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METALS AND CERAMICS DIVISION

THORIUM CERAMICS DATA MANUAL

Volume I - Oxides

Sigfred Peterson and C. E. Curtis

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PLAN OF COMPILATION

This Manual when completed should comprise separate volumes on the systems: borides, carbides, nitrides, oxides, phosphides, silicides, sulfides, and possibly others. Separate volumes will be issued when completed. The first completed, *Oxides*, accompanies this explanation. The *Nitrides* volume has been drafted and should appear next. Information is being collected for the other volumes.

Each volume will begin with an introduction that presents information on the overall system. This will be followed by Divisions on the individual compounds in the system. In the *Oxides* volume the only such compound is ThO_2 . The *Nitrides* volume at present includes Divisions on "Thorium Mononitride," " Th_3N_4 ," and " $\text{Th}_2\text{N}_2\text{O}$ and Other Complex Nitrides." The *Carbides* volume will have Divisions on ThC and ThC_2 .

In most cases, each Division will be subdivided into Parts:

- A. The compound
- B. Its binary with the uranium compound
- C. Its binary with the plutonium compound
- D. Binary systems with a common negative element
- E. Ternary and more complex systems with a common negative element
- F, G, etc. Systems with different negative elements

The *Oxides* volume will contain no information on systems with a second negative element; these will be treated in the volume for the other element. Thus Divisions for complex oxides or Parts beyond E will not be found in the *Oxides* volume.

Each Part will be further subdivided, when information warrants, into Sections according to the following property classifications:

1. Composition
2. Preparation
3. Crystal properties
4. Thermodynamic properties
5. Change of state
6. Electrical and magnetic properties
7. Heat and mass transport
8. Mechanical properties
9. Chemical properties
10. Surface properties

The following outline is a general, but not necessarily complete, description of the scope of the Sections.

1. Composition
Range of composition possible for the material
2. Preparation
Preparation of compound or mixture concerned
Fabrication methods for preparation of ceramic bodies (only enough given for interpretation of fabrication-related data)
3. Crystal properties
Structure
Lattice parameter
Density
Thermal expansion
Refractive index
Absorption spectra
4. Thermodynamic properties
Heat capacity, enthalpy, entropy, free energy, heat and free energy of formation

5. Change of state
 - Melting point
 - Boiling point
 - Vapor pressure
 - Heats of vaporization and melting
6. Electrical and magnetic properties
 - Conductivity
 - Dielectric constant
 - Magnetic susceptibility
7. Heat and mass transport
 - Diffusion coefficients
 - Thermal conductivity
 - Emissivities and other radiation properties
8. Mechanical properties
 - Strength, ductility, hardness, elastic constants
9. Chemical properties
 - Reactivity toward gases, liquids, solids; compatibility behavior
10. Surface properties
 - Electrokinetic potentials, wetting behavior, etc.

Each volume will have a separate bibliography, with references numbered approximately in order of first occurrence and not repeated (although references may be repeated in other volumes). When revisions are added, references will be added at the end of the sequence.

Volume I. Oxides

Sigfred Peterson and C. E. Curtis*

ABSTRACT

Physical, chemical, and mechanical properties of thorium oxide, alone and in combination with other oxides, are compiled from the literature through October 1969 (256 references). Thorium-oxygen phase information is followed by data collections on thorium oxide, binary systems with uranium and plutonium oxides, other binaries, and ternary and more complex systems. For each, sections on composition ranges and preparation and fabrication methods described as needed to understand their influence on properties are followed by compilations on crystal properties, thermodynamic properties, change of state, electrical and magnetic properties, heat and mass transport, mechanical properties, chemical properties, and surface properties.

Compilations on the other ceramic compounds of thorium and revisions to this compilation are planned for future issues.

The only oxide of thorium with useful stability is the dioxide, ThO_2 . The thorium-oxygen phase diagram reported by Benz¹ is given in Fig. 1. Systems containing a second negative element are deferred to the other appropriate volume.

THORIUM DIOXIDE SYSTEMS

A. Thorium Oxide

1. Composition

Thorium dioxide (thoria), ThO_2 , exists up to its melting point as a single cubic phase with the fluorite structure. No deviation from the composition indicated by the formula can be detected by chemical analysis. However, on prolonged heating to 1800 or 1900°C in vacuum, thoria blackens with loss of oxygen, although the loss is insufficient to be reflected in chemical analysis or lattice-parameter measurement. Reheating in air to 1200 or 1300°C restores the white color. In contact with molten thorium at sufficiently high temperatures, thoria shows deviations from stoichiometry.¹ The limiting oxygen-to-thorium ratio varies from 1.985 at about 1735°C to a low of 1.87 at about 2700°C, increasing to 1.997 at the melting point.

*Retired.

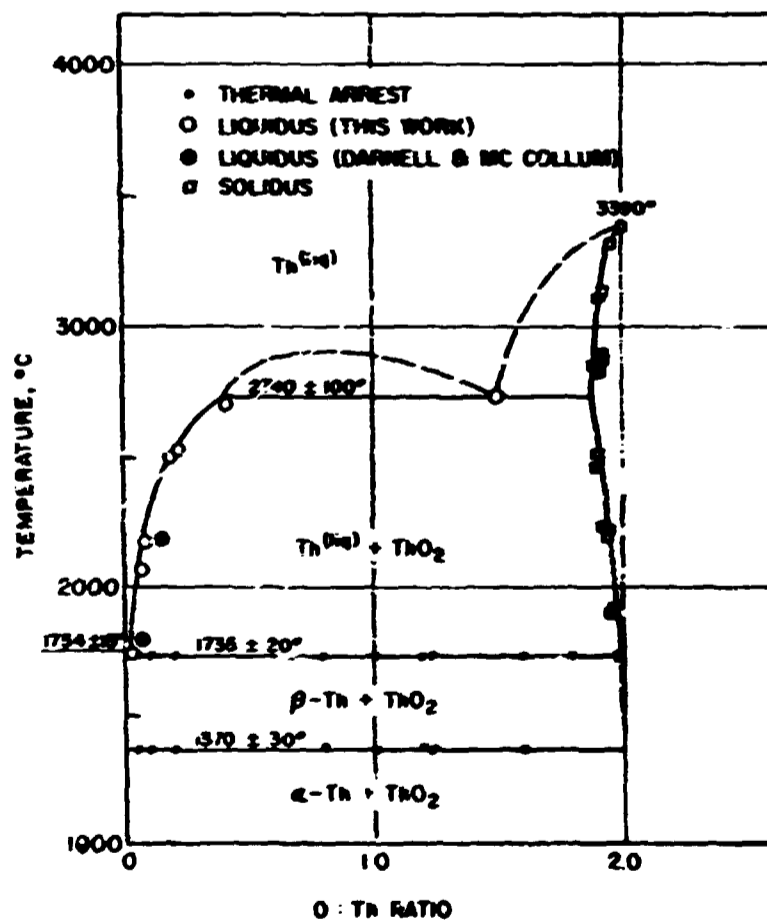


Fig. 1. The Th-ThO₂ Phase Diagram. From R. Benz.¹ Copyright by North-Holland Publishing Company and reproduced with permission.

2. Preparation

Thorium oxide is commonly prepared by the calcination of a salt. Usually the oxalate is precipitated under regulated conditions from a solution of the purified nitrate and then calcined at 900 to 1000°C. It may then be fired at higher temperatures to modify its properties.

Of increasing importance for the preparation of thoria, particularly for nuclear use, is the sol-gel process, which lends itself especially to the recycle of thorium fuels irradiated in nuclear reactors. First, the nitrate salt or its solution is decomposed by superheated steam. The resulting oxide is digested with nitric acid to form a sol (colloidal dispersion). The sol in turn is evaporated to form thoria gel chunks containing about 3% water. These can be crushed to powder for subsequent forming or fired at 1150°C to dense pieces for vibratory compaction into fuel rods. In an alternate process the sol is converted to gel by extraction of water by an organic liquid, usually an alcohol, that has an affinity for water but is immiscible with the sol. The gel so produced is a fine spherical powder.

In the fabrication of shapes from thorium oxide, two steps are usually regarded as essential: a forming stage and a subsequent high-temperature sintering (or firing) stage. Only the methods suitable for forming with thorium oxide ceramics are described here.

Cold Pressing. — Ceramic powders are formed into shapes at room temperature by exerting mechanical pressure on them in a steel die. Pressure is exerted along one axis only (uniaxial pressing); in the case of cylindrical shapes, the pressure is usually along the longitudinal axis. Lubricants such as polyvinyl alcohols (up to about 5 wt %) are often added to aid in the movement of the particles during compaction; the particles may be wet or dry. This method is generally restricted to the forming of simple shapes with a length-to-diameter ratio not greater than 1.

Isostatic Pressing. — Powders, possibly preshaped by cold pressing, are placed in a mold made of rubber or some other elastic material. Hydraulic pressure is applied to the mold to compact the powder. This

method is more amenable than uniaxial cold pressing to forming shapes of uniform density, shapes that are fairly complicated, and shapes that have a length-to-diameter ratio greater than 1. "Hot isostatic pressing" is the same in principle; however, because of the high temperatures necessary in the forming, the pressing medium may be a gas or a finely divided solid.

Extrusion. — Powders are wet with a liquid and are often also combined with a "plasticizer" to form a plastic mass. The mass is placed in an extrusion chamber and evacuated to remove air if improvement in plasticity is desirable. It is then forced as a column out of a steel die, the shape of which determines the cross section of the formed piece. Either of two types of extruding devices may be used: (1) the auger type, in which the material is forced through the die by an auger with much the same action as a meat grinder, and (2) the piston type, in which the material is forced through the die by a plunger. Extrusion is used primarily for making rod-shaped or tubular pieces.

Hot Pressing. — Powders are loaded into a mold, usually of graphite, and compacted by mechanical pressure at a temperature at which thermoplasticity is attained; heating is usually by resistance in the graphite mold to induced electrical currents of high frequency. This method is generally used for forming dense bodies from powders that have poor sintering characteristics or for forming large simple shapes that cannot be formed conveniently by other standard techniques.

Slip Casting. — Powders are suspended in a liquid (about 25 wt %) by means of a "deflocculant" (normally an acid or base) to form a "slip." This slip is poured into a plaster-of-paris mold that has been contoured to form the desired shape. Liquid is absorbed by the mold, resulting in a buildup of solids at the mold walls. For hollow shapes the slip is allowed to stay in the mold until the desired wall thickness of solids is built up, and then the excess is poured from the mold. For solid shapes, preferably a very thick slip is used, and all the slip is allowed to remain in the mold until most of the liquid is removed. This method is amenable to forming very complicated shapes, but pure oxides such as ThO₂ are difficult to suspend.

3. Crystal Properties

Structure. — Thorium oxide exists in only one crystal form, the cubic fluorite structure, space group O_h^5 or $Fm3m$, isomorphous with UO_2 and CeO_2 . Hurd² has measured lattice disorder by x-ray diffraction, and Willis³ has used neutron diffraction to verify the location of the oxygen atoms and measure their thermal motion up to 1100°C.

Lattice Parameter. — 5.5971 Å at 25°C. Most measurements aimed at accurate determination of this quantity are within ± 0.0002 Å of this value. Values ranging down to 5.590 are found for specific specimens, probably reflecting variations in purity. Figure 2 shows values of the parameter measured at various temperatures. Data of Kempter and Elliott,⁴ Brown and Chitty,⁵ and Mauer and Boltz⁶ show good agreement to 800°C. The parameters by Skinner⁷ appear low, but the variation with temperature agrees reasonably well.

Density. — 10.001 g/cm³ at 25°C, based on the above lattice parameter.

Thermal Expansion. — The direct measurements of thermal expansion by Chrysty and Rose⁸ cover the widest temperature range of any and are plotted in Fig. 3. Over the temperature ranges studied, these results are in good agreement with other direct measurements⁹⁻¹³ as well as with expansions derived from x-ray measurements.^{4-7,14}

Refractive Index. — Ellis and Lindstrom¹⁵ report the following:

Wavelength (Å)	Index of Refraction
5893	2.105 ± 0.005
5641	2.110 ± 0.005
4358	2.135 ± 0.005

Spectra. — Infrared, visible, and ultraviolet absorption spectra of single-crystal ThO_2 are given by Linares¹⁶ and Bates;¹⁷ Bates has also reported spectra of polycrystalline material. The ultraviolet edge of ThO_2 is at 38,000 cm⁻¹ (2600 Å), and a strong impurity band peaks at 32,000 cm⁻¹ (3100 Å).¹⁶ Annealing in hydrogen at 1725°C introduces¹⁷ absorption at 4030 and 7100 Å and decreases absorption at 3060 Å. Single-crystal thoria absorbs infrared at 2.21, 2.7, 4.9, 8.5, 9.8, and 11.4 μm; polycrystalline material has peaks at 9.6, 11.6, and 13.6 μm, with the short-wavelength peaks obscured by scattering from grain boundaries and porosity.¹⁷ Axe and Pettit¹⁸ measured the

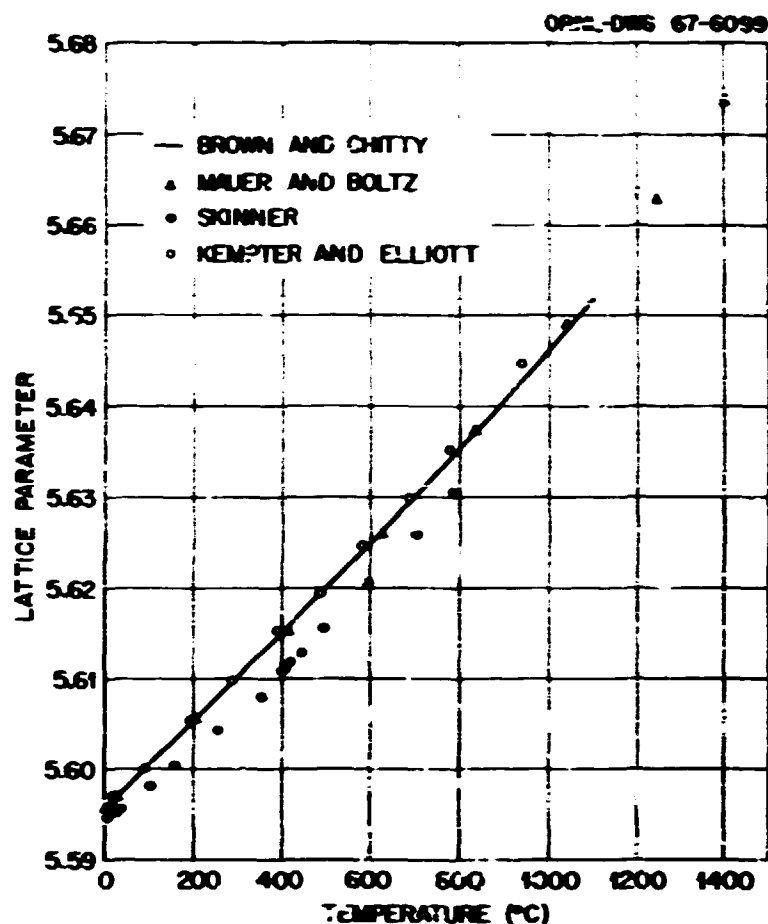


Fig. 2. Lattice Parameters of Thoria. Based on Kempter and Elliott,⁴ Brown and Chitty,⁵ Mauer and Boltz,⁶ and Skinner.⁷

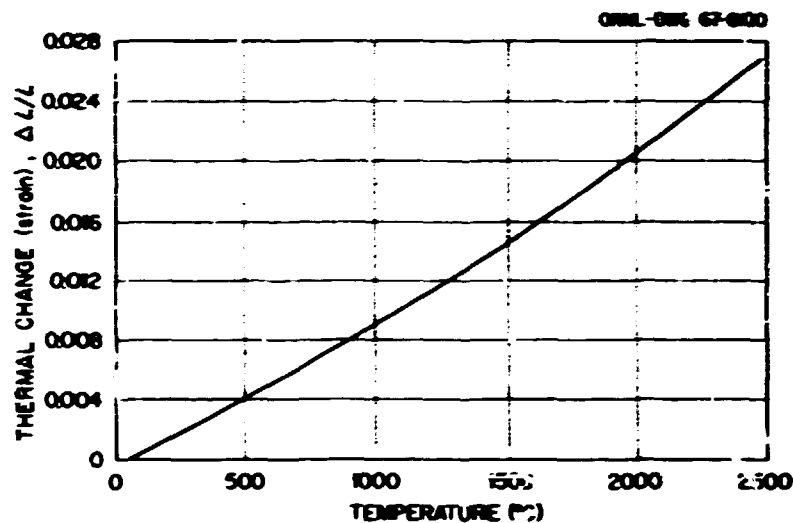


Fig. 3. Thermal Expansion of Thoria. Based on Chrysty and Rose.⁸

infrared reflection spectrum of single-crystal ThO_2 . The reflectivity rises from 40% at 50 cm⁻¹ (20 μm) to 90% at 290 cm⁻¹ (3.4 μm), drops to near zero between 550 and 600 cm⁻¹ (1.8–1.7 μm), and then rises some above 650 cm⁻¹. Tripp and Rodine¹⁹ have measured emission, excitation, and fluorescence spectra of thoria single crystals.

4. Thermodynamic Properties

Table 1 lists a selection of thermodynamic properties of ThO_2 . The values of the heat capacity, enthalpy, entropy, and free energy function up to 298.15°K are from Osborne and Westrum,²⁶ and those for higher temperatures are based on the analysis by Godfrey *et*

*al.*²¹ of data by Victor and Douglas,²² Southard,²³ and Hoch and Johnston.²⁴ Table 2 gives the heat and free energy of formation, based on the heat of formation at 25°C by Huber *et al.*²⁵ and thermodynamic functions of thorium, oxygen, and thoria from Hultgren *et al.*,²⁶ Stull and Sinke,²⁷ and Table 1 respectively.

Table 1. Thermodynamic Functions of ThO_2

Temperature (°K)	C_p° , Heat Capacity		$H^\circ - H_0^\circ$, Enthalpy		S° , Entropy		$-(G^\circ - H_0^\circ)/T$	
	$\left(\frac{\text{cal}}{\text{mole}^\circ\text{K}}\right)$	$\left(\frac{\text{J}}{\text{mole}^\circ\text{K}}\right)$	(cal/mole)	(J/mole)	$\left(\frac{\text{cal}}{\text{mole}^\circ\text{K}}\right)$	$\left(\frac{\text{J}}{\text{mole}^\circ\text{K}}\right)$	$\left(\frac{\text{cal}}{\text{mole}^\circ\text{K}}\right)$	$\left(\frac{\text{J}}{\text{mole}^\circ\text{K}}\right)$
10.00	0.032	0.134	0.08	0.33	0.011	0.046	0.003	0.013
50.00	2.430	10.167	38.63	161.5	1.058	4.469	0.296	1.238
100.00	6.246	26.133	257.3	1076.5	3.948	16.518	1.375	5.753
150.00	9.546	39.94	655.1	2740.9	7.129	29.828	2.762	11.556
200.00	11.97	50.38	1196.5	5006.2	10.227	42.790	4.244	17.757
250.00	13.64	57.07	1839.1	7694.8	13.088	54.760	5.732	23.98
298.15	14.76	61.76	2524.4	10562	15.593	65.241	7.126	29.82
300.00	14.79	61.88	2551	10673	15.68	65.605	7.18	30.04
400.00	16.08	67.28	4103	17167	20.14	84.27	9.88	41.34
500.00	16.80	70.29	5750	24058	23.81	99.62	12.31	51.51
600.00	17.29	72.34	7456	31196	26.92	112.63	14.49	60.63
700.00	17.68	73.97	9205	38514	29.61	123.89	16.46	68.87
800.00	18.01	75.35	10990	45982	32.00	133.89	18.26	76.40
900.00	18.30	76.56	12806	53580	34.13	142.80	19.91	83.30
1000.00	18.56	77.74	14650	61296	36.08	150.96	21.43	89.66
1100.00	18.84	78.83	16521	69124	37.86	158.41	22.85	95.60
1200.00	19.09	79.9	18417	77057	39.51	165.31	24.17	101.13
1300.00	19.34	80.9	20338	85094	41.05	171.75	25.40	106.27
1400.00	19.58	81.9	22284	93236	42.49	177.78	26.58	111.21
1500.00	19.81	82.9	24254	101479	43.85	183.47	27.68	115.81
1600.00	20.05	83.9	26247	109817	45.13	188.82	28.73	120.21
1700.00	20.28	84.9	28264	118257	46.36	193.97	29.74	124.43
1800.00	20.51	85.8	30304	126792	47.52	198.82	30.69	128.41
1900.00	20.74	86.8	32366	135419	48.64	203.51	31.50	132.21
2000.00	20.97	87.7	34452	144147	49.71	207.99	32.48	135.90
2100.00	21.20	88.7	36561	152971	50.74	212.30	33.35	139.45
2200.00	21.43	89.7	38693	161892	51.73	216.44	34.14	142.84
2300.00	21.66	90.6	40847	170904	52.69	220.45	34.92	146.11
2400.00	21.88	91.5	43024	180012	53.61	224.30	35.69	149.33
2500.00	22.11	92.5	45224	189217	54.51	228.07	36.42	152.38
2600.00	22.34	93.5	47446	198514	55.38	231.71	37.13	155.35
2700.00	22.56	94.4	49691	207907	56.23	235.27	37.83	158.28
2800.00	22.79	95.4	51958	217392	57.05	238.70	38.50	161.08
2900.00	23.01	96.3	54248	226974	57.86	242.09	39.19	163.97
3000.00	23.24	97.2	56560	236647	58.64	245.35	39.79	166.48

Table 2. Heat and Free Energy of Formation of ThO₂

Temperature (°K)	-ΔH _f		-ΔG _f	
	(kcal/mole)	(kJ/mole)	(kcal/mole)	(kJ/mole)
298.15	293.2	1227	279.4	1169
400	293.0	1226	274.7	1149
500	292.8	1225	270.2	1131
600	292.6	1224	265.7	1112
700	292.4	1223	261.2	1093
800	292.2	1223	256.8	1074
900	292.0	1222	252.4	1056
1000	291.8	1221	248.0	1038
1100	291.7	1220	243.6	1019
1200	291.6	1220	239.0	1000
1300	291.4	1219	234.9	983
1400	291.3	1219	230.6	965
1500	291.2	1218	226.0	946
1600	291.1	1218	221.9	928
1700	291.7	1220	217.5	910
1800	291.6	1220	213.2	892
1900	291.6	1220	208.8	874
2000	296.0	1238	204.3	855
2500	295.4	1236	181.5	759
3000	294.2	1231	158.8	664

5. Change of State

Melting Point. - 3300 ± 100°C (Lambertson *et al.*²⁴); 3390°C (Benz).¹

Boiling Point. - 4400°C (Mott).²⁹

Vapor Pressure. - Vapor pressure data from several investigators³⁰⁻³⁵ are presented in Fig. 4.

Heat of Fusion. - Based on 3R as the estimated entropy of fusion, the heat of fusion is estimated²⁸ as 21.4 kcal/mole (90 kJ/mole).

Heat of Vaporization. - The following values are derived from the temperature dependence of vapor pressure. Unless otherwise noted they are for the temperature range of the corresponding vapor pressures.

