements with $ThO_2$[3] as an electrolyte indicate that $ThO_2$ is substantially ionic. When $ThO_2$ crystals are doped with lower valent cations, *e.g.*, $La^{3+}$, anion vacancies are formed accompanied by a diminished crystal density[4] and an enhanced electrical conductivity.[2,5] In principle, anion vacancies may also be formed by incorporating higher valent anions such as $N^{3-}$ into the $ThO_2$ anion sublattice. In what follows, some conditions are described under which the oxygen atoms in the $ThO_2$ phase are replaced by nitrogen atoms. As the N:O ratio is increased, the hexagonal $Th_2N_2O$ and, ultimately, the rhombohedral $Th_3N_4$ phases are formed.[6] The existence of an appreciable composition range in the $Th_2N_2O$ and $ThO_2$ phases is established microscopically. Under the experimental conditions, the compositions of the $Th_3N_4$, $Th_2N_2O$, and $ThO_2$ phases and phase mixtures equilibrated under a variety of conditions fall on a plane in the Th–N–O phase diagram, and these compositions conform to those required for ionic valences.

## Experimental Section

**Procedure.** Various mixtures of Th + ThN + $ThO_2$ (3 to 50 mole % Th as $ThO_2$) were made by adding weighed quantities of $ThO_2$ to known amounts of Th + ThN powders that had been prepared by a method previously described.[7] Each mixture was pressed into a 3-g cylinder 6 mm in diameter, sintered *in vacuo*, and allowed to react with $N_2$ at selected pressures (up to 2 atm) and temperatures (800 to 2000°) in a tungsten crucible.

The products were analyzed for Th by ignition of samples to $ThO_2$ in air at 800°. For specimens that contained 25 mole % $ThO_2$ or less, the O:Th ratio of the product was taken to be the same as that of the original mixture; nitrogen was computed by difference. The N:Th ratios obtained in this way were reproducible within ±0.03. Specimens that were prepared from mixtures with more than 25 mole % $ThO_2$ suffered an appreciable loss of oxygen when heated to 2000°. This was evident because of the erosion of the tungsten crucible. Thus, the difference method described above is not a dependable method for computing the oxygen and nitrogen contents of the products with more than 25 mole % $ThO_2$. Additional information on the compositions of products was inferred from microscopic examinations as described below. Lattice parameters were determined from high-angle lines in photographs of X-ray diffraction powder patterns taken with Ni-filtered Cu K$\alpha$ radiation in a camera 115 mm in diameter.

## Results

The mixtures that were heated in the temperature range 800 to 1200° did not equilibrate, and X-ray diffraction powder patterns of samples revealed the presence of complex mixtures of $Th_3N_4$, $ThO_2$, and $Th_2N_2O$ phases in the products. The mixtures that were heated in the temperature range 1550 to 2000° reached equilibrium in the $N_2$ atmosphere within 1 day. Of the equilibrated mixtures, those containing 25 ± 2 mole % $ThO_2$ exhibited powder diffraction patterns of only the hexagonal $Th_2N_2O$ phase with $a_0 = 3.883 \pm 0.001$ and $c_0 = 6.187 \pm 0.002$ A, in agreement with that reported

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[1] This work was done under the auspices of the U. S. Atomic Energy Commission.

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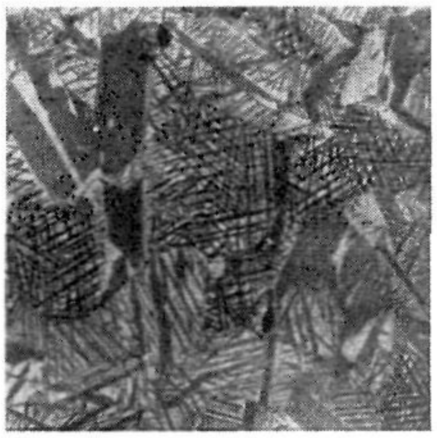

Figure 1. Photomicrograph of a specimen prepared from the mixture Th + ThN + 12 mole % $ThO_2$ by equilibrating 24 hr with 1.91 atm of $N_2$ at 1618°. The bulk composition is $ThN_{1.16}O_{0.24}$. The phases present at temperature were $Th_3N_4$ and nitrogen-rich $Th_2N_2O$. The large homogeneous grains are $Th_3N_4$. The relatively small needles are $Th_3N_4$ that formed by precipitation from $Th_2N_2O$ as the specimen cooled. An X-ray diffraction powder pattern of a sample contained lines corresponding to the hexagonal $Th_2N_2O$ and the rhombohedral $Th_3N_4$ phase (×300).