Heat of Vaporization		Reference
(kcal/mole)	(kJ/mole)	
158.7 ± 2.5	664 ± 10	32
171	715	31
170.3	713	30 (corrected to 25°C)
184	770	36 (from temperature dependence of relative rates of evaporation)

6. Electrical and Magnetic Properties

Resistivity. - At low to moderate temperatures thoria can be considered an insulating material. However, it

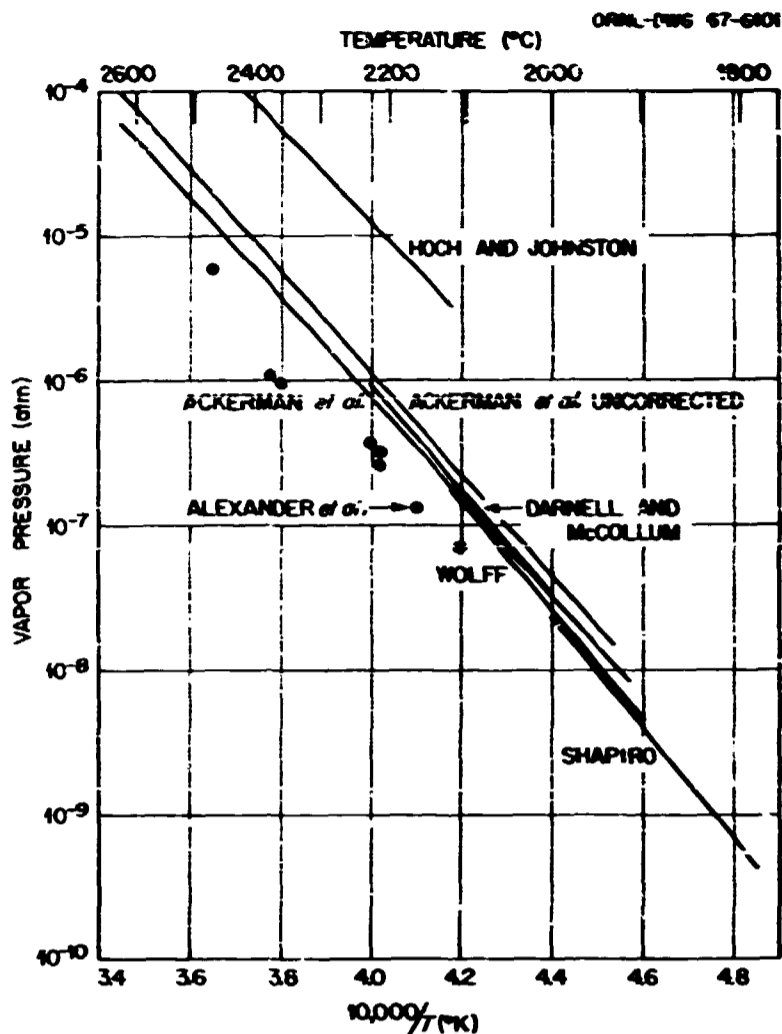


Fig. 4. Vapor Pressure of Thoria. Straight lines are taken from Hoch and Johnston,³⁰ Shapiro,³¹ Ackerman *et al.*,³² Wolff and Alcock,³³ and Darnell and McCollum³⁴ to fit their data over the ranges measured. The two lines from Ackerman *et al.* represent calculation neglecting decomposition and calculation correcting for formation of ThO + O as part of the vapor. Individual data points are shown for Alexander *et al.*³⁵ All measurements are based on rates of evaporation. To convert, 1 atm = 101,325 N/m².

has some of the characteristics of semiconductors, and its resistivity is sensitive to many conditions. The variation in values is illustrated by the collection of several measurements in Fig. 5 on specimens described in Table 3. As a transport property of a fabricated body, the resistivity depends on such features as porosity, grain size, and impurity content that depend on the fabrication history. That these factors are involved is clear from the figure, despite the incomplete characterization of the specimens. Also, a comparison of different results from the same investigator shows an effect of environment. More recent work has related this effect to the oxygen partial pressure, which can be varied to very low values by using mixtures of water vapor and hydrogen and the known dissociation equilibrium. At higher temperatures, increasing the oxygen pressure increases resistivity, as shown by the results

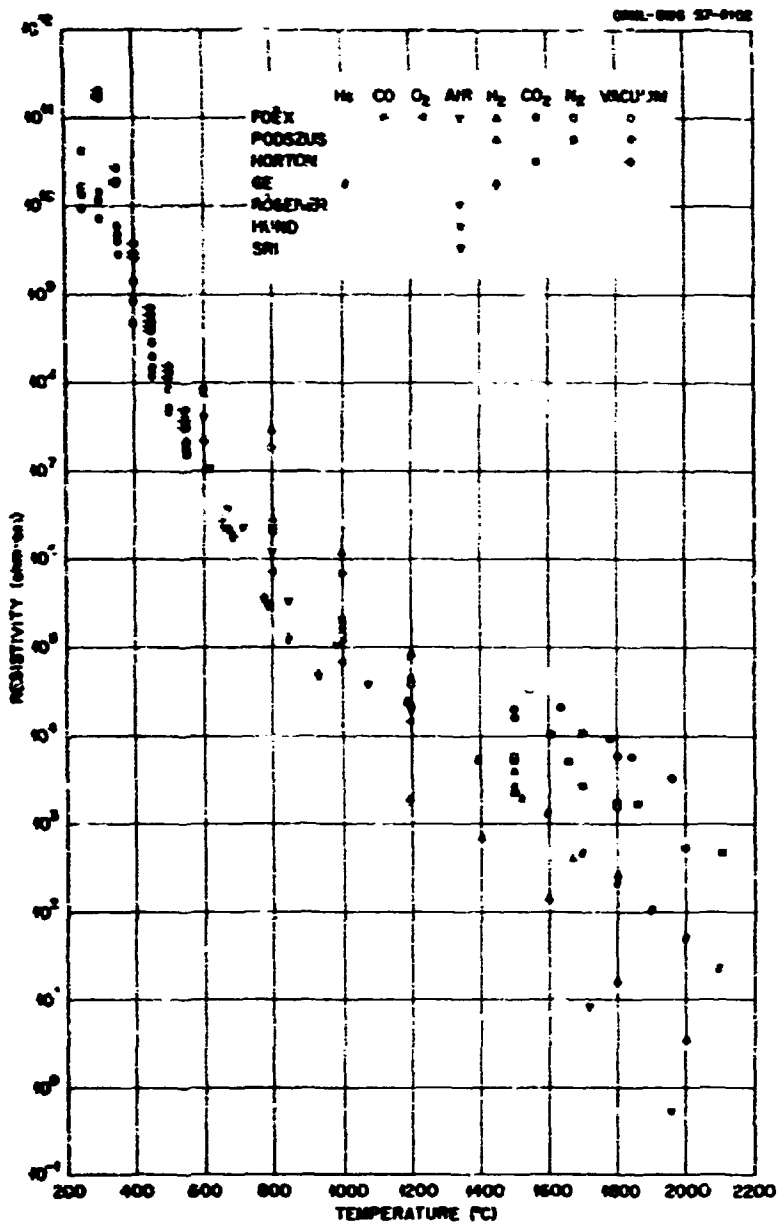


Fig. 5. Selected Measurements of the Electrical Resistivity of Thoria. References and data on specimens are in Table 3.

from General Electric⁴³ in Fig. 6. At lower temperatures the oxygen effect is reversed, as seen by the results of Bauerle⁴⁴ in Fig. 7 and of Lasker and Rapp⁴⁵ in Fig. 8. The latter also shows measurements by Steel and Alcock⁴⁶ and Rudolph.⁴⁷ Both figures show the different resistivities of specimens with different history. Bauerle⁴⁴ relates the conductivity to oxygen pressure by

$$\sigma = \sigma_1 + \sigma_2 P_{O_2}^{1/4}$$

Bates⁴⁸ reports conductivity values in Ar-8% H₂ ranging from 1 X 10⁻⁸ Ω-cm at 760°C to 5 Ω-cm at 2610°C, in reasonable agreement with other measurements under reducing conditions.

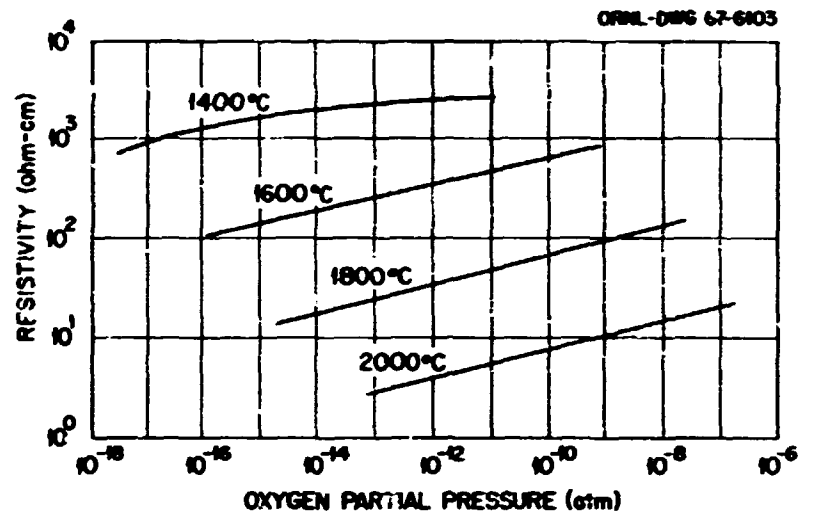


Fig. 6. Effect of Oxygen Activity on Electrical Resistivity of Thoria at High Temperatures. Data from General Electric.⁴³ To convert, 1 atm = 101,325 N/m².

Table 3. Specimens for Electrical Resistivity Shown in Fig. 5

Author and Reference	Pressing Pressure		Sintering		Dimensions (cm)		Density (g/cm ³)
	(kg/cm ²)	(tsi)	Temperature (°C)	Medium	Diameter	Length	
Poëx ³⁷	3,000	21	2100		1		7.8
Podzus ³⁸	Extruded		1500 2000	H ₂ -O ₂			
Horton et al. ³⁹	2,500	18		Not sintered			
General Electric ⁴⁰			2000 1400	H ₂ Air	1		
Rögenes ⁴¹					1.01	1	
Hend ²	10,000	71	1500	Air	1	0.5	
Southern Research Institute ⁴²	Commercial						9.69

The measurement history also affects the resistivity. Danforth and Morgan⁴⁹ subjected thoria to increasingly heavy electric currents between series of measurements of resistivity as a function of temperature for molded and sintered (7 g/cm^3) thoria. The resistivity decreased with use and abuse, finally reaching $10 \text{ } \Omega\text{-cm}$ at 730°C and $1 \text{ } \Omega\text{-cm}$ at 1630°C . Mesnard⁵⁰ found that the resistivity of thoria in vacuum at 1500°C ranged from 3×10^4 to $2 \times 10^6 \text{ } \Omega\text{-cm}$ after various treatments up to 1900°C . Mesnard and Uzan⁵¹ showed the resistance of thoria specimens in vacuum to increase with time.

Dielectric Constant. — Güntherschulze and Keller⁵² report 10.6. A low-frequency value (at 0.3 MHz) of 18.9 ± 0.4 is reported by Axe and Pettit.¹⁸

Magnetic Susceptibility. — Smith and Clark⁵³ report $-26.5 \pm 0.3 \times 10^{-6} \text{ cm}^3/\text{mole}$.

Thermoelectric Power. — Rudolph⁴⁷ plots thermoelectric power against reciprocal temperature for thoria under 370 torr oxygen. The value rises from about $1.1 \text{ mV}/^\circ\text{C}$ at about 610°C to a peak of $1.7 \text{ mV}/^\circ\text{C}$ at 790°C and then drops to $1.2 \text{ mV}/^\circ\text{C}$ at 1060°C .

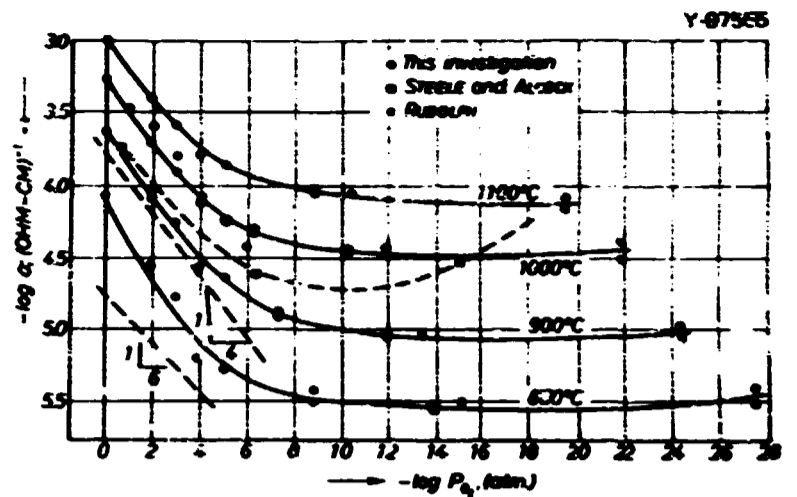


Fig. 8. Variation of Electrical Conductivity of Thoria with Temperature and Oxygen Activity. Copied from Lasker and Rapp⁴⁵ with permission of Akademische Verlagsgesellschaft. The specimens were 1-cm-diam by 0.3-cm disks fired 2.5 hr in vacuum at 2100°C and then 5 hr in air at 1400°C to a density of 9.3 g/cm^3 . Specimens of Steele and Alcock⁴⁶ were isostatically pressed at 30 ksi (4200 kg/cm^2) and sintered in vacuum at 2000°C to 9.5 g/cm^3 . Those of Rudolph⁴⁷ were pressed and sintered at 1500 to 1600°C . To convert, $1 \text{ atm} = 101,325 \text{ N/m}^2$.

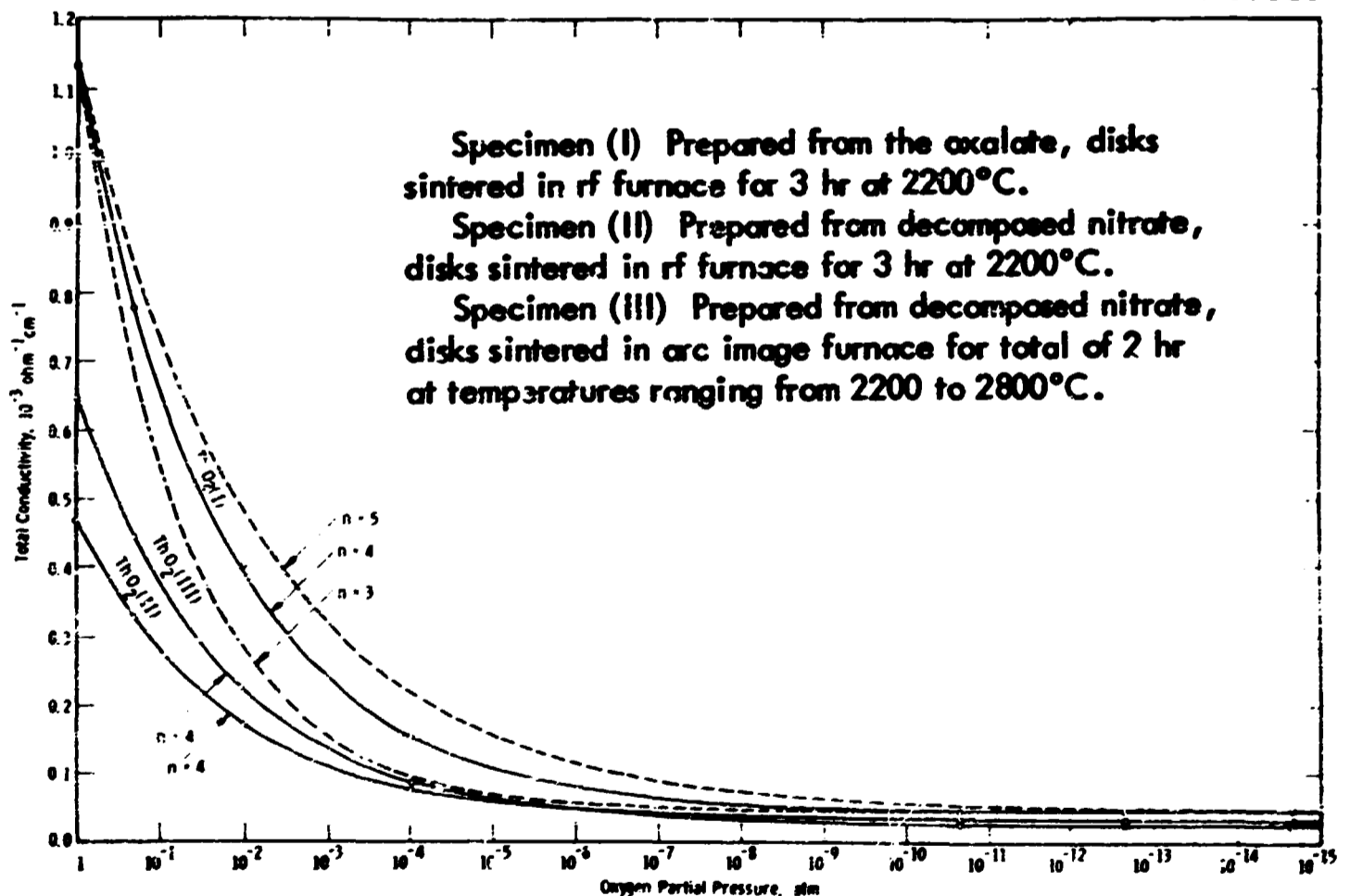


Fig. 7. Electrical Conductivity of Thoria as a Function of Oxygen Activity at 1000°C . Curves represent the theoretical equation $\sigma = \sigma_1 + \sigma_2 P_{\text{O}_2}^{1/n}$. Copied from J. E. Bauerle⁴⁴ with permission. Copyright by American Institute of Physics. To convert, $1 \text{ atm} = 101,325 \text{ N/m}^2$.

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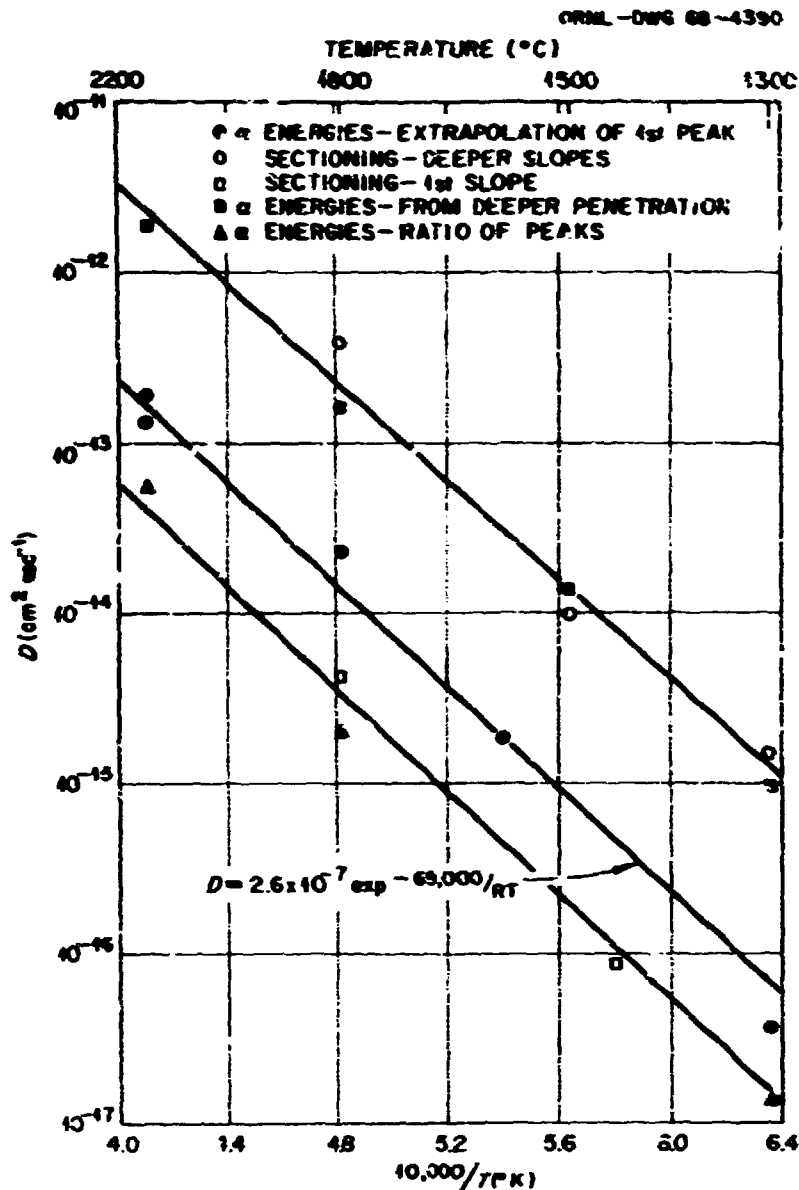


Fig. 9. Diffusion Coefficients for Thorium in Sintered Thoria. Data of Poteat and Morgan.⁵⁴

7. Heat and Mass Transport

Diffusion. — Figure 9 shows values of the diffusion coefficient of thorium in sintered polycrystalline thoria determined by Poteat and Morgan.⁵⁴ As much as a 100-fold variation with method of measuring penetration reflects a depth dependence. The same study showed that a substantial part of the diffusion was grain-boundary rather than lattice diffusion, since fine-grained sol-gel material showed much more rapid diffusion, and diffusion was slower in single-crystal thoria. For pressed thoria fired 5 hr at 1900°C in vacuum and then 4 hr at 2000 to achieve a 100- μ m grain size, Hawkins and Alcock⁵⁵ found the diffusion coefficient of thorium to follow

$$D = 1.25 \times 10^{-7} \exp(-Q/RT) \text{ cm}^2/\text{sec}$$

over the range 1600 to 2100°C, where Q is 53,800 cal/mole or 246,000 kJ/mole. Figure 10 gives results by Morgan and Yust⁵⁶ on diffusion of oxygen in fine-grained 10- μ m-diam thoria spheres, and Fig. 11 gives similar results by Edwards *et al.*⁵⁷ for coarser material.

Table 4 summarizes measurements by Furuya and Yajima⁵⁸ on protactinium and by Furuya⁵⁹ on uranium diffusion in thoria, and Table 5 gives results on uranium by Matzke.⁶⁰ Matzke also measured rates of migration of xenon in thoria, but his results did not permit calculation of diffusion coefficients.

Berman⁶¹ measured surface diffusion on high-density sintered polycrystalline ThO₂ specimens annealed 24 to 48 hr at 1750°C in hydrogen. The measurements over the range 1560 to 2500°C were fitted by

$$D_s = 5.21 \times 10^9 \exp(-Q/RT) \text{ cm}^2/\text{sec},$$

where Q is $141,900 \pm 17,200$ cal/mole or $594,000 \pm 72,000$ J/mole.

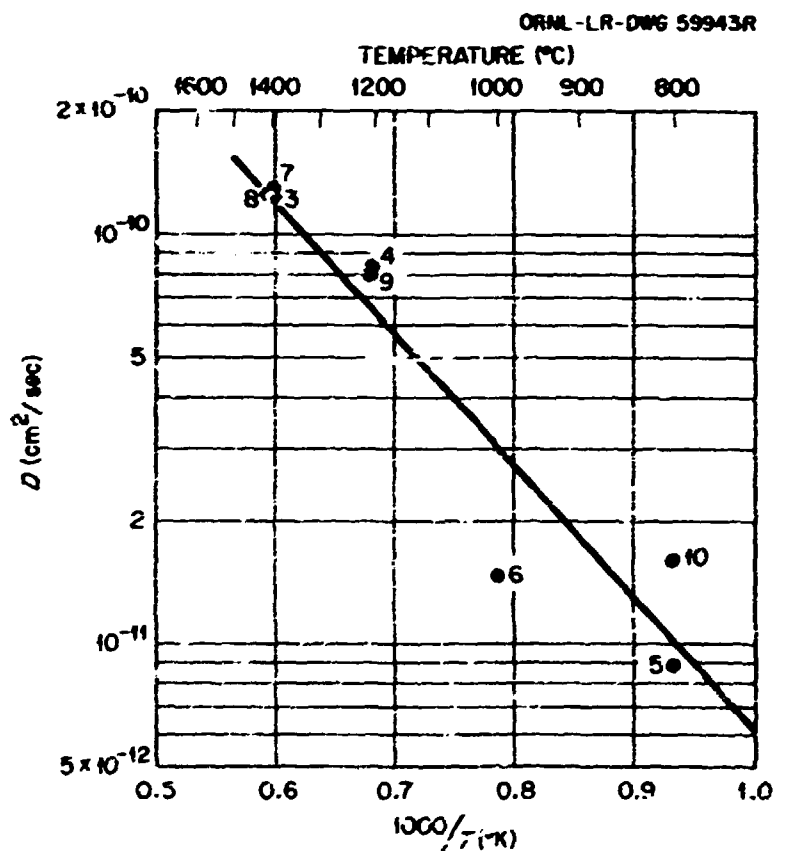


Fig. 10. Diffusion Coefficient of Oxygen in Thoria Microspheres. Data of Morgan and Yust.⁵⁶

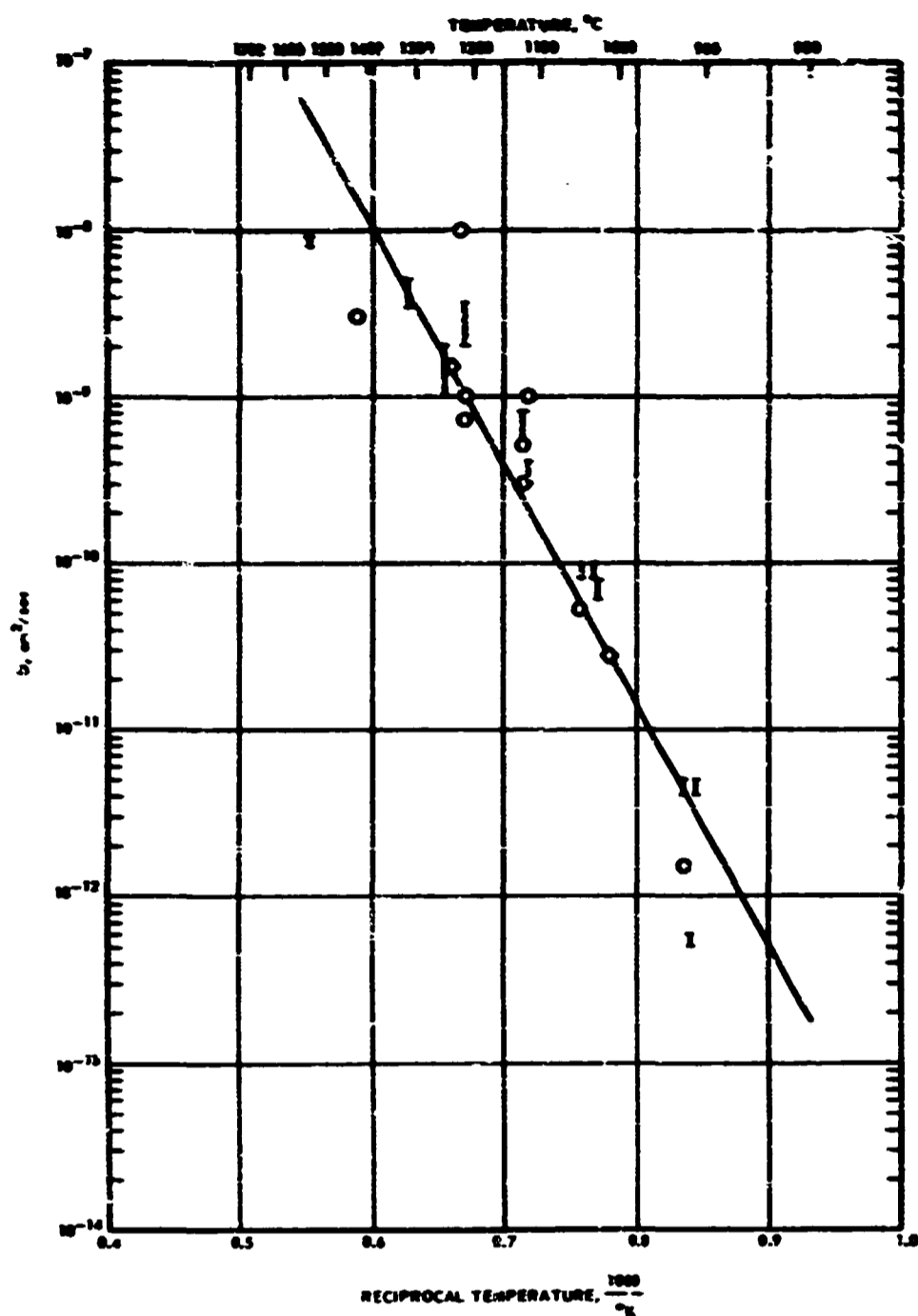


Fig. 11. Diffusion Coefficient of Oxygen in Thoria. Data of Edwards *et al.*⁵⁷

Table 4. Diffusion Coefficients of Protactinium and Uranium in Polycrystalline Thoria at 1800 to 2000°C^a

Mobile Atom	Component	Arrhenius Coefficients ^b		
		$D_0 \times A$	Q (cal/mole)	Q (J/mole)
Protactinium	Lattice	2.91×10^{-5}	75,400	316,000
	Grain boundary	6.66×10^{-11}	30,600	128,000
Uranium	Lattice	1.10×10^{-4}	76,400	320,000
	Grain boundary	2.35×10^{-9}	47,900	201,000

^aTaken from Feruya and Yajima.^{58,59} Specimens were pressed at 5000 kg/cm², sintered in vacuum 2 hr at 1700°C to a density greater than 9.6 g/cm³, and then sintered 2 hr at 2300°C in argon to a density greater than 9.8 g/cm³ and an average grain size over 60 μm. Results were analyzed into lattice and grain-boundary components.

^bConstants of $D = D_0 \exp(-Q/RT)$ cm²/sec and $2aD' = A \exp(-Q/RT)$ cm³/sec, where D' is the grain-boundary diffusion coefficient and $2a$ is the width of the grain boundary.

Table 5. Diffusion Coefficient of Uranium in Thoria^a

Medium	Diffusion Coefficient (cm ² /sec) at -	
	1400°C	1550°C
ThO ₂	2×10^{-14}	3×10^{-13}
ThO ₂ -0.1 mole % Y ₂ O ₃	5×10^{-15}	1.2×10^{-14}
ThO ₂ -0.1 mole % Nb ₂ O ₅	6.8×10^{-12}	6.2×10^{-11}

^aMeasured by Matzke⁶⁰ on material pressed and sintered 1 hr in H₂ at 1650°C.

Thermal Conductivity. — Data on the thermal conductivity of thoria are collected in Fig. 12; see also Table 6. The scatter largely reflects variations in porosity and other structural features of the specimens. Measured values, λ , of the thermal conductivity can be corrected to values λ_{TD} for theoretically dense material by

$$\lambda = \lambda_{TD}(1 - P)/(1 + \beta P),$$

where P is the pore volume fraction and β is an empirical parameter that depends on preparation method, presumably as reflected by pore shape. Belle *et al.*⁶² found that β varied from 0.5 to over 3 for a variety of specimens measured at 120°C. Table 7 relates the measurements of Moore *et al.*⁶³ to specimen history; they fitted their data with $\beta = 1.2$ for oxalate thoria and 6.5 for sol-gel thoria. Springer *et al.*¹³ fitted their data by

$$\lambda = (1 - P)/(1 + 1.49P)(0.79 + 0.0185T) \text{ W cm}^{-1} (\text{°C})^{-1}$$

Table 8 gives low-temperature results of Moore and McElroy.⁶⁴ Their results over the whole range, corrected to theoretical density with $\beta = 0.5$, have been reported.⁶⁵ The corrected results follow:

$$1/\lambda = 0.01935T - 0.1550, 200 \text{ to } 400^\circ\text{K},$$

$$1/\lambda = 0.02141T - 0.9800, 400 \text{ to } 1400^\circ\text{K}.$$

Table 6. Specimens for Thermal Conductivity Shown in Fig. 12

Investigator	Specimen Preparation	Density (g/cm ³)
Babcock and Wilcox ⁶	Not given	
Adams ⁶⁷	Slip cast	8.07 ^b
Moore and McElroy ⁶⁴	Commercial ^c	9.37
Springer <i>et al.</i> ¹³	Sintered 1750°C in H ₂	9.30 (1) 8.66 (2) ^d 7.36 (3) ^d
Moore <i>et al.</i> ⁶³	See Table 7	
Koenig ⁶⁸	Hot pressed at 1800°C	9.58
Kingery <i>et al.</i> ⁶⁹	Same as Adams	
Southern Research Institute ⁴²	Commercial	9.00
Jaeger <i>et al.</i> ⁷⁰	Sintered at 1500°C	8.5

^aAttributed by DeBoskey⁷¹ to Babcock and Wilcox Alliance Research Center.

^bBased on theoretical density of 10.00 and author's percentage; may be 7.82 if author used a lower theoretical density.

^cBrush Beryllium Co. "Thorox." Grain size 18 μm ; <400 ppm impurities.

^dSugar was incorporated before pressing to give added porosity after firing.

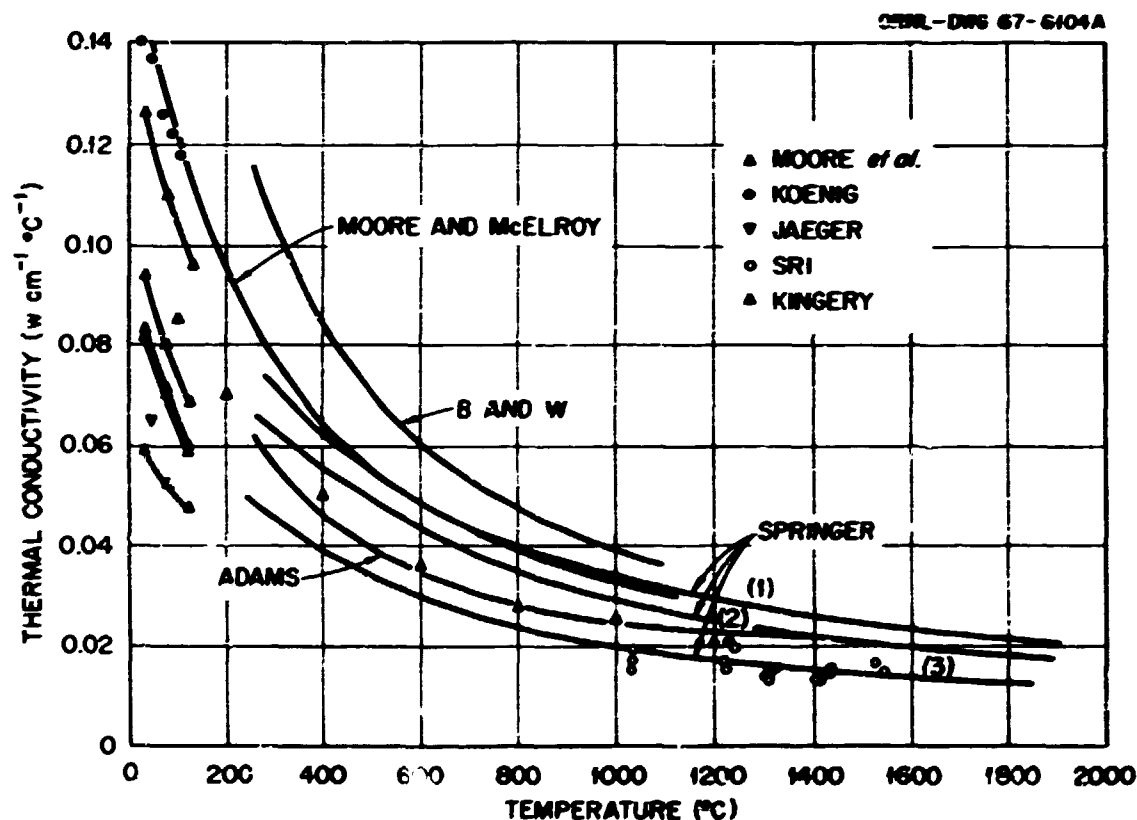


Fig. 12. Thermal Conductivity of Thoria. References and data on specimens are in Table 6.

Table 7. Thermal Conductivity of ThO₂ Specimens with Different Preparation Histories^a

Specimen Description	Density (g/cm ³)	Sintering Conditions	Thermal Conductivity ^b [W cm ⁻¹ (°C) ⁻¹] at -		
			30°C	75°C	120°C
Sol-gel thoria	9.046	In hydrogen at 1750°C	0.0828	0.0702	0.0596
Sol-gel thoria	9.046	In air at 1650°C	0.0817	0.0692	0.0509
Oxalate thoria	9.525	In air at 1650°C	0.1260	0.1100	0.0958
Oxalate thoria	8.582	In air at 1650°C	0.0934	0.0800	0.0683
Oxalate thoria	8.116	In air at 1650°C	0.0593	0.0523	0.0480

^aFrom Moore *et al.*, ref. 63.

^bSmoothed values are tabulated here. Measured values were precise to within ±0.25% and have a probable accuracy of ±1.75%. Some of these specimens were ground flat in a solution of ethylene glycol and water. The solution had a noticeable effect on the specimen conductivity when the measurements were made shortly after grinding. It was necessary, therefore, to thoroughly dry the samples by heating to 400 or 500°C in air before making measurements.

Table 8. Low-Temperature Conductivity of 93.7%-Dense Thoria^a

Temperature		Thermal Conductivity [W cm ⁻¹ (°C) ⁻¹]
(°K)	(°C)	
90	-183	0.614
100	-173	0.544
150	-123	0.333
200	-73	0.234
250	-23	0.186
300	27	0.154
350	77	0.131

^aData of Moore and McElroy.⁶⁴

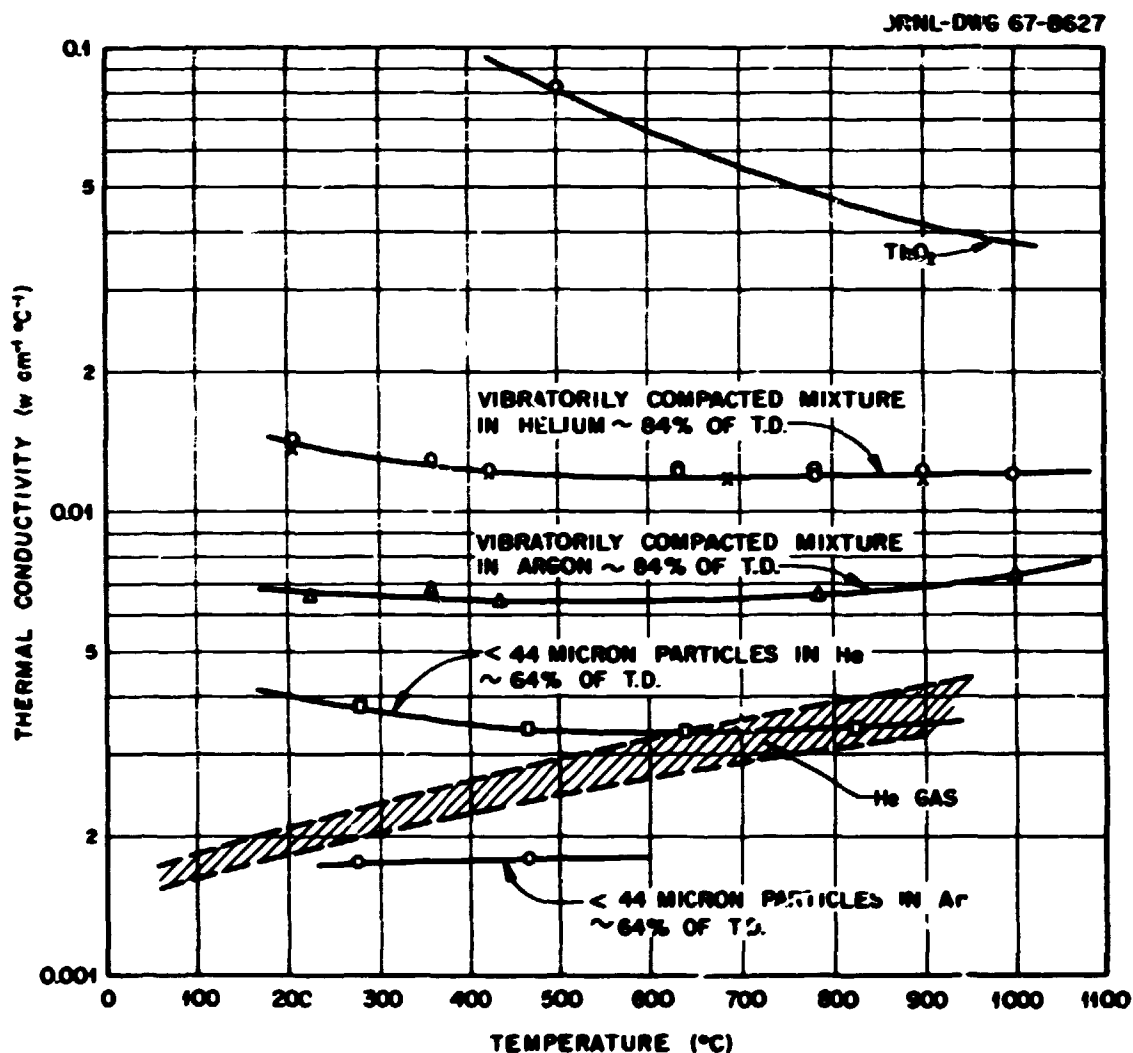


Fig. 13. Thermal Conductivity of Vibratorily Compacted Beds of ThO₂ Microspheres in Gases at Atmospheric Pressure. Data of McElroy *et al.*⁶⁵ Shown for comparison are values for theoretically dense ThO₂ and helium.

McElroy *et al.*⁶⁵ measured the thermal conductivity of vibratorily compacted beds of thorium microspheres. Figure 13 compares the values with those of helium gas and theoretically dense thorium. Figure 14 shows the effect of interstitial gas pressure. Table 9 lists measurements reported by Feith⁶⁶ on 75%-dense beds of thorium powder in vacuum and in various gases at atmospheric pressure.

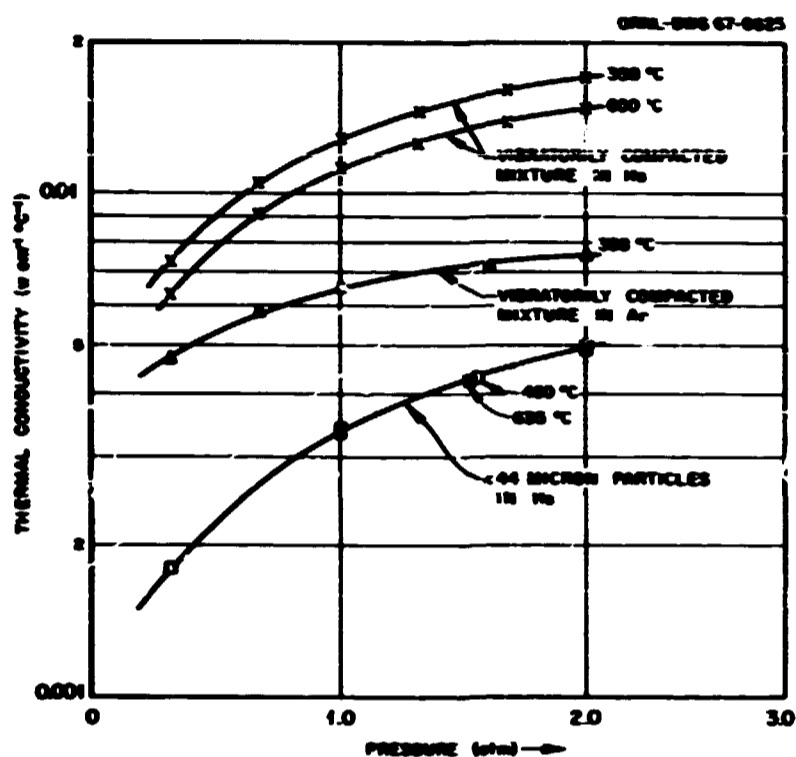


Fig. 14. Effect of Interstitial Gas Pressure on the Thermal Conductivity of Vibratorily Compacted Beds of ThO_2 Microspheres. Data of McElroy *et al.*⁶⁵ To convert, 1 atm = 101,325 N/m^2 .

Emissivity. - The total normal emissivity reported by Pirani⁷² for thorium sintered at about 1600°C is plotted in Fig. 15. Weinreich⁷³ reported the effect of various treatments on the spectral emissivity (at 0.65 and 1 μm) of thorium deposited on tungsten. The values varied considerably, depending on prior thermal and electrical treatment; he attributed the variation to reaction with the tungsten support at about 2500°C. He gives references to previous spectral emissivity measurements.

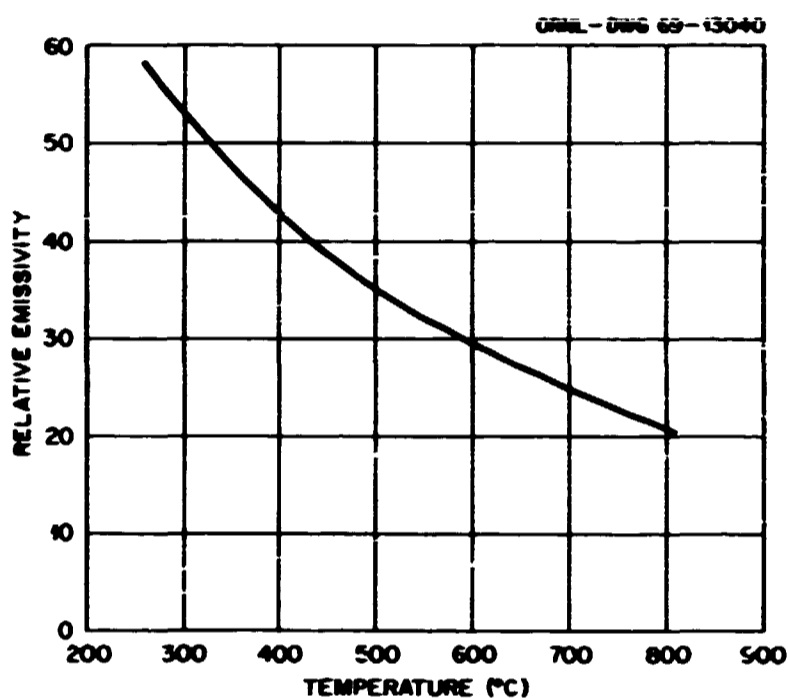


Fig. 15. Relative Emissivity of Thorium Perpendicular to Surface (black body = 100). Data of Pirani.⁷²

Table 9. Thermal Conductivity of 75%-Dense Beds of ThO_2 in Vacuum and in Gases at 1 atm (10^5 N/m^2)^a

Temperature (°C)	Thermal Conductivity [$\text{W cm}^{-1} (\text{°C})^{-1}$]				
	He	He-52% N_2	N_2	Ar	Vacuum ^b
400	0.0128	0.0130	0.0122	0.0107	0.004
500	0.0122	0.0122	0.0118	0.0101	0.0043
600	0.0119	0.0116	0.0107	0.0100	0.0047
700	0.0118	0.0113	0.0104	0.0105	0.005
800	0.0118	0.0113	0.0103	0.0125	
900	0.0122	0.0117	0.0106		
1000	0.0128	0.0122			
1100	0.0137	0.0132			
1200	0.0150	0.0146			

^aData of Feith.⁶⁶

^bApproximately 0.035 torr (4.7 N/m^2).

8. Mechanical Properties

The mechanical properties of thoria depend strongly on fabrication history. Curtis and Johnson⁷⁴ showed that the strength increased with decreasing porosity, achieved by increasing the firing temperature, incorporating 0.5 to 3% CaO, or both. Using powders with different characteristics, Knudsen⁷⁵ prepared thoria with independent variations in porosity and grain size and found that high strength was favored by low porosity, fine grain size, and high firing temperature. Thus, property values cited below are representative of particular preparations and are not characteristic of thoria in general. More modern preparations, because of their lower porosity, are generally stronger than the

older preparations on which the most frequently cited measurements have been made.

Bending Strength. — Values of the modulus of rupture determined from bending to fracture are listed in Table 10. Knudsen⁷⁵ obtained a reasonable fit to his data by

$$S = 69,700G^{-0.39} e^{-bP},$$

where S is the modulus of rupture in psi (to give S in N/m^2 the constant should be changed to 4.80×10^8), G is the grain size, P is the porosity, and b is a parameter that depends on the firing temperature. It was 5.5 for 1650°C, 4.7 for 1725°C, 3.8 for 1800°C, and 3.7 for 1850°C.

Table 10. Modulus of Rupture of Thoria

Reference	Fabrication History	CaO Content (%)	Firing Temperature (°C)	Porosity (%)	Grain Size (μm)	Modulus of Rupture at —			
						20°C		1000°C	
						(psi)	(N/m^2)	(psi)	(N/m^2)
75	0–2 μm precipitated powder prepared wet, isostatically pressed at 15 ton (200 MN/m ²), dried, fired in oxidizing atmosphere	0	1650	7.2	24.7	$\times 10^3$	$\times 10^7$	$\times 10^3$	$\times 10^7$
			1725	6.1	34.8	10.7	7.4		
			1800	6.7	25.1	14.5	10.0		
			1850	5.3	53.1	16.0	11.0	16.9	11.6
75	Same, except 0–5 μm arc-fused ThO ₂ powder was used	0	1650	8.7	11.8	16.3	11.3		
			1725	8.3	15.8	16.6	11.4		
			1800	8.6	16.4	18.7	12.9	17.2	11.9
			1850	8.6	17.4	15.8	12.0		
75	Same, except 5–10 μm arc-fused powder was used	0	1650	28.7	5.0	8.8	6.1		
			1725	25.0	5.1	10.5	7.2		
			1800	23.2	6.1	13.7	9.4	9.7	6.7
			1850	19.7	5.6	15.5	10.7		
75	Same, except 10–15 μm arc-fused powder was used	0	1725	30.8	9.9	6.5	4.5		
			1800	31.3	9.4	9.2	6.3	5.7	3.9
			1850	29.2	9.3	10.6	7.3		
75	Same, except 30–60 μm arc-fused powder was used	0	1650	31.3	35.6	2.8	1.9		
			1725	31.3	38.5	4.0	2.8		
			1800	31.1	42.9	4.6	3.2	2.4	1.7
			1850	30.8	36.2	5.6	3.9		
76 ^a	Powder blended, prepared dry, hydrostatically pressed at 15 ton (200 MN/m ²), fired in oxidizing atmosphere	0.5	1800	0.9	2	10.3	7.1	10.6	7.3
			1800	0.9	2	15.1	10.4	15.2	10.5
74	Calcined powder pressed at 12.7 ton (175 MN/m ²) with 2% dextrin and 5% H ₂ O, fired 2 hr in air	0	1400	46.9		0.7	0.5		
			1600	27.8		0.9	0.6		
			1800	17.6		1.3	0.9		
74	Same	0.5	1600	17.2		0.9	0.6		
			1800	0.0		1.9	1.3		
74	Same	1.0	1600	12.8		0.9	0.6		
			1800	0.0		2.0	1.4		
74	Same	3.0	1400	35.1		0.7	0.5		
			1800	0.0		2.6	1.8		
77	Air-calcined 33–600 μm powder sintered at 1700°C in H ₂ , isostatically pressed at 20 ton (200 MN/m ²), sintered 1.5 hr	0	1500	5		11.3	7.8	8.95	6.2

^aValues are for specimens of two sizes as required by different apparatus.