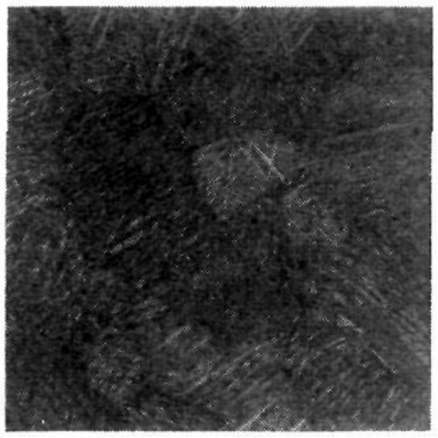

Figure 2. Photomicrograph of a specimen prepared from the mixture Th + ThN + 12 mole % $ThO_2$ by equilibrating 3 hr with 1.91 atm of $N_2$ at 2000°. The bulk composition is the same as that shown in Figure 1, but the large $Th_3N_4$ grains are absent. The needles are $Th_3N_4$ that were formed by segregation from the nitrogen-rich $Th_2N_2O$ phase as it cooled. An X-ray diffraction powder pattern of a sample was indistinguishable from that obtained with the preparation shown in Figure 1 (×300).

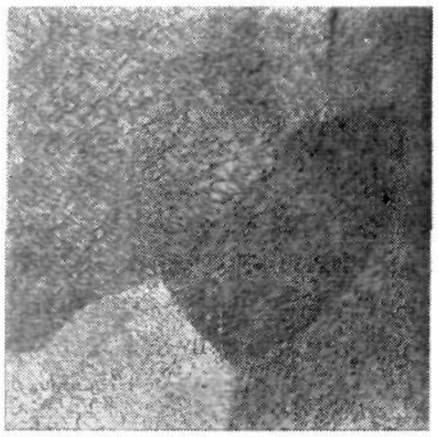

Figure 3. Photomicrograph of a specimen prepared from the mixture Th + ThN + 20 mole % $ThO_2$ by equilibrating 16 hr with 1.61 atm of $N_2$ at 1986°. The bulk composition is $ThN_{1.06}O_{0.40}$. The specimen was single-phase, nitrogen-rich $Th_2N_2O$ at temperature. The dark islands are $Th_3N_4$ particles that precipitated as the specimen cooled. An X-ray diffraction powder pattern of a sample contained lines corresponding to the $Th_2N_2O$ phase and only faint lines corresponding to the $Th_3N_4$ phase (air etched, ×1000).

for pure $Th_2N_2O$.[6] The X-ray diffraction powder patterns of samples taken from the other equilibrated mixtures corresponded to two phases. The phases thus identified were either $Th_3N_4$ (observed cell dimensions, $a_0 = 3.869 \pm 0.001$ and $c_0 = 27.41 \pm 0.03$ A) and $Th_2N_2O$ or $ThO_2$ (observed cell dimension, $a_0 = 5.597 \pm 0.001$ A) and $Th_2N_2O$, depending on whether the initial percentage of $ThO_2$ was less or more than 25, respectively. The stated cell dimensions agree with those reported, respectively, for $Th_3N_4$[6] and $ThO_2$.[8] The weights of the specimens that were prepared from mixtures containing less than 25 mole % $ThO_2$ did not vary perceptibly (less than 0.1%) with changes in $N_2$ pressures in the range 0.05 to 2.0 atm at 1600° or 0.6 to 2.0 atm at 2000°. Some representative results are listed in Table I. At the same temperatures but at lower $N_2$ pressures, the $Th_2N_2O$ phase decomposed to mixtures of ThN and $ThO_2$.

$Th_2N_2O$ grains that had been equilibrated at selected temperatures between 1550 and 2000° and $ThO_2$ grains that had been equilibrated at 2000° were found to be inhomogeneous at room temperatures. The inhomogeneities formed micro patterns that indicated that each specimen had been a homogeneous solid solution at temperature, but that phase segregation had occurred as they were rapidly cooled. These observations are in accord with the absence of an appreciable variation in the room-temperature lattice parameters as reported above; the solid solutions that were formed at elevated temperatures were not retained in the cooled products. By equilibrating a series of different compositions and identifying phases in the products microscopically, the $Th_2N_2O$ phase was found to range in composition from $ThN_{1.22}O_{0.20}$ to $ThN_{1.0}O_{0.5}$ at 1600 ± 40° and from $ThN_{1.28}O_{0.10}$ to $ThN_{1.0}O_{0.5}$ at 2000 ± 48°. No perceptible range of composition was found in the $ThO_2$ phase at 1600°; however, the composition coexisting with $Th_2N_2O$ at the higher temperature (2000°) was found micrographically to be approximately $ThN_{0.1}O_{1.85}$, corresponding to an appreciable nitrogen solubility. No evidence for solubility of oxygen in the $Th_3N_4$ phase was observed.

**Table I.** Analyses of the Mixtures Th + ThN + $ThO_2$ after Equilibration with Different $N_2$ Atmospheres[a]

| Initial Th as $ThO_2$, mole % | Time, hr | $p_{N_2}$, atm | Temp, °C | Product bulk compn | Minor phase | |
|---|---|---|---|---|---|---|
| | | | | | By X-ray | By optical microscopy |
| 5 | 24 | 0.93 | 2000 | $ThN_{1.26}O_{0.10}$ | $Th_3N_4$ | $Th_3N_4$ |
| 12 | 8 | 1.91 | 2000 | $ThN_{1.16}O_{0.24}$ | $Th_3N_4$ | $Th_3N_4$ |
| 22 | 16 | 1.60 | 1986 | $ThN_{1.05}O_{0.44}$ | $Th_3N_4$ | $Th_3N_4$ |
| 25 | 8 | 1.91 | 1790 | $ThN_{0.98}O_{0.50}$ | None | None |
| 40 | 24 | 2.00 | 2000 | $ThN_{0.91}O_{0.63}$[b] | $ThO_2$ | $ThO_2$ |

[a] The chief phase in all the products was $Th_2N_2O$. [b] This formula was computed from the Th content as determined by ignition, the O + N content as computed by difference neglecting the difference between the atomic weights of O and N, and the formula given in the Discussion.

Figure 1 is a photomicrograph of a specimen that consisted of the two phases $Th_3N_4$ + nitrogen-rich $Th_2N_2O$ at 1618°. Figure 2 is a photomicrograph of a specimen with the same bulk composition as that in Figure 1; however, the specimen had been equilibrated in $N_2$ at the higher temperature, 2000° and cooled. The latter specimen was single phase at temperature.

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(8) W. A. Lambertson, M. H. Mueller, and F. H. Gunzel, Jr., *J. Am. Ceram. Soc.*, **36**, 397 (1953); R. J. Ackermann, E. G. Rauh, R. J. Thorn, and M. C. Cannon, *J. Phys. Chem.*, **67**, 762 (1963).

The photomicrograph in Figure 3 shows a specimen consisting of large $Th_2N_2O$ grains containing small (dark) particles, probably $Th_3N_4$, that were formed by precipitation as the specimen cooled. The bulk composition is more nearly that of the formula $Th_2N_2O$ than is that shown in Figure 2, and a corresponding smaller proportion of $Th_3N_4$ precipitate is seen. Specimens prepared from mixtures containing 25 mole % $ThO_2$ were found to have the composition $ThN_{0.99}O_{0.50}$ after being equilibrated 24 hr in 2 atm of $N_2$ at selected temperatures 1700 to 1800°. The specimens were virtually single phase by microscopic examination. No evidence was obtained for the (O + N):Th ratio exceeding 1.5 in the $Th_2N_2O$ phase.

Mixtures with 40 to 50 mole % $ThO_2$ that had been equilibrated at temperature and cooled contained two microscopically distinct regions corresponding to two distinct phases at temperature. The first region was translucent and appeared light orange to yellow in color. It consisted mostly of the $ThO_2$ phase in which needles or platelets of precipitate, probably $Th_2N_2O$ had formed. The second region appeared homogeneous. It had a gray to maroon color, depending on grain size, and consisted of the $Th_2N_2O$ phase. The two coexisting regions are shown in Figure 4.