Table 11. Compressive Strength of Thoria at Room Temperature

Reference	Porosity (%)	Grain Size (μm)	Firing Temperature ($^{\circ}\text{C}$)	Dimensions (mm)		Compressive Strength		Number Tested
				Cross Section	Height	(psi)	(N/m^2)	
75 ^a	6.7	25.1	1800	10.2 diam	20.3	$\times 10^3$ 220	$\times 10^8$ 15.2	8
	8.6	16.4	1800	10.2 diam	20.3	227	15.7	8
	23.2	6.1	1800	10.2 diam	20.3	139	9.6	9
	31.3	9.4	1800	10.2 diam	20.3	73	5.1	9
	31.1	42.9	1800	10.2 diam	20.3	31.6	2.18	9
78 ^b	8		1950	6 square	6	214	14.8	1
76 ^c	0.9	2	1800	8.7 diam	19.8	222	15.3	5

^aPrepared from five different starting powders as described in Table 10.

^b99.5% pure thoria fired in an oxidizing atmosphere.

^c ThO_2 -0.5% CaO prepared as in Table 10.

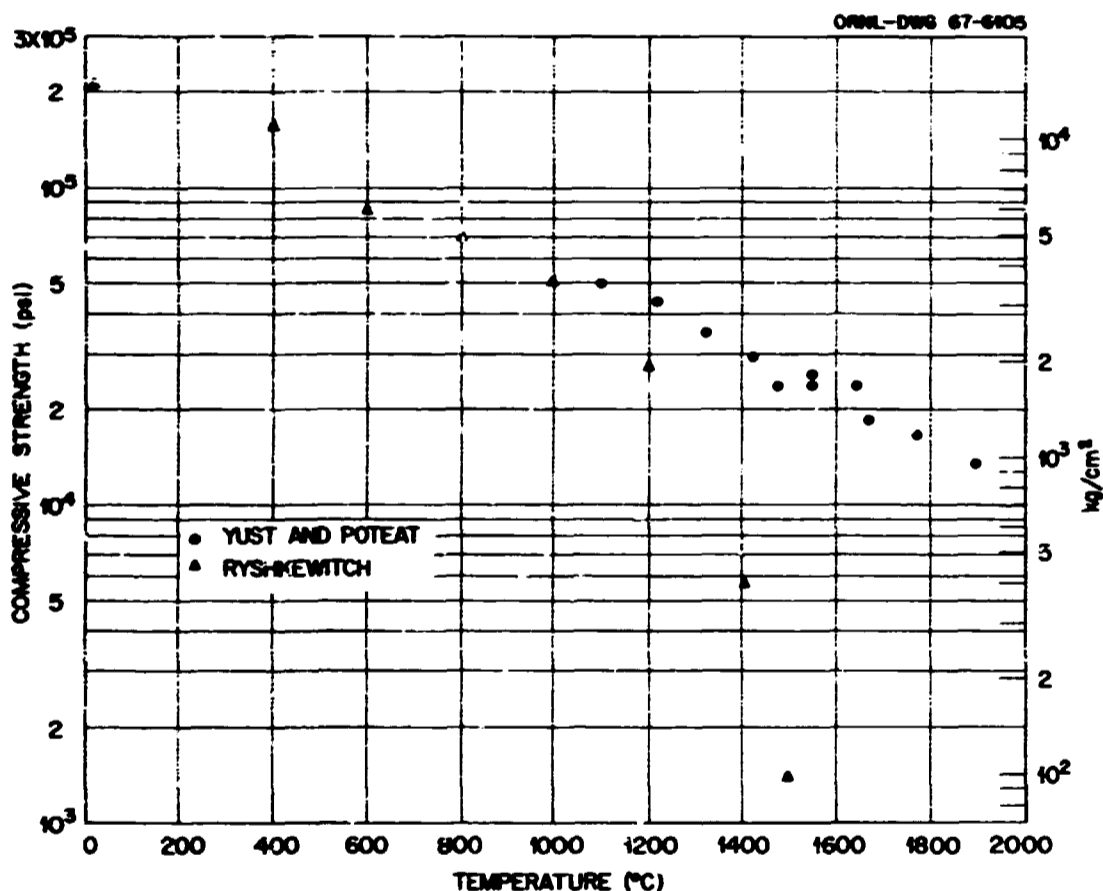


Fig. 16. Compressive Strength of Thoria at Elevated Temperatures. The data of Ryshkewitch⁷⁸ are for 99.5% pure material fired at 1950 $^{\circ}\text{C}$ in an oxidizing atmosphere and having 8% porosity. Yust and Poteat⁷⁹ isostatically pressed high-purity 0.5- μm powder at 17.5 tsi and fired in air at 1800 $^{\circ}\text{C}$ for 2 hr. Specimens had density 97.5% of theoretical and average grain diameter of 10 μm . To convert, 1 psi = 6895 N/m^2 .

Compressive Strength. — Compressive strengths of thoria measured at room temperature and elevated temperatures are presented in Table 11 and Fig. 16

respectively. The denser material retains much more strength above 1200 $^{\circ}\text{C}$.

Compressive Stress-Strain Relationships. — Morgan *et al.*⁸⁰ report compressive stress-strain curves for iso-statically pressed and sintered sol-gel ThO_2 at different temperatures; Fig. 17 shows their results. Figure 18 compares the 1450°C curve with comparable curves for uniaxially pressed and sintered oxalate ThO_2 of different densities.

Tensile Strength. — Ryskewitch⁷⁸ reports “just below 1000 kg/cm^2 ” ($14,000 \text{ psi}$, 10^8 N/m^2) for 2-mm-diam rods fired at 1950°C in an oxidizing atmosphere to a porosity of 8%.

Shear Strength. — Wygant⁸¹ tested, with a torsion apparatus, thoria isostatically pressed under $25,000 \text{ psi}$ ($1.7 \times 10^8 \text{ N/m}^2$) and fired to 1830°C for 5 hr to a density of 9.53 g/cm^3 . Strengths were 3500 psi ($2.4 \times 10^7 \text{ N/m}^2$) at 1100°C and 1200 psi ($8 \times 10^6 \text{ N/m}^2$) at 1300°C .

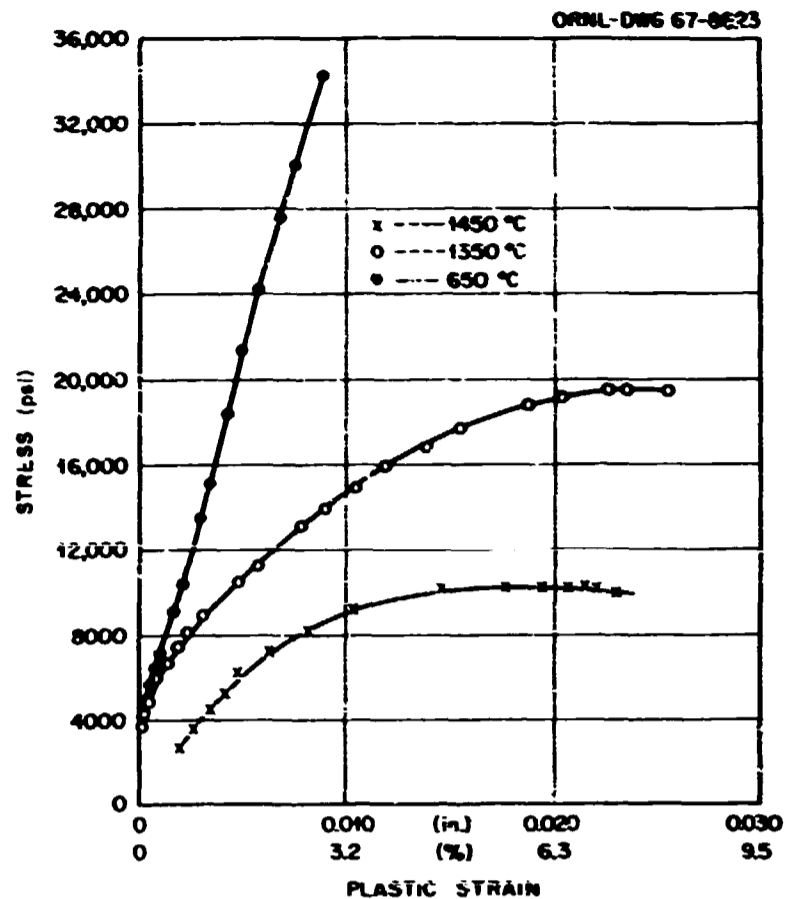


Fig. 17. Stress-Strain Relationships for 9.1-g/cm^3 Sol-Gel ThO_2 Pellets Tested at a Constant Compressive Strain Rate of 0.0007 in./min. Taken from Morgan *et al.*⁸⁰ To convert, $1 \text{ psi} = 6895 \text{ N/m}^2$.

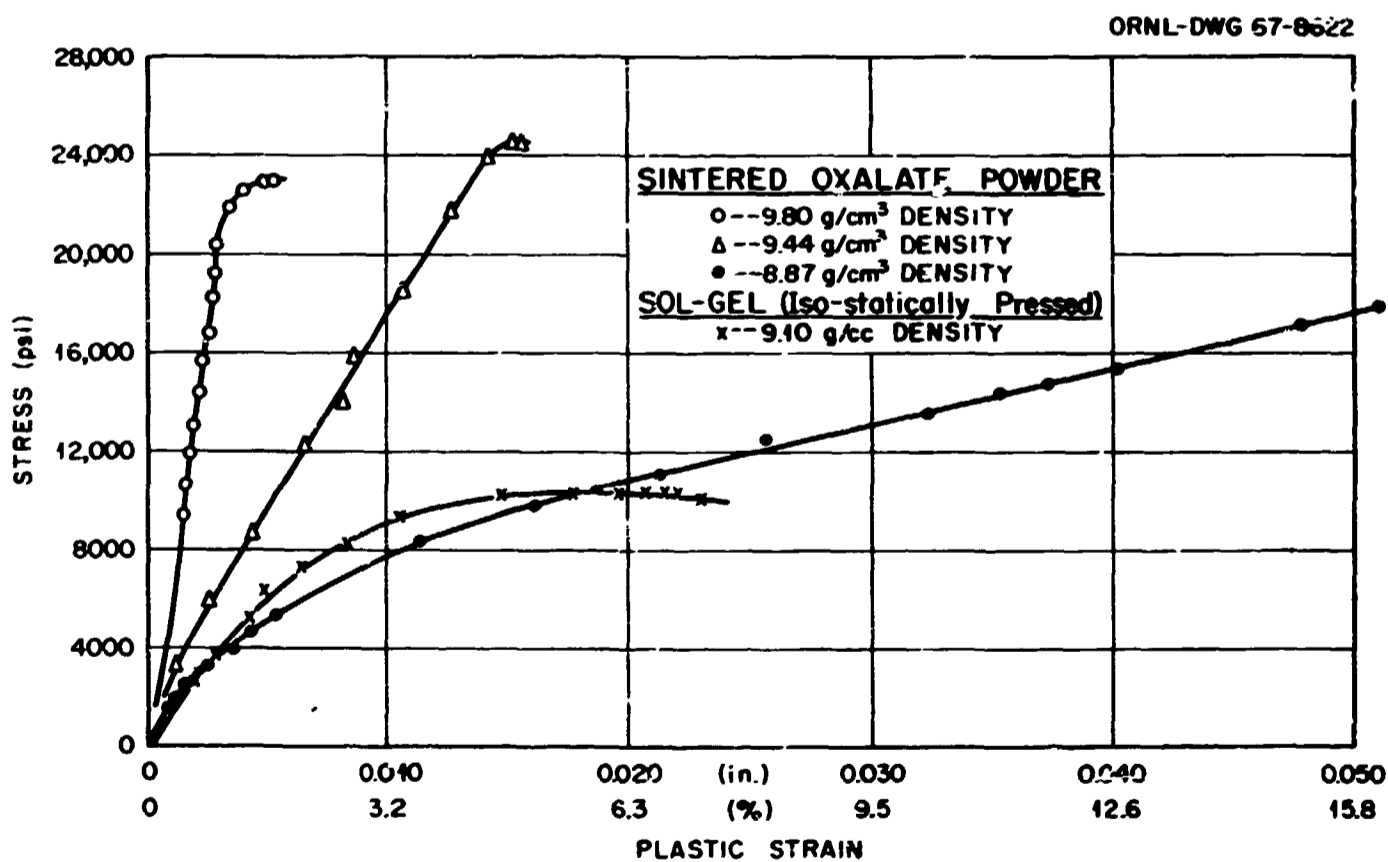


Fig. 18. Effect of Density on Stress-Strain Relationship for ThO_2 Pellets Tested at 1450°C with a Constant Compressive Strain Rate. Taken from Morgan *et al.*⁸⁰ To convert, $1 \text{ psi} = 6895 \text{ N/m}^2$.

Creep Rate. - Wygant⁸¹ found a torsional creep rate of 2.06×10^{-6} /hr at 1100°C under a load of 1200 psi (8.3×10^6 N/m²) for specimens similar to his shear strength specimens described above Poteat⁸² and Yust report the creep rates in Fig. 19 for specimens similar to their compressive strength specimens (Fig. 16), tested in compression by application of a constant load in the range 4000 to 11 000 psi (2.8 to 7.6×10^7 N/m²) at temperatures from 1400 to 1800°C. Wolfe and Kaufman⁸³ showed a striking effect of grain size on steady-state creep rate; their results are shown in Fig. 20 with comparable ORNL results. Morgan and Hall⁸⁴ found a compressive creep rate of 1.3×10^{-4} /hr at 1465°C and 8000 psi (5.5×10^7 N/m²) for cold-pressed bushings sintered 2 hr in air at 1800°C to density between 9.7 and 9.8 g/cm³. Incorporation of CaO decreased the creep strength considerably. They observed⁸⁵ creep at as low as 650°C for 9.1-g/cm³ sol-gel ThO₂. A creep curve for this material at 1500°C

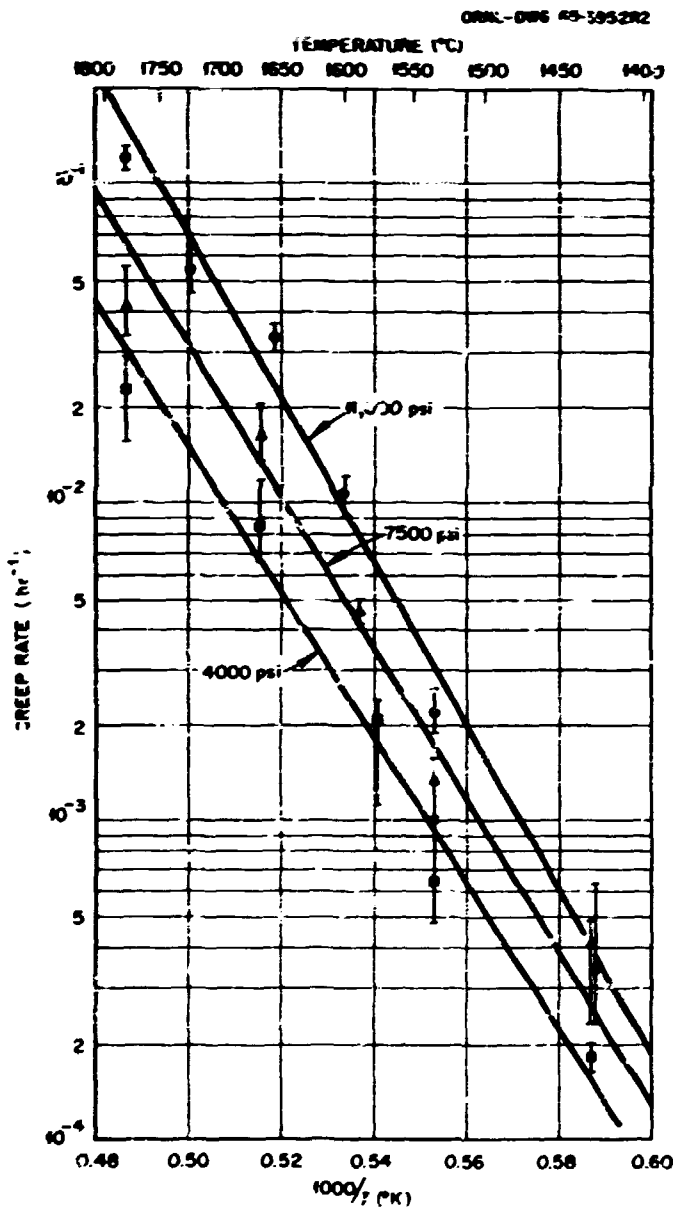


Fig. 19. Creep Rate of Thoria. Taken from Poteat and Yust.⁸² Specimens are like the same authors' specimens described in Fig. 17. The stresses are 28, 52, and 76 MN/m².

is compared⁸⁶ in Fig. 21 with a similar curve for oxalate-derived ThO₂. Kaufman⁸⁶ determined creep rates from data on hot pressing low-density specimens.

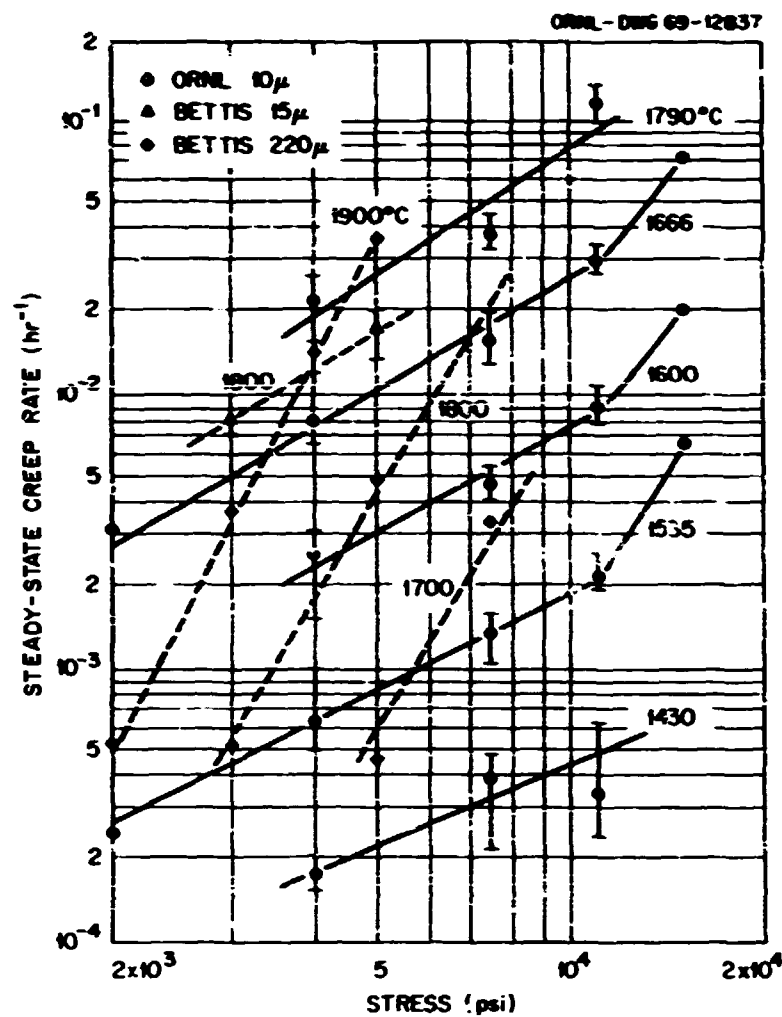


Fig. 20. Effect of Stress and Grain Size on Steady-State Creep Rate of High-Density Thoria. Taken from Wolfe and Kaufman.⁸³ Bettis results are by Wolfe on specimens cold pressed and sintered to a density 98.5% of theoretical; the large grain size was obtained by annealing 4 hr at 2300°C. The ORNL results are by Poteat and Yust, mostly reproduced,⁸² on specimens like those of Fig. 16. To convert, 1 psi = 6895 N/m².

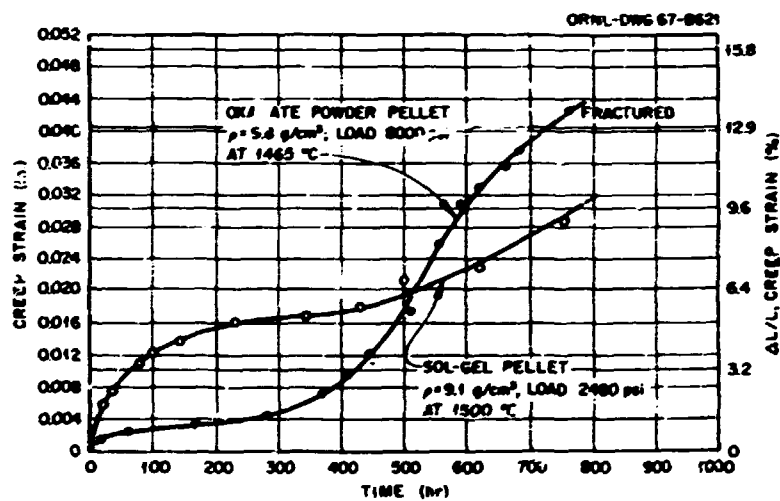


Fig. 21. Creep Curves for ThO₂ Pellets with Constant Compressive Loading. Taken from Morgan *et al.*⁸⁰ The loads are 55 and 17.1 MN/m².

Impact Strength. — Lang and Knudsen⁷⁶ found an average impact strength of 1.53 ft-lb/in.² (3.3 kg-cm/cm²) on unnotched Charpy specimens (dimensions 5.5 X 1.0 X 1.0 cm) of ThO₂-0.5% CaO pressed at 3000 psi (2.1 X 10⁷ N/m²), re-pressed hydrostatically at 30,000 psi (2.1 X 10⁸ N/m²), and fired 1 hr at 1800°C after slow heating.

Young's Modulus. — Like many other properties, the elastic constants of thoria depend on both porosity and other microstructural features. The most extensive measurements of Young's modulus at room temperature are by Spinner *et al.*,⁸⁷ in which the porosity was varied systematically in three series of samples. As shown in Fig. 22, the porosity dependence was greater for the material pressed from the finest powder. Other room-temperature values of Young's modulus are collected in Table 12. Elevated temperature measurements by Spinner *et al.*⁹⁰ are shown in Fig. 23 and those by

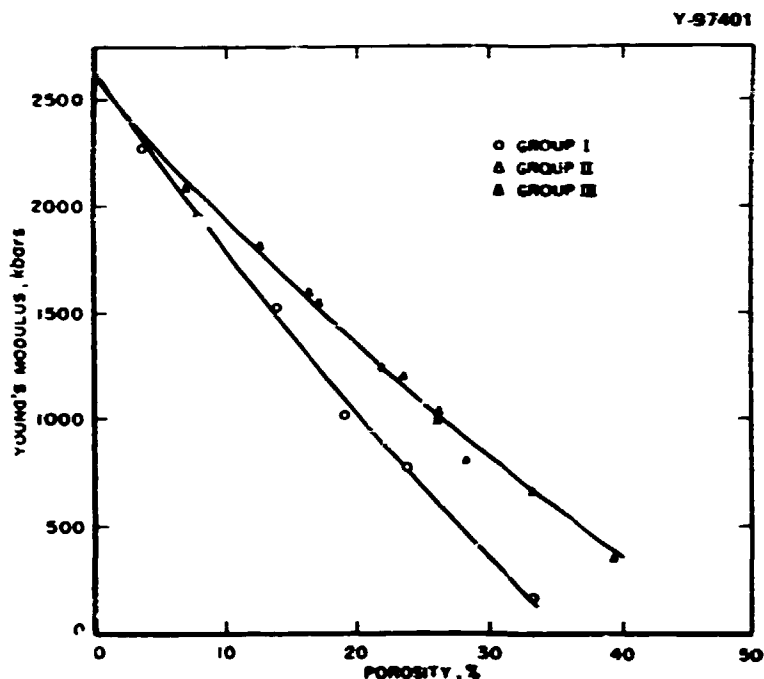
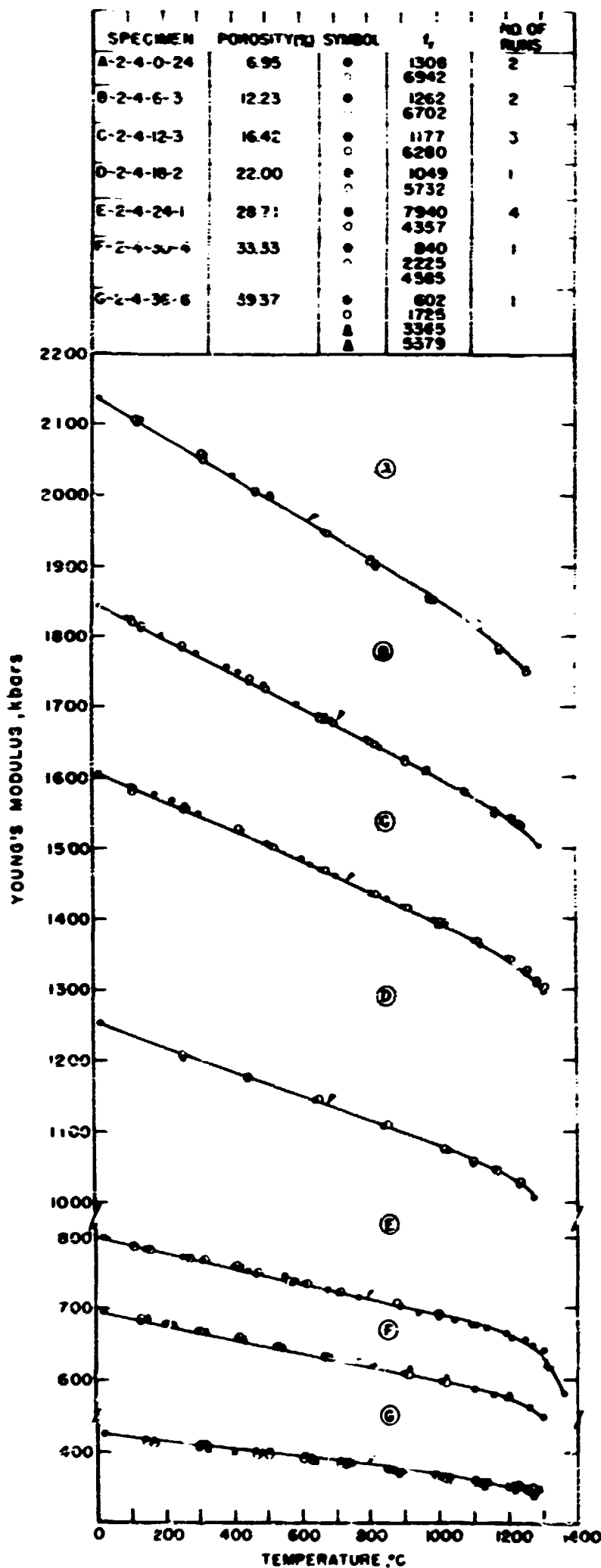


Fig. 22. Variation of Young's Modulus of ThO₂ with Porosity. Taken from Spinner *et al.*⁸⁷ Group I specimens were pressed from 0- to 2- μ m powder with cross-linked polystyrene beads added to introduce porosity on firing. Those of group II were similarly prepared from 2- to 4- μ m powder. Specimens of group III were prepared from powders of different particle sizes without filler. All were hydrostatically cold pressed and sintered at 1750°C for 17 hr. One bar is 14.5 psi, or 100,000 N/m².