## Discussion

The above experimental results can be systemized with a simple interpretation. The first four products listed in Table I were single-phase, nitrogen-rich $Th_2N_2O$ at temperatures. Considering these in reversed order, the fourth to the first as listed, which is the order of increasing deviations from the $Th_2N_2O$ composition, the N:Th ratio increases from 0.98 to 1.26, while the anion to cation ratio, *i.e.*, (N + O):Th ratio, decreases from 1.48 to 1.36. Thus, we were led to inquire if the compositions of $Th_2N_2O$ phase may be simulated by replacing $O^{2-}$ with $N^{3-}$ ions on lattice sites and simultaneously creating anion vacancies. Now, neither the $Th_2N_2O$ nor the $Th_3N_4$ phase can be heated directly by electromagnetic induction in eddy-current heaters indicating a low electrical conductivity characteristic of ionic compounds. The unit cell of the stoichiometric $Th_2N_2O$ phase contains two Th atoms, two equivalent nitrogen atoms, and one oxygen atom. Coulombic energy requirements make anion–cation substitutional defects improbable, and changes of composition are tentatively assumed to be describable in terms of the number and kinds of atoms on the anion sites of the $Th_2N_2O$ lattice. The charge neutrality condition demands that two $N^{3-}$ ions and one anion vacancy be substituted for every three $O^{2-}$ ions removed. Accordingly, the chemical compositions of ionic $Th_2N_2O$, $Th_3N_4$, and, in addition, $ThO_2$ are expressible with the single formula $ThN_{4/3-(2z/3)}O_z$ $(0 \leq z \leq 2)$, where $z$ is the composition variable, valid for single-phase regions and two-phase mixtures. When $z$ is allowed to take on the values 2, $^1/_2$, and 0, the respective compositions $ThO_2$, $Th_2N_2O$, and $Th_3N_4$ are obtained. Further, it may be seen that the compositions of the first four products listed in Table I are, indeed, describable with the above formula. These are typical results. The compositions of other products equilibrated at intermediate pressures and temperatures were also found to agree with the above formula within the stated uncertainty of the analyses. Thus, the above formula describes the compositions of all the products that were equilibrated with $N_2$ at pressures sufficiently high that the ThN phase did not exist, and the atoms in the $ThO_2$, $Th_2N_2O$, and $Th_3N_4$ phases exhibit valences identical with those of the corresponding ions $Th^{4+}$, $N^{3-}$, and $O^{2-}$. The solid solutions were observed to segregate rapidly as they were cooled, and this is apparently achieved by exchange of $O^{2-}$ and $N^{3-}$ ions.

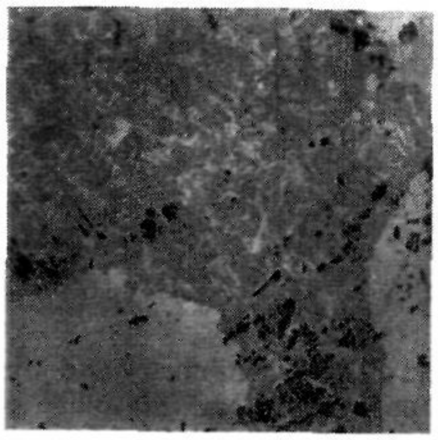

Figure 4. Photomicrograph of the mixture Th + ThN + 40 mole % $ThO_2$ after being equilibrated for 1 hr at 2000° in 1.91 atm of $N_2$. The specimen was visually inhomogeneous and contained two distinct regions: (1) a light orange to yellow region (area of intermediate darkness) which consisted of $ThO_2$ with platelets of precipitate, probably $Th_2N_2O$, and (2) a gray to maroon region that consisted of $Th_2N_2O$. The dark areas are cavities (air etched, ×300).

In contrast to the above results, a nitrogen-deficient $Th_3N_4$ phase (1600 to 2000°) has been reported.[7] Appreciable deviations from the ionic valences are therefore to be expected in the $Th_3N_4$ phase at the nonstoichiometric compositions.

The electrical conductivity of $ThO_2$ in nitrogen-rich $N_2 + O_2$ mixtures at different temperatures (862–1497°) has been reported by Rudolph.[5] According to his results, the conductivity increases with temperature more rapidly for higher $N_2$ pressures (lower $O_2$ pressure). Considering the relatively high $O_2$ pressures involved, 0.1 to 760 torr, it seems possible that the enhanced electrical conductivity in the presence of $N_2$ gas resulted from exchange of $N^{3-}$ ions for $O^{2-}$ ions with formation of anion vacancies which have a relatively high mobility. Thus, the electrical conductivity data of Rudolph suggests that an appreciable extent of nitrogen–oxygen exchange (and range of composition) may occur in the $ThO_2$ phase at temperatures as low as 1200°, which is lower than that observed by us with the less sensitive microscopic method.

**Acknowledgments.** The author thanks M. G. Bowman for discussions.