Fig. 23. Variation of Young's Modulus of ThO₂ with Temperature for Different Porosities. From Spinner *et al.*⁹⁰ The values are for Group II specimens of Fig. 22; the temperature dependence was similar for other specimens. f_r is the flexural resonance frequency (fundamental or overtones). One bar is 14.5 psi, or 100,000 N/m².



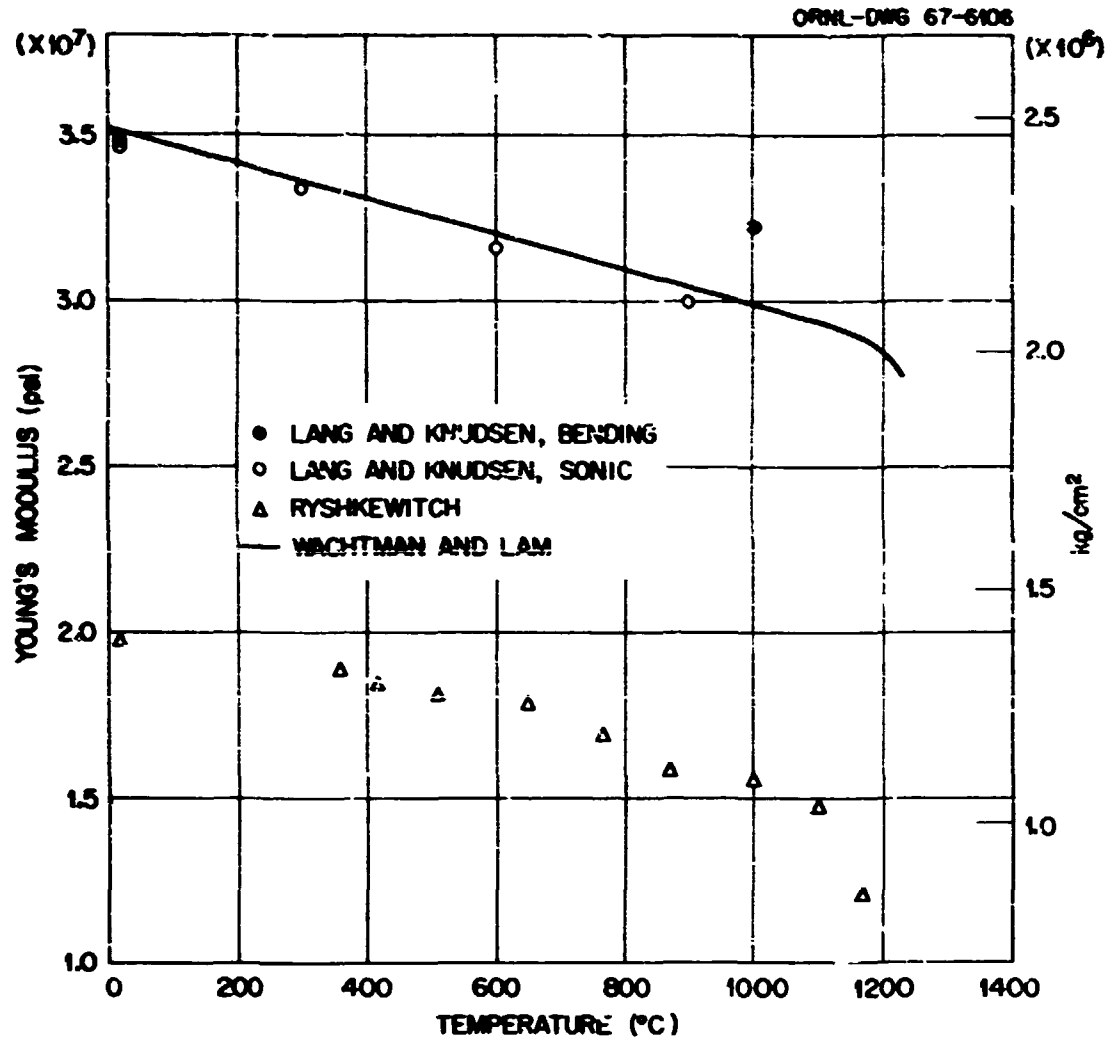


Fig. 24. Variation of Young's Modulus of ThO₂ with Temperature. Data of Lang and Knudsen,⁷⁶ Ryshkewitch,⁷⁸ and Wachtman and Lam⁸⁸ on specimens described in Table 12. To convert, 1 psi = 6895 N/m².

Table 12. Various Values of the Young's Modulus of ThO₂ at Room Temperature

Reference	Pressing		CaO (%)	Sintering Conditions			Porosity (%)	Measurement Method	Young's Modulus	
	Method	(tsi)		(°C)	(hr)	Medium			(psi)	(N/m ²)
78			0	1950		Oxidizing	8	Bending	19.8	1.37
76	Isostatic	15	0.5	1800	1	Oxidizing	0.9	Bending	34.8	2.40
76	Isostatic	15	0.5	1800	1	Oxidizing	0.9	Sonic	34.58	2.383
88	Commercial		0.5				1.4	Sonic	34.9	2.41
89	Commercial		0				9.3	Sonic	29.0	2.00
74	a	12.7	0	1400	2	Air	46.9	Sonic	7.3	0.50
				1600			27.8		12.8	0.88
				1800			17.6		19.6	1.35
			0.5	1600			17.2		20.7	1.43
				1800			0.0		20.9	1.44
			1.0	1600			12.8		19.9	1.37
				1800			0.0		33.9	2.34
			3.0	1400			35.1		10.7	0.74
				1800			0.0		43.6	3.01

^aSpecimens of Curtis and Johnson⁷⁴ were mixed with 2% dextrin and 5% H₂O, then pressed and sintered as indicated.

other investigators in Fig. 24. The measurements by Wachtman *et al.*⁸⁹ over the range -196 to 580°C are reported only to fit the equation

$$E = E_0 - BT \exp(-181/T),$$

where $E_0 = 2.0416 \times 10^{12}$ dynes/cm² (2.961×10^7 psi, 2.0416×10^{11} N/m²), $B = 2.73 \times 10^8$ dynes cm⁻² (°K)⁻¹ [3.96×10^3 psi/°K, 2.73×10^7 N m⁻² (°K)⁻¹], and T is the absolute temperature; their specimen is described in Table 12.

Shear Modulus. - The extensive measurements by Spinner *et al.* show effects of porosity, structure, and temperature similar to those found in their measurements of Young's modulus; values are in Fig. 25 for room temperature⁸⁷ and in Fig. 26 for elevated temperatures.⁹⁰ Other investigators' values are collected in Table 13.

Y-97398

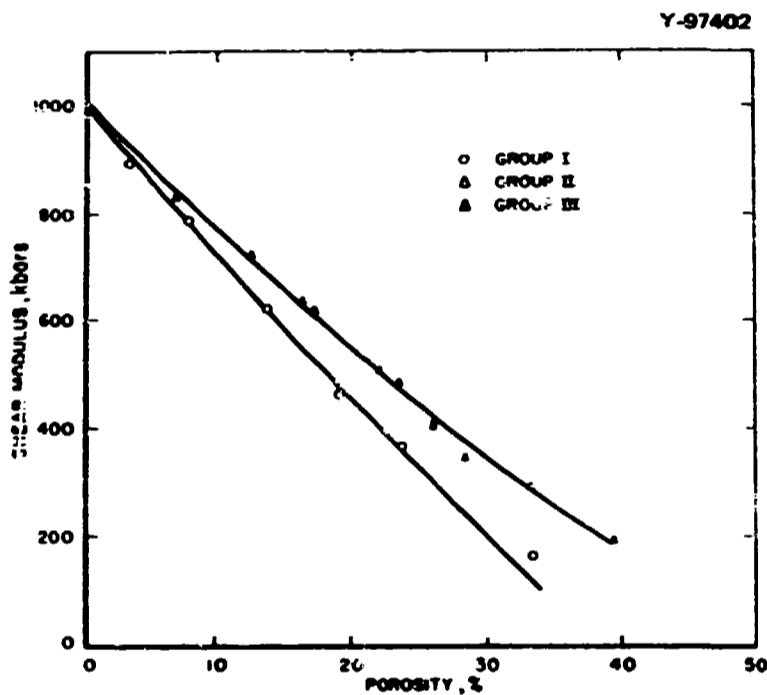
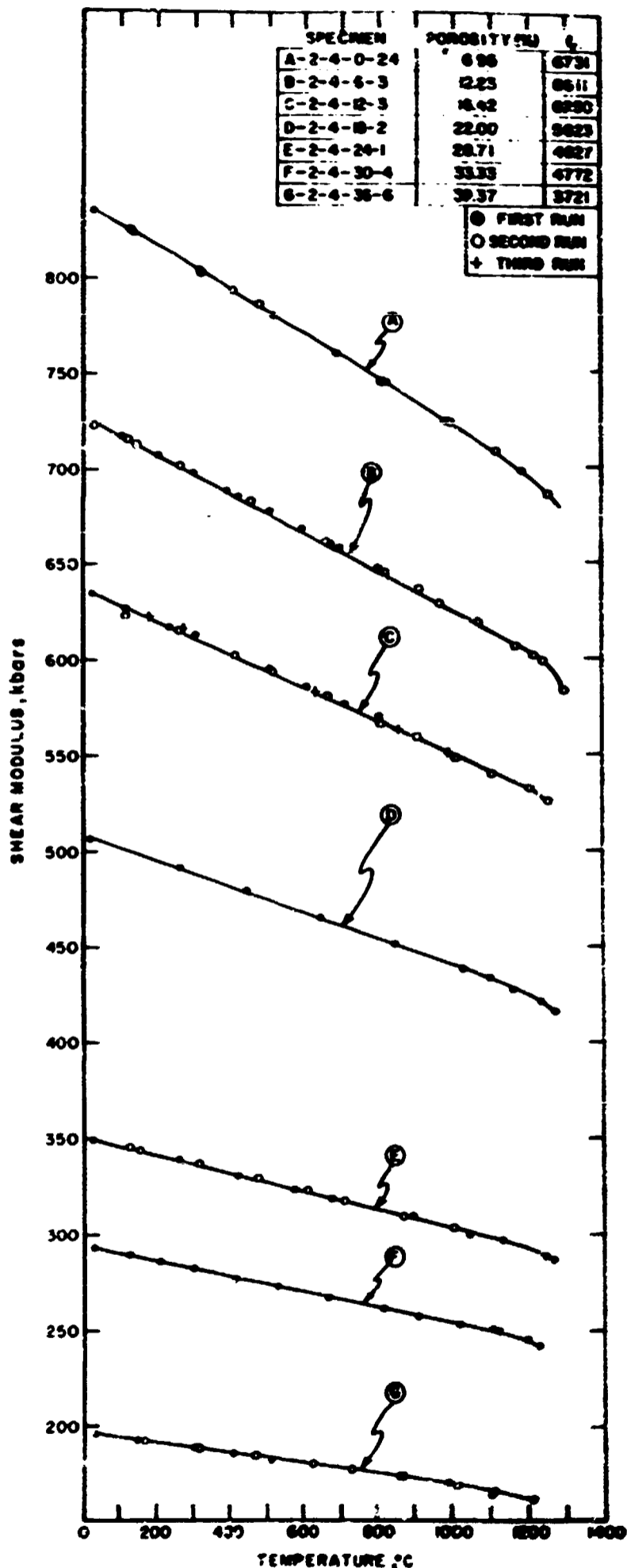


Fig. 25. Variation of the Shear Modulus of ThO₂ with Porosity. Taken from Spinner *et al.*⁸⁷ The specimens are described in Fig. 22. One bar is 14.5 psi, or 100,000 N/m².

Fig. 26. Variation of the Shear Modulus of ThO₂ with Temperature for Different Porosities. From Spinner *et al.*⁹⁰ The values are for Group II specimens of Fig. 22; the temperature dependence was similar for other specimens. f_r is the fundamental torsional resonance frequency. One bar is 14.5 psi, or 100,000 N/m².



Y-97402

Poisson's Ratio. — Values reported are collected in Table 13.

Bulk Modulus. — The value by Lang and Knudsen⁷⁶ is in Table 13.

Hardness. — Wolfe and Kaufman⁸³ have summarized two sets of Vickers hardness measurements on high-density thoria, as shown in Fig. 27. More details of the high-temperature set have appeared elsewhere.⁹² Finlay⁹³ reported a Knoop 100-g hardness of 945 kg/mm² for undescribed material. Lang and Knudsen⁷⁶ measured Knoop 500-g hardness on specimens of the ThO₂-0.5% CaO preparation used in several properties reported above. Values ranged from 330 to 810 about an average of 640. Within the wide spread in values, the hardness appeared independent of whether the specimen was unstressed or stressed, tested on a high-stress or no-stress area when stressed, or tested at room temperature or 1000°C. Wolfe and Kaufman⁸³ report mutual indentation hardnesses for two batches of thoria pellets as a function of load from 1000 to 2000°C; the batch with the larger grain size showed lower hardness and fractured at lower loads.

Cleavage. — Campbell *et al.*⁹⁴ found cleavage planes in a commercial 0.5-in. single crystal of thoria to be principally {100}. By electron microscopy of thoria platelets extracted from a deformed thoriated refractory alloy, Gilbert⁹⁵ found cleavage principally on {111} planes but occasionally on {011} or {201}.

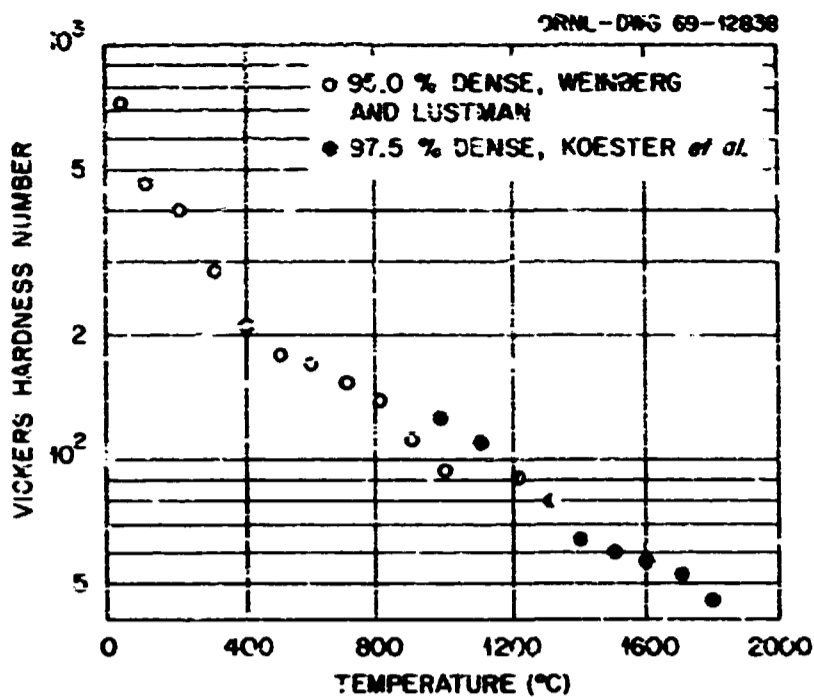


Fig. 27. Hardness of ThO₂. Reported by Wolfe and Kaufman⁸³ and attributed to J. G. Weinberg and E. Lustman of Westinghouse Atomic Power Department and to R. Koester *et al.* of Battelle Memorial Institute.

Table 13. Shear Modulus, Poisson's Ratio, and Bulk Modulus of ThO₂

Reference	Method (Shear)	Temperature (°C)	Shear Modulus		Poisson's Ratio	Bulk Modulus	
			(psi)	(N/m ²)		(psi)	(N/m ²)
			$\times 10^6$	$\times 10^{10}$		$\times 10^6$	$\times 10^{10}$
91 ^a	Bending	Room	8.5	5.9	0.17		
81 ^b	Torsion	30	14.3	9.8			
		700	11.4	7.9			
		1100	8.6	5.9			
		1300	5.6	3.9			
76 ^c	Sonic	Room	13.49	9.30	0.282	26.4	18.2
		300	13.0	9.0	0.28		
		600	12.3	8.5	0.28		
		900	11.7	8.1	0.28		

^aMaterial described for ref. 78 in Table 12.

^bMaterial described above under *Shear Strength*.

^cThO₂-0.5% CaO described for ref. 76 in Table 12.

9. Chemical Properties

Thermal Stability. — Thoria is exceedingly stable to quite high temperatures. Some decomposition to ThO and oxygen occurs^{30,32} on vaporization above 2000°C. Solid ThO on cooling in vacuum changes to metal and dioxide. Specimens so discolored (gray to black) by vacuum heating are restored to white by heating in air.^{30,33} The composition ThO_{1.998} is reported³² for thoria heated above 2500°C.

Reactions with Nonmetallic Solids. — Mixing of powdered thoria with various oxides and halides affects the densification on sintering at 1500°C after pressing.⁹⁶ Thoria combines in 20 hr in O₂ at 1200°C with Pa₂O₅ to form a single fluorite phase.⁹⁷ Heating pressed mixed compacts of ThO₂-30 vol % UN 25 hr in the range 600 to 1100°C gave no reaction.⁹⁸ Similar compacts did not react in 2 hr at 2400°C under 500 torr N₂, but the thoria dissolved the UO₂ impurity from the nitride.⁹⁹

Kroll and Schlechton¹⁰⁰ found that mixtures of thoria and graphite powders started to react in vacuum at 1380°C. Nadler and Kempter¹⁰¹ found a similar mixture to react in helium at 1650 to 1730°C. Greenwood¹⁰² found reaction between thoria and "retort carbon" at 1500°C in a poor vacuum (by modern standards). The differences may be due to

differences in subdivision, since Johnson¹⁰³ found a temperature of 2000°C required for reaction between large specimens of thoria and carbon in contact. The product is invariably a carbide and not thorium metal.

Benz¹⁰⁴ found reaction between ThO₂, ThN, and thorium to form Th₃N₄ and Th₂N₂O. Although some reaction occurred at 800 to 1200°C, 1550 to 2000°C was required to reach an equilibrium mixture that depended on the initial ThO₂ content.

Fries *et al.*¹⁰⁵ observed reaction between W₂C and ThO₂ at 2200°C or higher; melting occurred at 2400°C.

Compatibility of thoria with borides was tested⁵⁷ with duplex pellets of thoria with boride centers, made by simultaneously cold pressing the powders and sintering in hydrogen 4 hr at 1700°C. Heated in dry hydrogen for 1 hr at 2500 or 2700°C, compacts containing HfB₂ showed melting at both temperatures, while those with ZrB₂ did only at the higher temperature. Heated similarly in moist hydrogen, both borides formed a glassy product at 2400°C and reacted completely at 2600°C. Also, TiB₂ reacted completely at 2600°C.

Fired thoria bodies appear quite resistant to nearly all nonmetallic oxides. Some interactions reported¹⁰³ are: with BeO, liquid formation at 2100°C and complete fusion at 2200°C; with MgO, some vapor reaction at

Table 14. Interaction of Thoria with Liquid Metals

Metal	Reference	Result ^a
Bismuth	111	Slight attack ^b in 167 hr at 1000°C
Cerium	106	Cerium dissolved completely in thoria at 810 to 1000°C
Cobalt	112	No chemical reaction but complete penetration in 0.5 hr at 1930–2130°C
Iridium	113	Thoria crucibles withstood several meltings
Iron	112	No chemical reaction; 0.01 mm penetration in 0.5 hr at 1930–2280°C
Lanthanum	108	Penetrated grain boundaries at 950–1200°C
Platinum	114	Thoria crucibles withstood several meltings
Sodium	115	Less than 0.001 in. corrosion in 100 hr (<0.0025 cm)
	111	Practically no corrosion in 168 hr
Titanium ^c	116	Very little attack
Uranium	117	Darkened zone penetrated 8 mm in 1 hr
Bi-0.1% Mg-0.025% Zr	118	ThO ₂ slurry circulated 1376 hr without reaction at 460–550°C
Bi-0.54% Mg-0.025% Zr	118	ThBi ₂ plugged loop in 152 hr at 430–550°C
Pb-0.1% Mg-0.01% Zr	118	No reaction in 78 hr circulation of ThO ₂ slurry at 500–550°C
Pb-2.2% Mg-0.01% Zr	118	ThPb ₃ plugged loop in 89 hr at 360–550°C
Pb-46.7% Bi-0.1% Mg-0.01% Zr	118	No reaction in 2136 hr circulation of ThO ₂ slurry at 330–550°C

^aUnless otherwise indicated, result is for melting metal in contact with thoria.

^bCompilers note: since author reported color change from gray to white, reaction is probably just purification.

^cTitanium severely attacks Th-ThO₂ compacts.^{119,120}

2200°C, erosion but no adherence; with ZrO_2 , slight adherence at 2200°C, no liquid phase at 2300°C. Thoria specimens heated with silicon carbide powder 2 hr at 2000°C showed no visual, metallographic, x-ray diffraction, or microhardness evidence of interaction.¹⁰⁶

Reactions with Metals. - Thoria is unreactive to common metals under their conditions of use. It reacts with thorium to form ThO at 1850°C and above; the reaction is reversed on cooling.³⁰ That calcium reduces thoria is well-known. Molten Zn-5% Mg at 750 to 850°C reduces thoria,¹⁰⁷ and so do solutions of

Table 15. Interaction of Thoria with Solid Metals

Metal	Reference	Exposure			Result
		(°C)	(hr)	Medium	
Beryllium	121	1400	0.25		No reaction
		1600	0.25		Some penetration of thoria
Iridium	122	1800-2300		Vacuum	Thoria blackened; attributed to tungsten present
Molybdenum	121	1800	0.25		No reaction
	103	1900	0.07		Visible reaction (but little reaction to 2300°C)
	123	2155			Reacts on rapid heating to this temperature
Nickel	121	1800	0.25		No reaction
Niobium	124	1540	1000		No reaction
	121	1800	0.25		Some corrosion
	123	2135			No reaction on rapid heating to temperature
Rhenium	125	2350	2	Vacuum	No reaction
	123	1350			Initial reaction on rapid heating; no rapid reaction to 2280°C
Silicon	121	1400	0.25		Slight reaction
		1600	0.25		Grain-boundary penetration and grain discoloration
Tantalum	124	1540	1000		No reaction
	24	2500			Very little attack to Ta on prolonged use with ThO ₂
	123	2795			No reaction on rapid heating to temperature
	105	2550	1		No reaction with ThO ₂ in capsule, C + H ₂ outside
	105	2600	1		Severe reaction, ThO ₂ in capsule, C + H ₂ outside
Titanium	121	1400-1800	0.25		Slight reaction
Tungsten	103	2200	0.07		Visible reaction ^d
	125	2350	2		No reaction
	122	2350-2400	Several		Thoria severely pitted ^d
	30	2100-2400			No reaction of equimolar mixture; 2 hr at peak temperature ^d
	99	2400			No reaction
	27	1900-2600			ThO ₂ satisfactorily contained in W crucibles during prolonged experiments ^d
	123	2645			No reaction on rapid heating to temperature
	105	2100	1		No reaction with ThO ₂ in capsule, C + H ₂ outside
Zirconium	121	1800	0.25		Very slight corrosion
Mo-40% Re	125	2350	2	Vacuum	No reaction
Nb-1% Zr	124	1540	1000		No reaction
W-5% Re	124	1540	1000		No reaction
W-26% Re	124	1540	1000		No reaction
	126	2215-2290	168		No reaction

^dHoch and Johnson³⁰ and Ackerman *et al.*³² attribute previously observed reactions of ThO₂ with tungsten, respectively, to decomposition of ThO₂ to ThO followed by disproportionation of ThO and to reduction of ThO₂ by carbon impurity in the tungsten.

calcium and magnesium in molten bismuth.⁵ Mixed with thoria powder, cerium reacted slightly at 500°C and extensively at 810°C; at 600 and 924°C lanthanum dissolved in the thoria.¹⁰⁸ Novak and Asano¹⁰⁹ found no interaction of ThO₂ insulation with tungsten-rhenium thermocouples in prolonged tests to over 2800°C and in a nuclear reactor¹¹⁰ to 1200 hr over 2300°C. Other behavior of thoria with liquid and solid metals is summarized in Tables 14 and 15 respectively.

Reaction with Liquids. — Dissolution reactions of thoria have been collected by Bachman and Banks.¹²⁷ In summary, thoria that has not been heated over 550 or 600°C will dissolve readily in 8 to 16 M HNO₃ with a small amount of fluoride present. Increasing the firing temperature makes dissolution more difficult. Oxide ignited at over 1000°C requires concentrated nitric acid 0.03 M in fluoride at 100°C, and dissolution is slow. Digestion with fuming sulfuric acid or fusion with NaHSO₄ or Na₂S₂O₇ converts ThO₂ to the water-soluble sulfate. Hydrochloric acid, even with added fluoride, is ineffective toward high-fired ThO₂.

Small samples of ThO₂ can be dissolved in 36% HCl with added HClO₄ at 310°C in a sealed tube.¹²⁸ Thoria ignited at 2000°C can be converted by fusion with ammonium bisulfate to a clear melt that is soluble in sulfuric acid.¹²⁹ Bishop *et al.*¹³⁰ dissolved thoria (both unirradiated and irradiated) in 1 to 8 hr in refluxing 13 M HNO₃–0.05 M HF. Phillips and Huber¹³¹ have related dissolution rate to the concentrations of titanium nitrate, aluminum nitrate, and hydrofluoric acid. Russell *et al.*¹³² showed that thoria dissolves three to six times as fast if 1% MgO is incorporated in it.

Reaction with Gases. — Thoria is apparently stable to most gases up to its melting point. Exposed to air at low temperature,⁵ it picks up water and carbon dioxide. The water escapes below 150°C; the CO₂ requires higher temperatures. The carbon dioxide pick-up is substantial for unfired powder, is decreased 75% by firing at 1400°C, and is nearly eliminated by firing at 1800°C. Grossman and Kaznoff¹³³ report no interaction of thoria with cesium vapor in 300 hr at 1 torr (500 N/m²) to 1600°C.

10. Surface Properties

Surface Energy. — Benson *et al.*¹³⁴ have calculated cohesive and surface energies of thoria from atomic and structural parameters. Their estimates for the surface energy are 810 and 1150 ergs/cm² by different methods. Lively and Murray¹³⁵ estimate a value of 530 ergs/cm² to ±20%. All values are for 0°K.

Interaction with Aqueous Systems. — Heats of immersion of thoria in water were measured by Holmes *et al.*¹³⁶ The data shown in Fig. 28 reveal a complex dependence on the specific surface area, crystallite size, and temperature of prior outgassing. The latter effect reflects reversal of the removal of chemisorbed water during outgassing. After being outgassed at 500°C, some of the samples were measured for heat of immersion as a function of presorbed water content, and the functions were differentiated to give differential heats of immersion. The samples are described in Table 16.

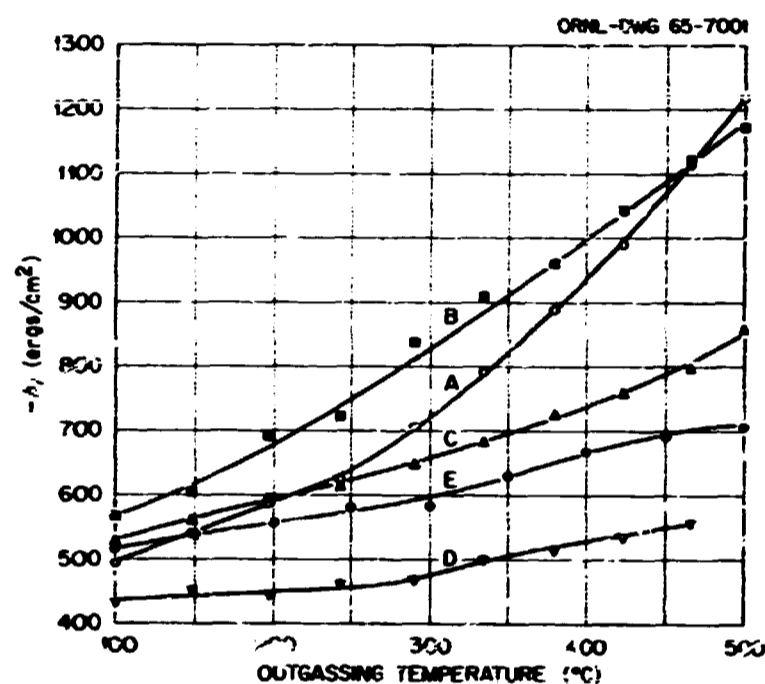


Fig. 28. Heat of Immersion of ThO₂ in Water at 25.0°C. From Holmes *et al.*¹³⁶ Copyright by the American Chemical Society; reprinted with permission.

Table 16. Characteristics of ThO₂ Samples for Heat of Immersion Measurements¹³⁶

Sample	Calcining Temperature (°C)	Nitrogen Surface Area (m ² /g)	Geometric Mean Particle Diameter (μm)	Crystallite Size (Å)
A	650	14.7	2.63	194
B	800	11.5	2.67	220
C	1000	5.64	2.20	682
D	1200	2.20	2.97	1700
E	1600	1.24	1.20	2500

The interaction of thoria surfaces with various aqueous electrolyte solutions has been studied electrokinetically and expressed in terms of zeta potentials and other properties.¹³⁷⁻¹³⁹ Fuller *et al.*¹⁴⁰ used infrared absorption to find that water on thoria surfaces exists in four forms.

Wetting by Liquid Metals. — Table 17 lists information on the wetting of thoria by liquid metals.

Absorption of Gases. — Holmes *et al.*¹⁴⁴ measured adsorption of water, nitrogen, and argon on various thoria powders. Adsorbed water was a very important factor in the adsorption of the gases.

Table 17. Wetting of Thoria by Liquid Metals

Metal	Reference	Reported Temperature (°C) of —		Other Information in Reference
		Nonwetting ^a	Wetting ^a	
Aluminum	141		>900	
Beryllium	141		>1000	
Bismuth	141		>1000	
	5	<1100 ^b		
Cadmium	141		>800	
Calcium	141		>1000	
Cerium	108		>1000	c
Cobalt	112		1930–2130	
Copper	141		>1250	
Iron	142	1550		c, d, e
	143	<1800	>1800	c
Lanthanum	108		950–1200	c, d
Lead	141		>1000	
Magnesium	141		>1000	
Mo–40% Re	143		2500–2750 ^f	c
Nickel	142	1500		c, d, e
Platinum	143		1770–2240	c
Rhodium	143	1940	1990–2250	c
Silicon	141		>1000	
Silver	141		>1000	
Sodium	141		>400	
Tin	141		>1200	
Uranium	117	Mp		
U–4% Mo	117	Mp		
U–4.6% Re	117	Mp		
Vanadium	143		>1970	c
Zirconium	141		>1000	

^aUnless wetting or nonwetting is cited by the author, wetting is taken as occurring if the contact angle is less than 90°.

^bBismuth containing low concentrations of metals that reduce CO₂ would wet thoria.⁵ Such metals are Al, Ba, Ca, Fe, Mg, Na, Th, Ti, U, Zn, and Zr.

^cContact angle.

^dWork of adhesion.

^eSurface tension.

^fBarely wetting; contact angles near 90°.

B. Thorium-Uranium Oxides

1. Composition

The dioxides of thorium and uranium form a continuous series of solid solutions over the entire range of composition. Such properties as melting point and lattice parameter reflect near-ideal solution behavior over nearly the whole range; sharp negative deviations occur in a narrow range near 98% UO_2 . Neeb and Peehs¹⁴⁵ demonstrated that a temperature gradient at very high temperature induced a composition gradient in $(\text{Th,U})\text{O}_2$; uranium migrated from a 2500°C region to a 2090°C region.

Heated in air or other oxidizing media the mixed dioxides can take up oxygen to an extent that depends on temperature and oxygen activity and increases with uranium content. An example by Claudel and Brau¹⁴⁶ is given in Table 18. This oxidation occurs without a phase change until the uranium oxide content exceeds 50 or 60%. Uranium-rich oxide can form a second phase of, or similar to, U_3O_8 . Figure 29 shows the limiting compositions given by Gilpatrick *et al.*¹⁴⁷ Other data on the system are given by Gilpatrick and Secoy,^{148,149} Gilpatrick *et al.*,¹⁵⁰ Friedman and Thoma,¹⁵¹ Cohen and Berman,¹⁵² Lynch,¹⁵³ and Christensen.¹⁵⁴ The compounds $\text{Th}_2\text{U}_2\text{O}_9$ (ref. 155) and UThO_5 (ref. 156) have been identified under special conditions, but no compounds appear to form for the compositions and conditions of nuclear use.

Table 18. Effect of Uranium Content and Heat Treatment on the Composition of $\text{Th}_{1-y}\text{U}_y\text{O}_{2+x}$
From Claudel and Brau¹⁴⁶

y, Uranium Fraction	x, Oxidation	
	As Prepared ^a	Treated ^b
0.0112	0.0071	0.0060
0.028	0.019	0.016
0.052	0.036	0.032
0.065	0.047	0.042
0.094	0.071	0.062
0.192	0.151	0.133

^aFrom mixed oxalate by calcination 24 hr in air at 500°C.

^bHeated 4 hr in air at 400°C, then 24 hr at 450°C and 10^{-6} torr.

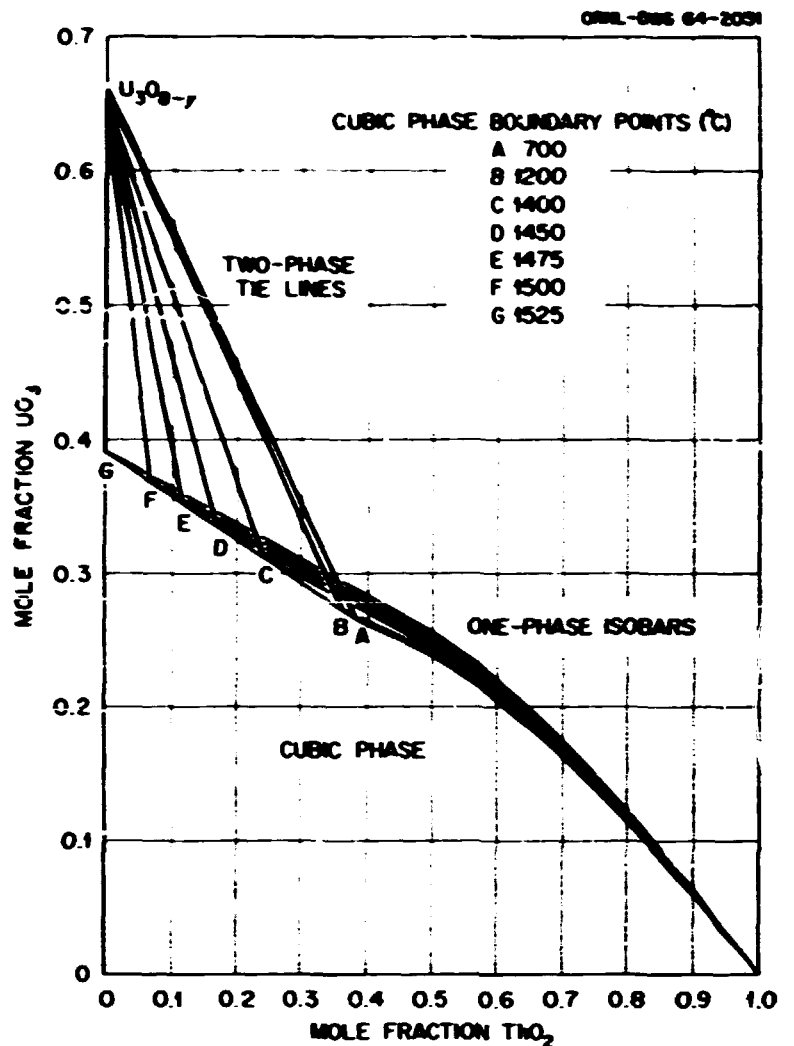


Fig. 29. Limiting Composition of Phases in the Thorium Oxide-Uranium Oxide System. Taken from Gilpatrick *et al.*¹⁴⁷

2. Preparation

Thorium-uranium mixed oxides can be prepared by the calcination of solid solutions such as $(\text{Th,U})(\text{C}_2\text{O}_4)_2$ precipitated from thorium-uranium(IV) solutions or by the sol-gel method. Ceramic bodies may be fabricated from such mixed oxides or from mixtures of thorium and uranium dioxide powders by the same consolidation and firing methods used for pure thorium. Firing temperatures are affected by the composition. Firing must be in inert gas, vacuum, or hydrogen if the oxide is to be stoichiometric (unoxidized).

3. Crystal Properties

Structure. — The $\text{ThO}_2\text{-UO}_2$ solid solutions have the cubic fluorite structure of ThO_2 , with uranium atoms substituted for thorium atoms. In oxidized solid solutions, the added oxygen atoms are in the octahedral interstices. Highly oxidized uranium-rich oxide contains the second phase orthorhombic U_3O_8 or in some cases the cubic U_4O_9 .

Lattice Parameter and Density. — Considerable variation exists among most reported values of the lattice parameters of thoria-urania solid solutions, probably reflecting unrecognized variations in purity or oxidation. Cohen and Berman¹⁵² appear to have maintained good control of these variables; Table 19 gives their values for the lattice parameter of stoichiometric oxides and corresponding theoretical densities. Their parameters for oxidized thoria-rich solid solutions are plotted in Fig. 30 and compared with an empirical equation that correlates them. Kempter and Elliott⁴ have measured the lattice parameter of a mixed oxide as a function of temperature. From the preparation method, their material is very likely stoichiometric equimolar $\text{ThO}_2\text{-UO}_2$, although this was not verified by analysis. Their values are listed in Table 20 and are correlated by the equation

$$a_0 = 5.53298 + 4.882 \times 10^{-5}t + 7.35 \times 10^{-9}t^2.$$

Table 19. Lattice Constants and Theoretical Densities of $(\text{Th,U})\text{O}_2$
From ref. 152

Composition (mole % UO_2)	Lattice Parameter ^a (Å)	Theoretical Density (g/cm^3)
100	5.4704	10.96
90.0	5.4341	10.65
80.1	5.4969	10.75
69.9	5.5098	10.65
60.1	5.5225	10.55
50.1	5.5355	10.46
40.3	5.5475	10.37
30.1	5.5590	10.28
20.2	5.5726	10.18
10.1	5.5846	10.09
0	5.5975	10.00

^aStandard error of deviation ± 0.0003 Å.

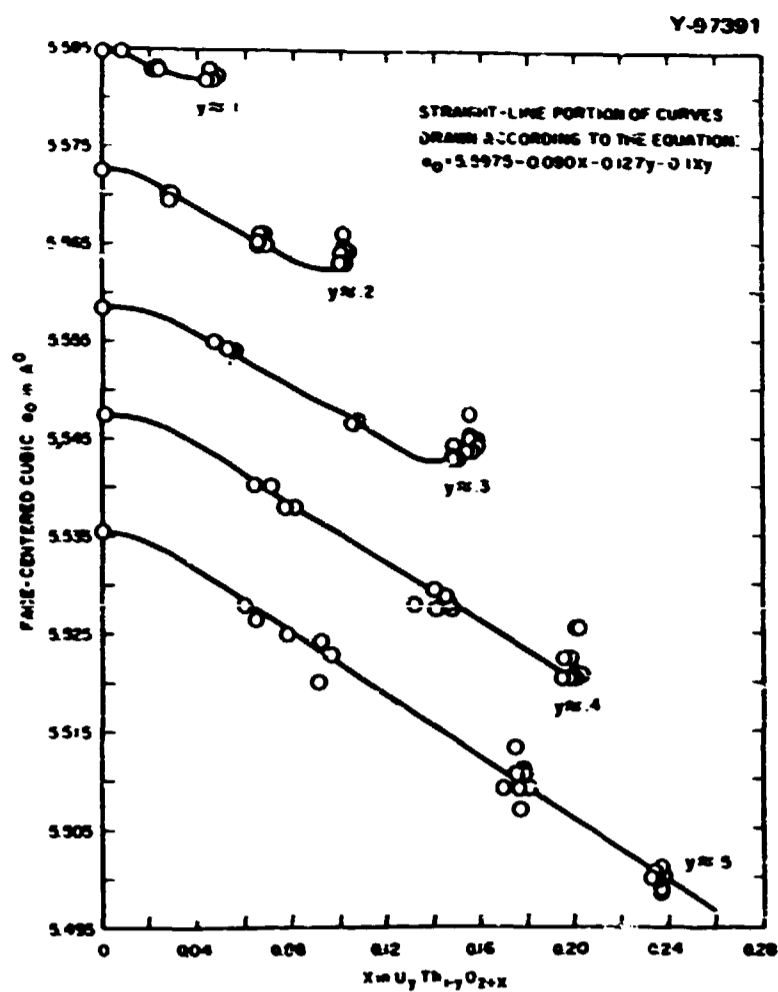


Fig. 30. Change of Lattice Parameter with Oxidation in $\text{Th}_{1-y}\text{U}_y\text{O}_{2+x}$. From Cohen and Berman.¹⁵² Copyright by North-Holland Publishing Company and reproduced with permission.

Table 20. Lattice Constant of Equimolar $\text{ThO}_2\text{-UO}_2$
From ref. 4

Temperature (°C)	a_0 (Å)
13	5.5337
19	5.5343
95	5.5376
195	5.5426
290	5.5476
389	5.5534
488	5.5582
583	5.5642
682	5.5699
776	5.5753
875	5.5809
942	5.5857

Table 21. Thermal Expansion Coefficients of (Th,U)O₂

UO ₂ (%)	Reference	Coefficient	Range (°C)	Value [(°C) ⁻¹]
6.4	157	Mean	25-800	9×10^{-6}
20	157	Mean	25-800	8×10^{-6}
50	4	Mean	26- <i>t</i>	$8.8553 \times 10^{-6} + 1.229 \times 10^{-9}t$
50	4	Instantaneous	26-1000	$8.821 \times 10^{-6} + 2.658 \times 10^{-9}t$

Thermal Expansion. — Reported thermal expansion coefficients for (Th,U)O₂ are listed in Table 21. Thermal expansion measured by Springer *et al.*¹³ is given in Table 22, and that by Turner and Smith¹⁵⁸ for ThO₂-9% UO₂ is fitted by:

$$\begin{aligned} \text{Percent expansion} = & 9.99 \times 10^{-4}(t - 20) \\ & - 2.45 \times 10^{-7}(t - 20)^2 \\ & + 2.33 \times 10^{-10}(t - 20)^3 \pm 0.0125, \end{aligned}$$

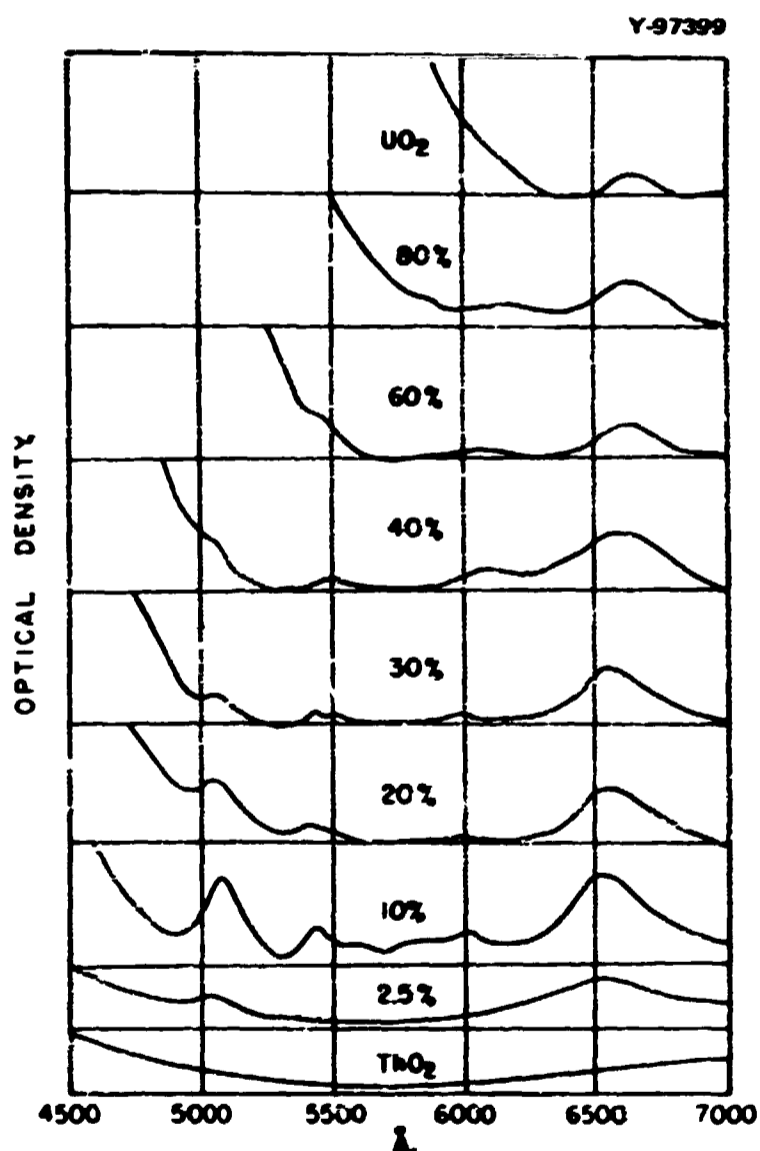


Fig. 31. Absorption Spectra of (Th,U)O₂. From Gruen.¹⁶⁰ Copyright by the American Chemical Society; reprinted with permission.

where *t* is in °C.

Refractive Index. — Table 23 lists values by Thoma and Weaver.¹⁵⁹

Absorption Spectra. — Absorption spectra of ThO₂-UO₂ mixtures pressed and fired in hydrogen 8 hr at 1750°C were measured by Gruen¹⁶⁰ and are reproduced in Fig. 31.

Table 22. Thermal Expansion of (Th,U)O₂
From ref. 13

Temperature (°C)	Linear Expansion (%)	
	10.3% UO ₂	20.4% UO ₂
20	0	0
200	0.17	0.16
400	0.36	0.35
600	0.57	0.55
800	0.77	0.76
1000	0.99	0.99
1200	1.21	1.22
1400	1.44	1.47
1600	1.67	1.72
1800	1.90	1.98
2000	2.14	2.24

Table 23. Index of Refraction of (Th,U)O₂
From ref. 159

UO ₂ Content (mole %)	Index of Refraction	
	Type 1 ^a	Type 2 ^b
0	2.10	2.11
10	2.11	2.11
20	2.15	2.11
30	2.17	2.14
40	2.18	2.16
50	2.21	2.18
60	2.22	2.22
70	2.25	2.22
80	2.28	2.25
90	2.34	2.30
100	2.36	2.36

^aMixed powders fired 2 hr in H₂ at 1750°C.

^bCoprecipitated mixtures fired in H₂ at 1100°C.

4. Thermodynamic Properties

Table 24 gives specific heats of $(\text{Th,U})\text{O}_2$ measured by Springer *et al.*¹³

The most extensive measurements of the partial molal thermodynamic quantities for solution of oxygen in

Table 24. Specific Heats of $(\text{Th,U})\text{O}_2$
From ref. 13

Temperature (°C)	[cal g ⁻¹ (°C) ⁻¹]		[J g ⁻¹ (°C) ⁻¹]	
	10.3% UO ₂	20.4% UO ₂	10.3% UO ₂	20.4% UO ₂
0	0.056 ₂	0.056 ₁	0.236	0.235
100	0.061 ₁	0.061 ₅	0.255	0.257
200	0.063 ₂	0.064 ₂	0.266	0.268
400	0.066 ₂	0.067 ₂	0.280	0.281
600	0.068 ₀	0.069 ₁	0.285	0.289
800	0.069 ₆	0.070 ₇	0.291	0.296
1000	0.071 ₁	0.072 ₂	0.297	0.302
1200	0.072 ₅	0.073 ₅	0.303	0.307
1400	0.073 ₈	0.074 ₃	0.309	0.313
1600	0.075 ₂	0.076 ₂	0.315	0.319
1800	0.076 ₅	0.077 ₅	0.320	0.324
2000	0.077 ₈	0.079 ₇	0.325	0.329

Table 25. Partial Molal Thermodynamic Quantities for Solution of Oxygen at 1250°K in $\text{Th}_{1-y}\text{U}_y\text{O}_{2+x}$

From ref. 161

y	x	\bar{G}_{O_2}		\bar{S}_{O_2}		\bar{H}_{O_2}	
		kcal/mole	kJ/mole	cal/mole °K	J/mole °K	kcal/mole	kJ/mole
0.90	0.042	51.8	217	8	33	62	259
0.90	0.042	52.4	219	13	54	69	288
0.90	0.076	48.7	204	17	71	70	293
0.90	0.081	48.4	202	17	71	70	293
0.90	0.123	44.7	187	23	96	73	305
0.90	0.126	44.7	187	21	88	71	297
0.90	0.157	40.7	170	29	121	77	322
0.71	0.046	50.9	213	14	59	68	284
0.71	0.049	50.9	213	14	59	68	284
0.71	0.084	47.2	197	21	88	74	310
0.71	0.092	46.9	196	28	117	82	343
0.71	0.121	44.0	184	34	142	85	356
0.71	0.133	42.9	179	29	121	80	334
0.71	0.152	40.3	168	34	142	83	347
0.71	0.154	40.2	168	35	146	84	351
0.52	0.044	47.5	199	20	84	72	301
0.52	0.045	46.8	196	22	92	74	310
0.52	0.079	43.4	182	22	92	72	301
0.52	0.087	44.4	186	31	130	83	347
0.52	0.119	39.8	166	35	146	84	351
0.52	0.122	39.5	165	34	142	82	343
0.52	0.152	35.7	149	40	167	85	356
0.52	0.152	35.2	147	35	146	78	326
0.29	0.019	45.4	190	22	92	72	301
0.29	0.027	43.2	181	19	79	67	280
0.29	0.046	37.3	156	24	100	67	280
0.29	0.053	36.2	151	26	105	69	288
0.29	0.053	36.8	154	30	125	74	297
0.29	0.069	33.5	140	30	125	71	297
0.29	0.073	33.1	138	34	142	76	318

thorium-uranium oxides are those of Aronson and Clayton¹⁶¹ listed in Table 25. Figure 32 is their plot of equilibrium oxygen pressures derived from these values. Figure 33 shows Roberts¹⁶² partial molal quantities for oxygen in $\text{Th}_{1-y}\text{U}_y\text{O}_{2+x}$ for $x/y = 0.175$ at an unspecified temperature. Table 26 lists the partial molal heats of solution and equilibrium oxygen pressures of Roberts *et al.*,¹⁶³ and Fig. 34 shows the oxygen pressures of Anderson *et al.*¹⁶⁴

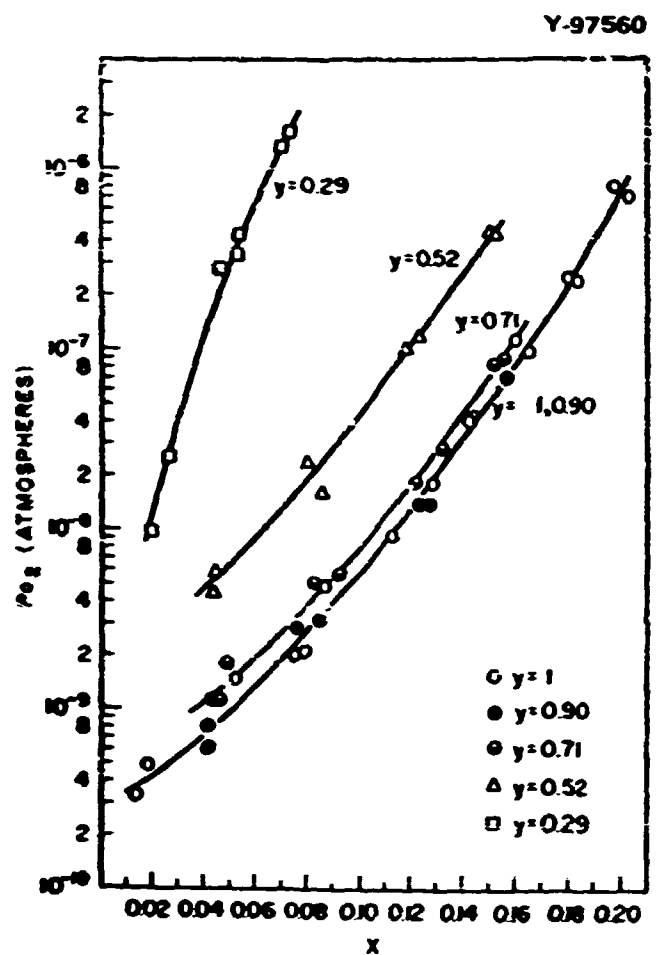


Fig. 32. Pressures of Oxygen in Equilibrium with $\text{Th}_{1-y}\text{U}_y\text{O}_{2+x}$ at 1250°C. From Aronson and Clayton.¹⁶¹ Copyright by the American Institute of Physics; reprinted with permission. To convert, 1 atm = 101,325 N/m².

Table 26. Partial Molal Enthalpy and Equilibrium Oxygen Pressures for Thorium-Uranium Oxide

From ref. 163

UO ₂ Content (mole %)	\bar{H}_{O_2}		P_{O_2} at 850°C	
	(kcal/mole)	(kJ/mole)	(torr)	(N/m ²)
0.53	14.5	61	30	4000
0.76	17.5	73	20	2700
1.2	25	105	16	2100
1.87	33	138	5	670
3.3	35	146	1	130
5.97	44	184	0.13	17

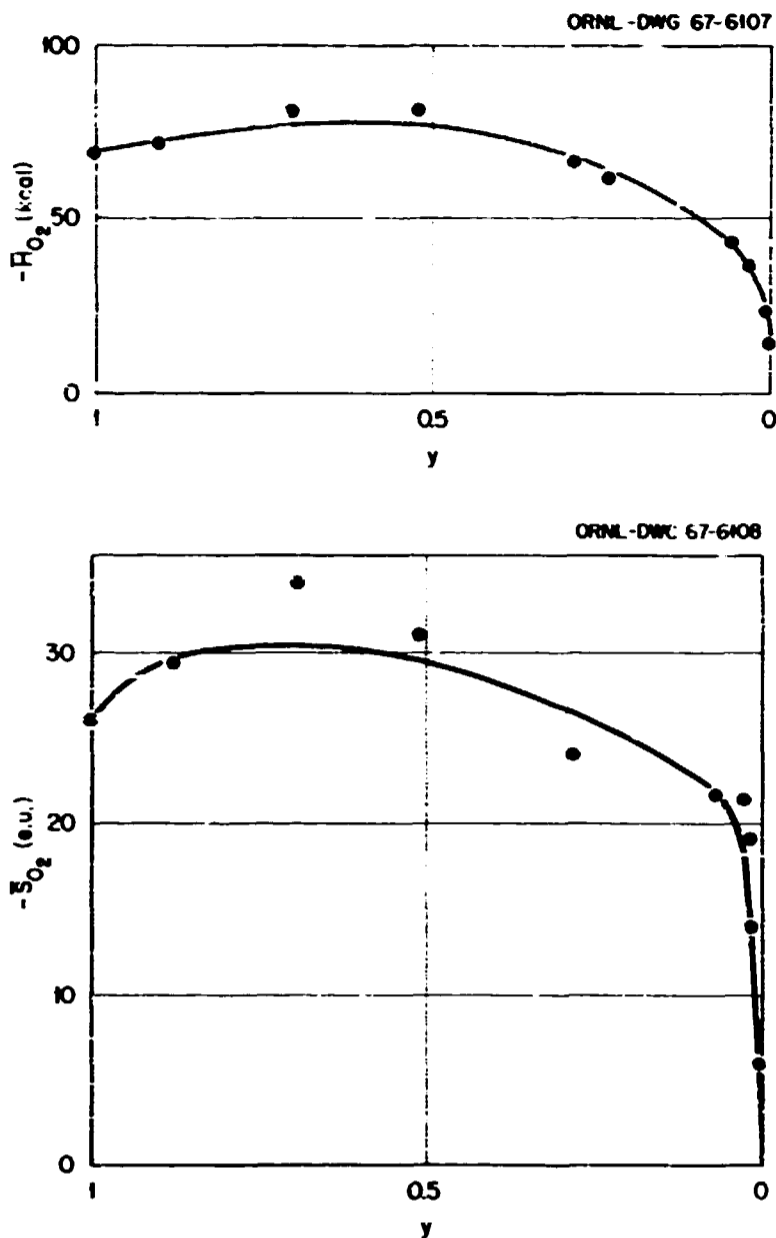


Fig. 33. Partial Molal Enthalpy (a) and Entropy (b) of Oxygen in $Th_{1-y}U_yO_{2+x}$; $x/y = 0.175$. Adapted from Roberts.¹⁶² To convert, 1 kcal = 4.184 kJ; 1 e.u. = 1 cal mole⁻¹ (°K)⁻¹ = 4.184 J mole⁻¹ (°K)⁻¹.

Aitken *et al.*¹⁶⁵ measured the volatilization of uranium oxide from thorium-uranium oxides in a stream of dry air at 1200 to 1600°C. Assuming that the uranium vaporizes as UO_3 , they derived the results in Table 27 for their four compositions. Figure 35 shows their derived free energies of formation for the stoichiometric solid solution and for the solid solutions in equilibrium with oxygen at 0.2 atm (2×10^4 N/m²) and 1:00°C.

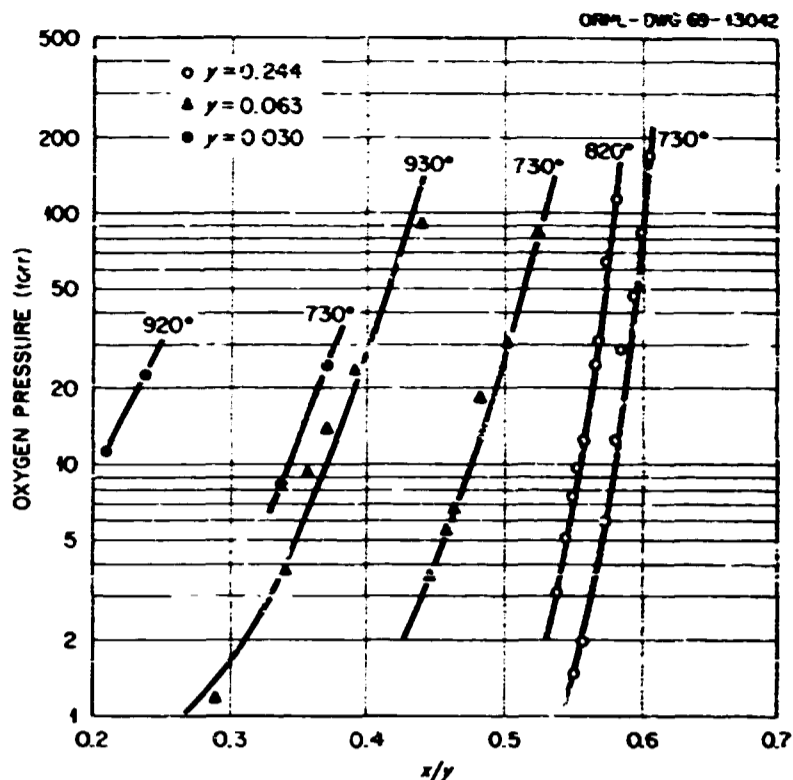


Fig. 34. Equilibrium Oxygen Pressures over $Th_{1-y}U_yO_{2+x}$. Adapted from Anderson *et al.*¹⁶⁴ To convert, 1 torr = 133.3 N/m².

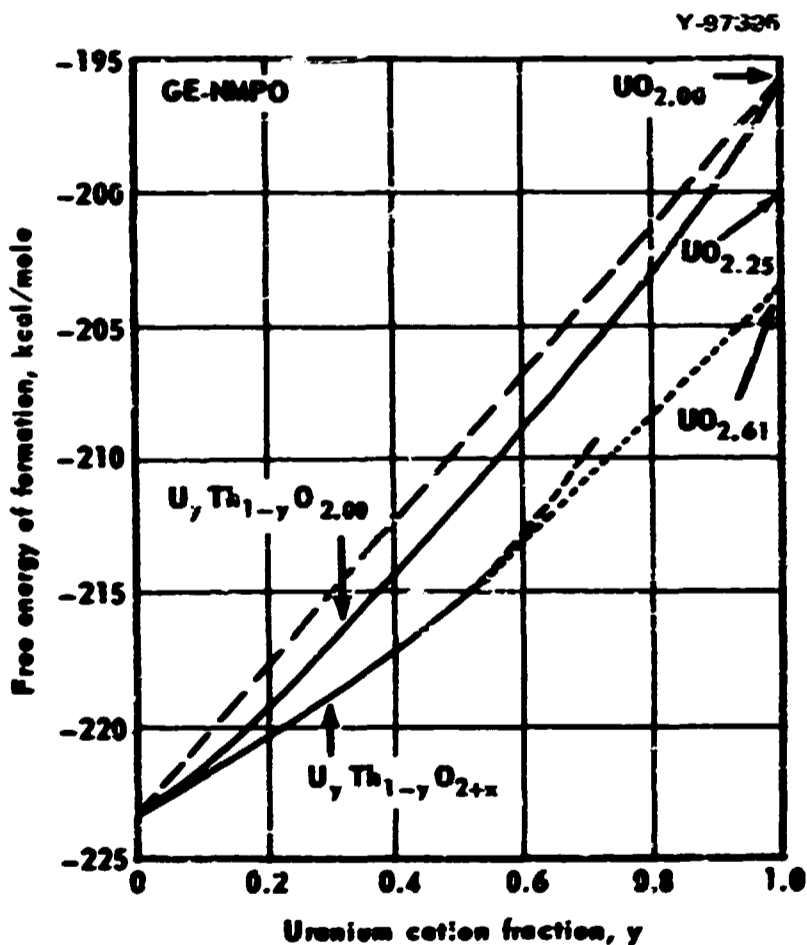


Fig. 35. Free Energy of Formation of $Th_{1-y}U_yO_{2+x}$. From Aitken, Edwards, and Joseph.¹⁶⁵ Copyright by the American Chemical Society; reprinted with permission.

Table 27. Volatility of UO_2 at 1200 to 1600°C and UO_2 Activity at 1300°C for $Th_{1-y}U_yO_{2+x}$
From ref. 165

Composition	2.34	2.13	2.10	2.03
y	0.5	0.25	0.20	0.063
Partial pressure,° atm				
$\ln P = A - B/T, A$	15,20	13,82	11,43	8,32
$\ln P = A - B/T, B$	42,568	39,888	37,313	33,198
Heat of sublimation				
Value, cal/mole	84,580	79,100	74,143	65,968
Standard deviation	1,488	888	1,588	1,988
ΔH_{sub} , kJ/mole	353.9	331.8	318.2	276.0
Standard deviation	5.8	3.3	6.3	7.9
Entropy of sublimation				
Value, cal/mole ^o (°K) ⁻¹	38.28	25.87	22.71	16.53
Standard deviation	0.85	0.45	0.95	1.2
Value, J/mole ^o (°K) ⁻¹	126.4	108.2	95.8	69.2
Standard deviation	3.6	1.9	4.8	5.8
UO_2 activity in 0.2 atm O_2 ^b at 1300°C				
For given composition	0.891	0.861	0.859	0.836
Corrected to $x = 0$	0.5	0.24	0.28	0.95
UO_2 activity coefficient for $x = 0$	1.0	0.96	1.0	0.83

^aFor P in N/m^2 , add 11.53 to A .
^b $2 \times 10^6 N/m^2$.

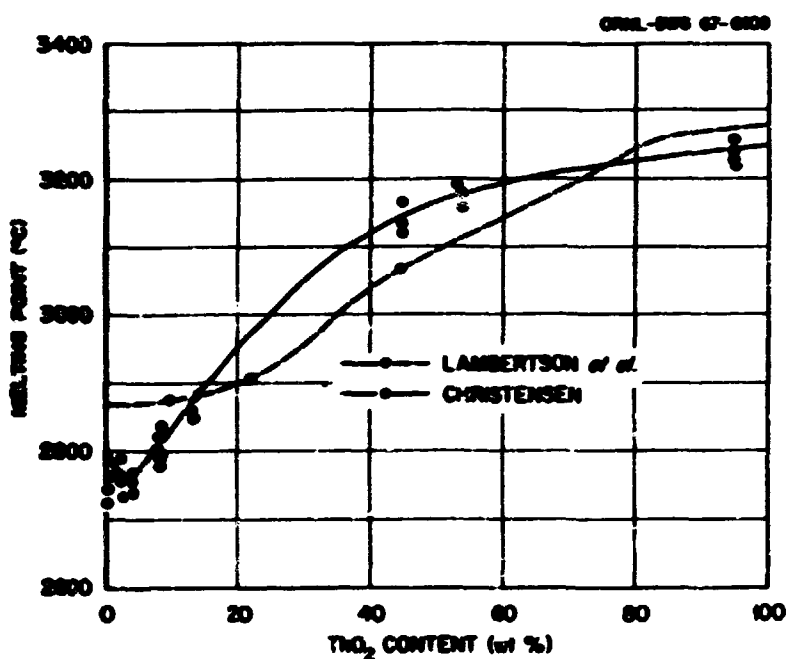


Fig. 36. Melting Point of $(Th,U)O_2$. Data from Lambertson et al.²⁸ and Christensen.¹⁵⁴

5. Change of State

Figure 36 shows the melting point vs composition curves for stoichiometric $(Th,U)O_2$ as determined by Lambertson et al.²⁸ and Christensen.¹⁵⁴ Partial pressures of UO_2 over $(Th,U)O_2$, determined by Alexander et al.³⁵ using a transpiration method with argon or

hydrogen, are plotted in Fig. 37. Other gas-solid equilibria involving thorium-uranium oxides are given in Sections 1 and 4.

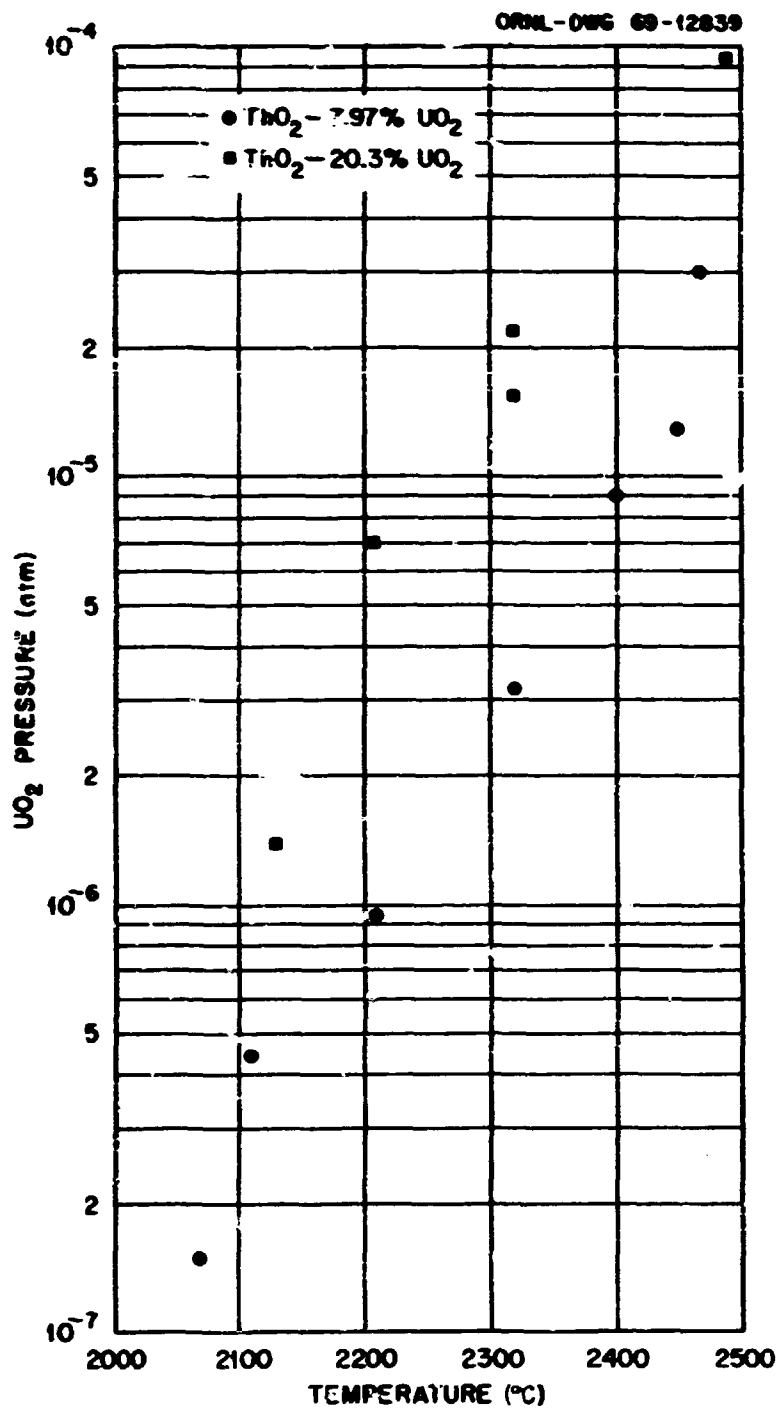


Fig. 37. Partial Pressures of UO_2 over $(Th,U)O_2$. Measured by Alexander et al.³⁵ To convert, 1 atm = $101,325 N/m^2$.

6. Electrical and Magnetic Properties

Electrical Resistivity. — Figure 38 shows Gruen's¹⁶⁰ measurements of electrical conductivity of mixed oxide fired 8 hr in hydrogen at 1750°C. Figure 39 shows the isotherm for 300°C and activation energies for conductivity.

Magnetic Susceptibility. — Several studies have been made of the magnetic susceptibility of thorium-uranium solid solutions. The results of Dawson and Lister¹⁶⁶ for stoichiometric material are listed in Table 28; a similar extensive set of data was obtained by Slowinski and Elliott¹⁶⁷. The variation with temperature and composition are consistent with a magnetic moment of about

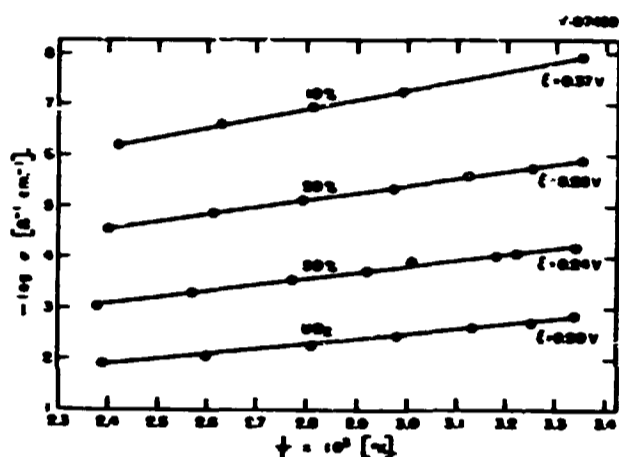


Fig. 38. Electrical Resistivity of $(\text{Th,U})\text{O}_2$. From Gruen.¹⁶⁰ Copyright by the American Chemical Society; reprinted with permission.

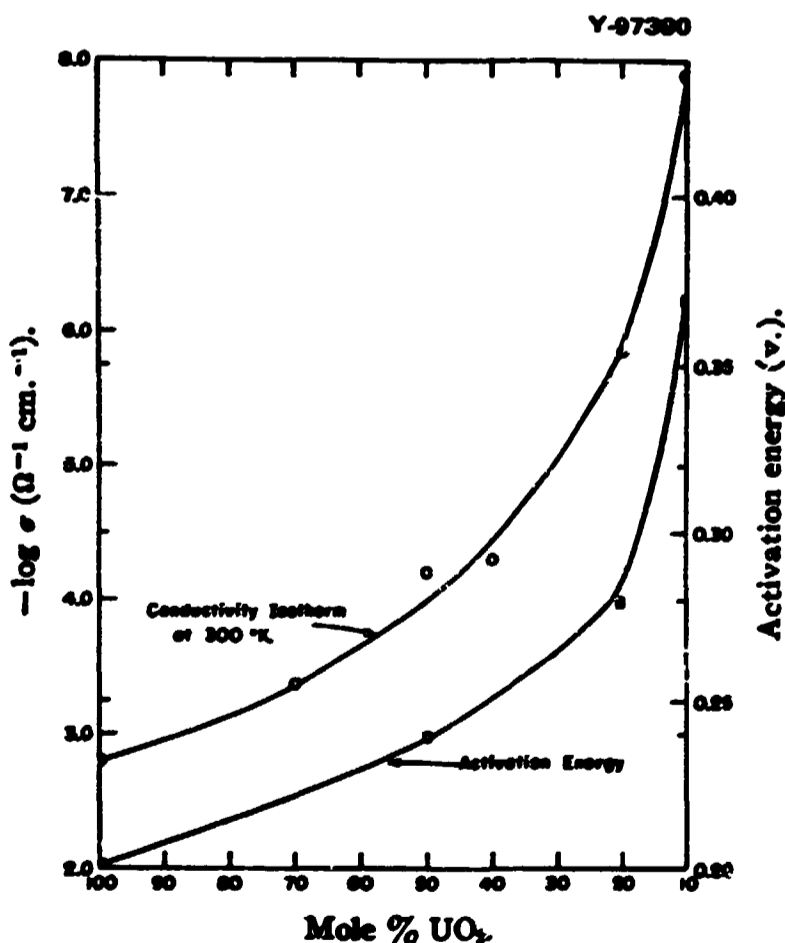


Fig. 39. Electrical Conductivity Isotherm of $(\text{Th,U})\text{O}_2$ at 300°C and Activation Energy for Conductivity. From Gruen.¹⁶⁰ Copyright by the American Chemical Society; reprinted with permission.

3 for uranium, increasing somewhat with uranium content. Comly¹⁶⁸ has extended measurements down to 1.7°K and finds the same trend continuing for material dilute in uranium; a magnetic transition occurs if the ThO_2 content drops below 42%. The susceptibility decreases with oxidation; typical results by Dawson and Roberts¹⁶⁹ are given in Table 29; Goto¹⁷⁰ found similar behavior.

Table 28. Magnetic Susceptibilities of $(\text{Th,U})\text{O}_2$
From ref. 166

UO_2 (%)	Temperature (°K)	Susceptibility per Gram
		$\times 10^{-6}$
90	197	9.81
	293	7.90
	337.5	7.22
	402	6.45
80	493	5.57
	197	9.07
	293	7.25
	338	6.59
	398	5.95
70	442.5	5.47
	197	7.98
	293	6.35
	334	5.87
	401	5.19
	60	197
293		5.62
330.5		5.16
352.5		4.95
393		4.58
417		4.39
50	197	6.11
	293	4.75
	335.5	4.30
	398	3.94
40	450	3.50
	197	5.20
	293	3.92
30	327	3.64
	353	3.41
	397	3.19
	417	3.01
	433	2.94
	20	197
293		3.05
337		2.72
398		2.38
10	405.5	2.15
	197	2.94
	293	2.14
	338	1.89
	400	1.64
	452	1.48
10	293	1.05

Table 29. Magnetic Susceptibilities
of $\text{Th}_{1-y}\text{U}_y\text{O}_{2+x}$ at 300°K
From ref. 149

y	x	Susceptibility per Gram
		$\times 10^{-6}$
0.148	0.000	1.83
	0.050	0.93
	0.067	0.62
	0.088	0.36
	0.108	0.26
0.279	0.000	2.94
	0.063	2.14
	0.138	1.05
	0.191	0.61
0.431	0.000	4.35
	0.069	3.51
	0.220	1.47
	0.259	1.02

7. Heat and Mass Transport

Diffusion. — Table 30 summarizes measurements by Furuya and Yajima⁵⁸ on protactinium and Furuya⁵⁹ on uranium diffusion in equimolar $\text{ThO}_2\text{-UO}_2$. Berman⁶¹ found for surface diffusion in $(\text{Th,U})\text{O}_2$

$$D_s = 0.889 \exp(-Q/RT) \text{ cm}^2/\text{sec}$$

from 1510 to 2050°C, where $Q = 51,800 \pm 11,100$ cal/mole or 217 ± 46 kJ/mole. Within the scatter, no effect of composition could be found in the range 3 to 30% UO_2 . The specimens were high-density sintered polycrystalline material annealed 24 to 48 hr in hydrogen.

Table 30. Diffusion Coefficients^a of Protactinium and Uranium
in Polycrystalline $\text{Th}_{0.5}\text{U}_{0.5}\text{O}_2$

Mobile Atom	Temperature Range (°C)	Component	Arrhenius Coefficients ^b		
			D_0 or A	Q (cal/mole)	Q (kJ/mole)
Protactinium	1800–2000	Lattice	1.88×10^{-3}	91,800	384,000
		Grain boundary	5.64×10^{-8}	59,700	250,000
Uranium	1800–2300	Lattice	7.59×10^{-4}	85,900	359,000
		Grain boundary	1.04×10^{-7}	64,200	269,000

^aTaken from Furuya and Yajima.^{58,59} Specimens were pressed at 5000 kg/cm², sintered in vacuum 2 hr at 1700°C to a density greater than 9.6 g/cm³, and then sintered 2 hr at 2300°C in argon to a density greater than 9.8 g/cm³ and an average grain size over 60 μm. Results were analyzed into lattice and grain-boundary components.

^bConstants of $D = D_0 \exp(-Q/RT) \text{ cm}^2/\text{sec}$ and $2aD' = A \exp(-Q/RT) \text{ cm}^2/\text{sec}$, where D' is the grain-boundary diffusion coefficient and $2a$ is the width of the grain boundary.

Thermal Conductivity. — Springer *et al.*¹³ measured the thermal conductivity of thorium containing 10 and 20% UO_2 and ranging in density from 73 to 95% of theoretical. Specimens were hydrostatically pressed \approx 60,000 psi, calcined in CO_2 to remove binder, and fired 14 hr in flowing dry hydrogen. Porosity was varied by incorporating sucrose in the pressed rods. The results, including some without uranium given in Fig. 12, are fitted by the equation

$$\lambda = \left[\frac{(1 - P)(0.67 + 0.282U)}{0.67 + 0.282U + P(1 + 0.092U)} \right] \times \left[\frac{1}{0.79(1 + 0.09U) + 0.0185T} \right] \times \left(\frac{1 + 0.291U}{1 + 0.400U} \right) \text{W cm}^{-1} (\text{K})^{-1},$$

where P is the fraction porosity and U is the weight percentage UO_2 . The same equation gives a fair representation of data of Springer and Lagedrost¹⁷¹ on similarly prepared specimens containing from 3.1 to 30% UO_2 with porosity varied by incorporation of dextrose before firing; deviations were significant for the lowest and highest UO_2 contents and greatest for a specimen with differently introduced porosity. The effect of UO_2 concentration on the thermal conductivity up to 500°C is seen in the results of Murabayashi *et al.*¹⁷² given in Fig. 40. Other results on the thermal conductivity of thorium-uranium oxides are collected in Fig. 41; the specimens measured are described in Table 31.

Jacobs¹⁷⁵ measured the thermal conductivity of $(\text{Th,U})\text{O}_2$ containing 3 to 10% UO_2 during reactor irradiation. At doses up to 1.4×10^{19} fissions/ cm^3 , the conductivity over the range 400 to 1000°C was about the same as that of similar unirradiated specimens measured by Springer and Lagedrost.¹⁷¹ From 1000 to 1700°C the conductivity under irradiation seemed somewhat greater. Kjaerheim and Rolstad¹⁷⁶ also found the in-reactor thermal conductivity of

ThO_2 -10% UO_2 to be about the same as that of unirradiated material. MacEwan and Stoute¹⁷⁷ found that irradiation at relatively low temperature to 3.8×10^{18} neutrons/ cm^2 halved the thermal conductivity of ThO_2 -1.3% UO_2 at 60°C . Values of their unirradiated 93- to 94%-dense specimens ranged from 0.118 to $0.127 \text{ W cm}^{-1} (\text{K})^{-1}$. Annealing at 1000°C restored most of the loss.

Effective thermal conductivities of 0.021 and $0.017 \text{ W cm}^{-1} (\text{K})^{-1}$ at average temperatures 990 and 1325°C , respectively, were found for vibratouly compacted sol-gel ThO_2 -2.9% UO_2 during ORR irradiation.¹⁷⁸

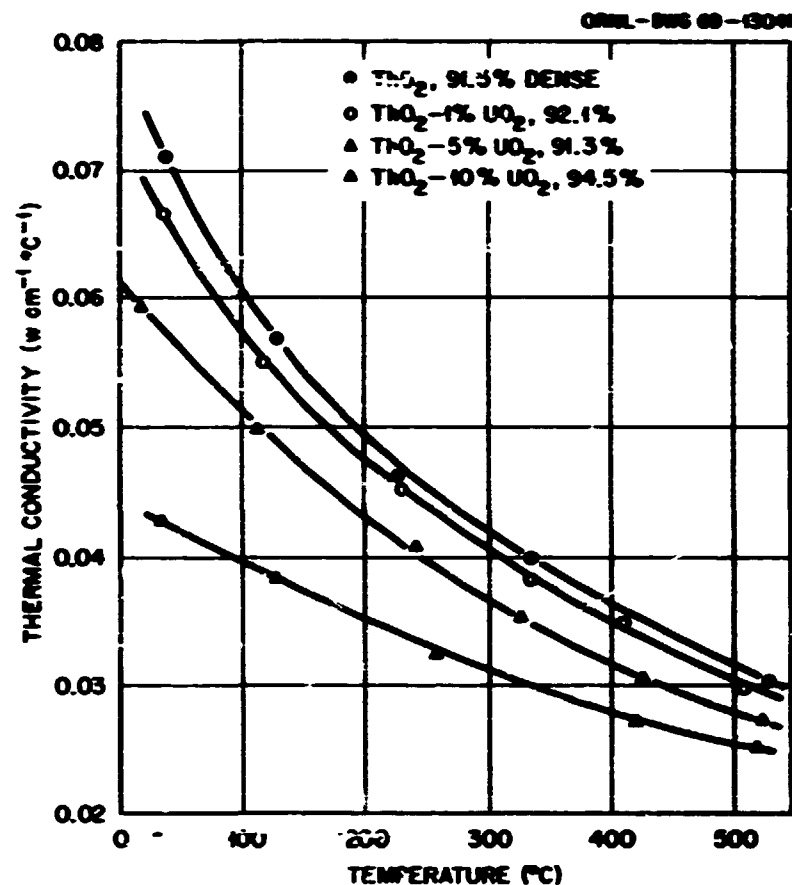


Fig. 40. Effect of UO_2 Content on the Thermal Conductivity of $(\text{Th,U})\text{O}_2$. Based on Murabayashi *et al.*¹⁷² The values were adjusted to zero porosity by dividing by $1 - P$, where P = pore fraction.

Table 31. Data on Thorium-Uranium Oxide Specimens with Thermal Conductivity Plotted in Fig. 41

Plet	Reference	UO ₂ (%)	Density (g/cm ³)	Oxidation	Preparation
1	Moore <i>et al.</i> ⁶³	4.7	8.733	Stoichiometric	Sol-gel, fired in H ₂ 1750°C
2	Moore <i>et al.</i> ⁶³	4.7	9.067	Oxidized	Sol-gel, fired in air 1650°C
3	Moore <i>et al.</i> ⁶³	6.1	9.043	Oxidized	Sol-gel, fired in air 1650°C
4	Moore <i>et al.</i> ⁶³	6.3	8.796	Stoichiometric	Sol-gel, fired in air 1650°C, then in H ₂ 1750°C
5	Kingry ¹⁷³	10	8.89	Oxidized	Not given
6	Kingry ¹⁷³	25	9.48	Stoichiometric	Not given
7	Kingry ¹⁷³	25	9.48	Oxidized	Not given
8	Kingry ¹⁷³	30	8.16	Oxidized	Not given
9	Harrison and Walker ^{174a}	10	9.08	Stoichiometric	Sintered
10	Belle <i>et al.</i> ^{62b}	10	9.51	Stoichiometric	Hydrostatically pressed
11	Belle <i>et al.</i> ^{62b}	10	9.47	Stoichiometric	Hydrostatically pressed
12	DeBokey ^{71c}	10		Not reported	Not given
13	DeBokey ^{71c}	8		Not reported	Not given

^aMean values for a 200°C range, measured with an apparatus that simulates behavior in a reactor.

^bValues attributed to Legendre of BMI; the higher values for each temperature are for axial heat flow, the lower radial.

^cValues attributed to the Babcock and Wilcox Alliance Research Center.

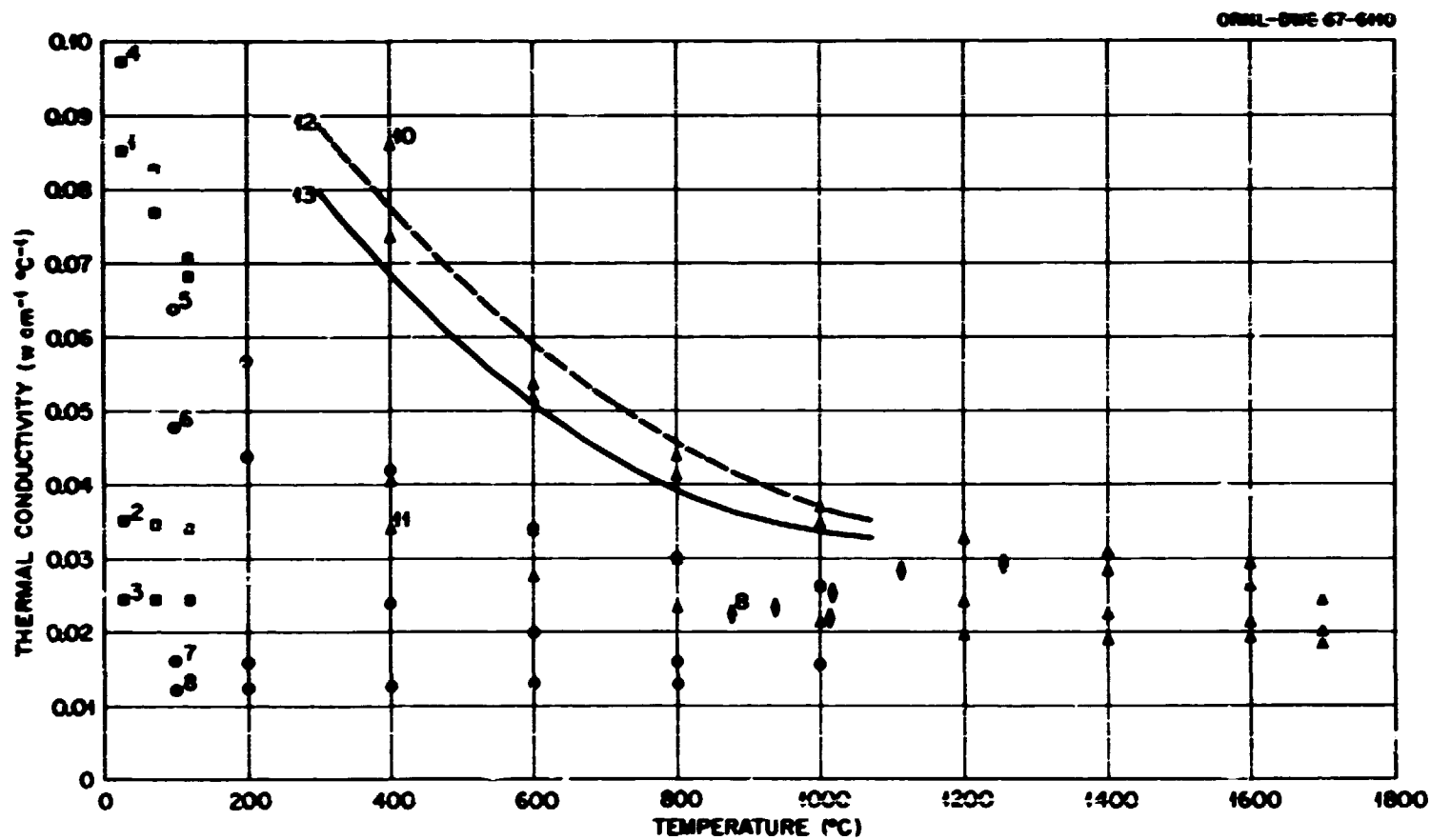


Fig. 41. Several Measurements of the Thermal Conductivity of Thorium-Uranium Oxides. Specimens and references are identified in Table 31. Where the published value included a correction for porosity, the values were recalculated to the actual specimen.

8. Mechanical Properties

For 96%-dense ThO_2 -5% UO_2 of unspecified history, Sylvania-Corning¹⁵⁷ reports a Young's modulus of 3.5×10^7 psi (2.4×10^{11} N/m²) and a compressive strength of 7.4×10^4 psi (5.1×10^8 N/m²).

Figure 42 shows Vickers hardness measurements on $(\text{Th,U})\text{O}_2$, taken from Wolfe and Kaufman⁸³ and including some results of Koester *et al.*¹⁷⁹ The latter report measurements from 1000 to 1800°C on similarly prepared specimens containing from 1.5 to 30% UO_2 .

Compressive creep rates on ThO_2 -10% UO_2 from Wolfe and Kaufman⁸³ are collected in Fig. 43. Their pressed and sintered specimens had a grain size of 30 μm . Some were annealed 4 hr in helium at 2200 or 2600°C to increase the grain size. Kaufman⁸⁶ has derived creep rates from hot pressing data on $(\text{Th,U})\text{O}_2$ low-density specimens containing from 2 to 25% UO_2 .

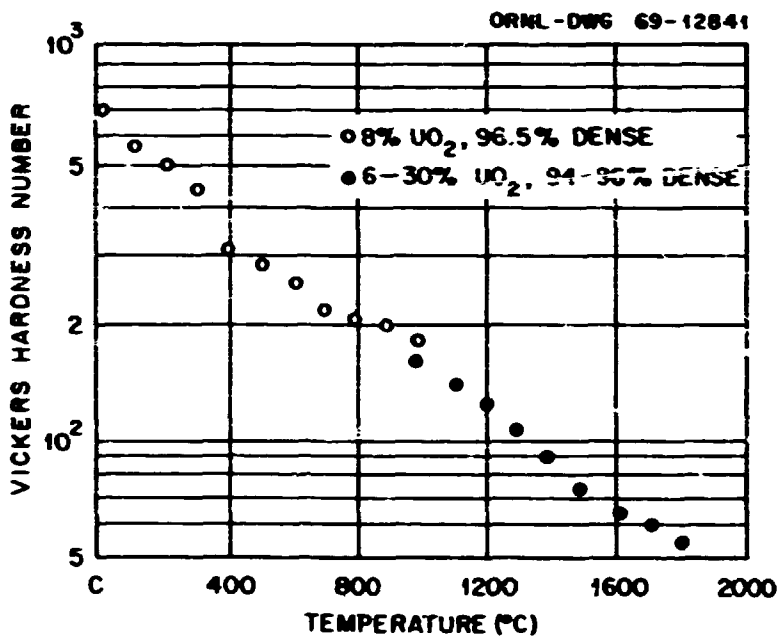


Fig. 42. Vickers Hardness Values for $(\text{Th,U})\text{O}_2$. Taken from Wolfe and Kaufman.⁸³ The high-temperature values (filled circles) are data of Koester *et al.*¹⁷⁹

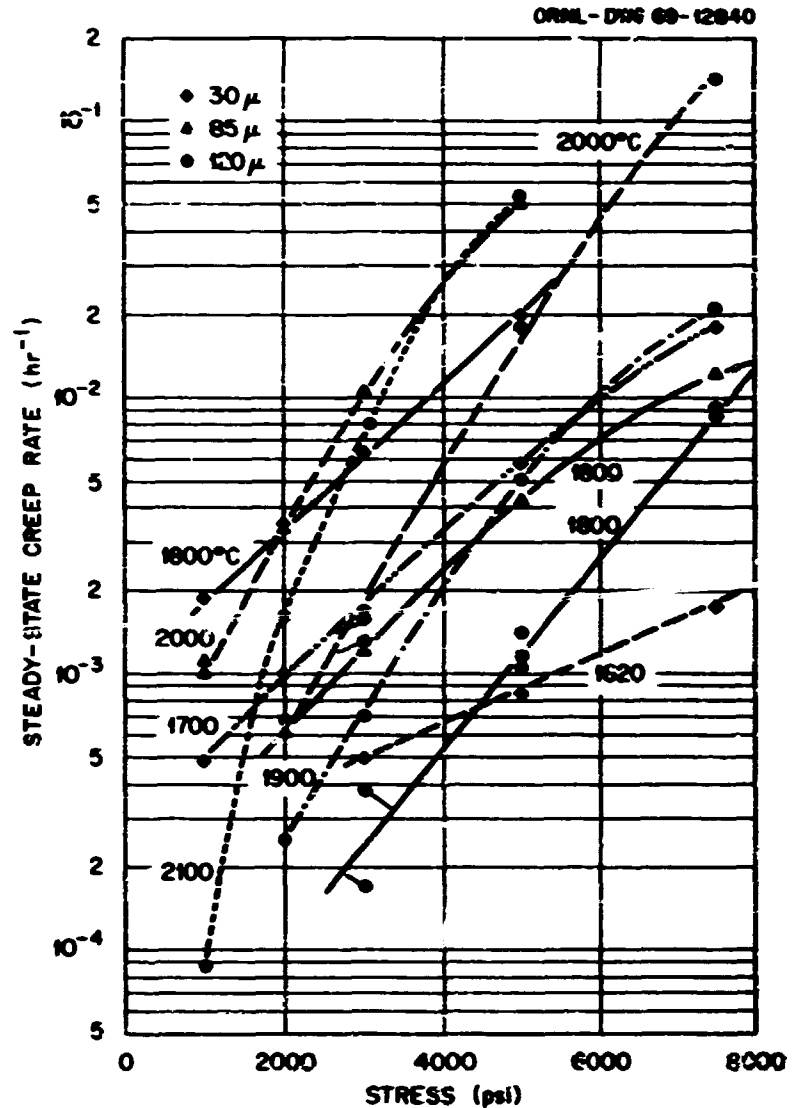


Fig. 43. Steady-State Compressive Creep Rates of ThO_2 -10% UO_2 . Based on Wolfe and Kaufman.⁸³

9. Chemical Properties

Reactions with Solids. — Little is available on the reactivity of $\text{ThO}_2\text{-UO}_2$ bodies with solids in contact with them. Because of the unreactivity of ThO_2 , the mixed oxides can be presumed compatible with any material compatible with UO_2 . Anderson *et al.*¹⁶⁴ calcined the mixed oxide in alumina boats. Lambertson *et al.*¹⁸ melted specimens in contact with tungsten, presumably without interaction. Cuneo *et al.*¹⁸⁰ found no reaction between pellets of $\text{ThO}_2\text{-9.2% UO}_2$ or $\text{ThO}_2\text{-33% UO}_2$ and graphite disks during nuclear reactor irradiation at 1370 to 1650°C. In the form of sol-gel microspheres dispersed in thorium, $\text{U}_{0.5}\text{Th}_{0.5}\text{O}_2$ reacted slightly at 800°C and extensively at 1000°C, while $\text{U}_{0.25}\text{Th}_{0.75}\text{O}_2$ at 1000°C reacted slightly on 100 hr heating.¹⁸¹

Selective Reactions. — Baskin *et al.*¹⁸² found that at 1300°C B_2O_3 selectively removed ThO_2 from $(\text{Th,U})\text{O}_2$ containing less than 60% UO_2 . When $(\text{U,Th})\text{O}_2$ is equilibrated with molten $\text{LiF-BaF}_2\text{-ThF}_4\text{-UF}_4$ at 600°C, the Th/U ratio in the fluoride phase is 1000 to 2000 times that in the oxide.¹⁸³ Venkateswarlu *et al.*¹⁸⁴ found that CCl_4 vapor in flowing nitrogen preferentially volatilized UCl_4 .

Reactions with Liquids and Gases. — Robertson¹⁸⁵ found no significant weight gains in 65 hr in distilled water at 360°C. His specimens were $\text{ThO}_2\text{-10% UO}_2$ of 9.1 and 9.7 g/cm^3 density prepared by cold pressing mixed ThO_2 and U_3O_8 and firing in air at 1750°C. Sylvania-Corning¹⁸⁷ found very small weight changes on $(\text{Th,U})\text{O}_2$ in steam at 336°C. Bishop *et al.*¹³⁰ found that unirradiated and irradiated $\text{ThO}_2\text{-3% UO}_2$ dissolved at a satisfactory rate (1 to 8 hr) in refluxing 13 *M* $\text{HNO}_3\text{-0.05 M HF}$. The behavior of thorium-uranium oxides on exposure to oxidizing and reducing gases is described in Section 1.

10. Surface Properties

Braz and Claudel¹⁸⁶ have studied the chemisorption of O_2 , CO , and CO_2 on $\text{Th}_{0.948}\text{U}_{0.052}\text{O}_{2.032}$ and shown that this mixed oxide catalyzes oxidation of carbon monoxide in the chemisorbed state. They further showed¹⁴⁶ that the activation energy of the reaction varied with mixed oxide composition, decreasing from 10.0 ± 0.3 kcal/mole (42 ± 1 kJ/mole) on $\text{Th}_{0.9888}\text{U}_{0.0112}\text{O}_{2.0060}$ to 4.5 ± 0.2 kcal/mole (21 ± 1 kJ/mole) on $\text{Th}_{0.808}\text{U}_{0.192}\text{O}_{2.133}$. Pichat and Braz¹⁸⁷ have followed the course of the reaction by infrared absorption of the chemisorbed reactants.

C. Thorium-Plutonium Oxides

1. Composition

The dioxides of thorium and plutonium form a continuous series of solid solutions over the entire range of composition. At the plutonium-rich end of the range, mixed oxide may be heterogeneous if prepared under reducing conditions, as a result of the formation of Pu_2O_3 .

2. Preparation

Powders of the mixed oxide have been prepared by precipitation of the mixed hydroxides with ammonia^{188,189} followed by calcination at 800 or 1000°C or by calcination at 500°C of plutonium oxalate premixed with thoria.¹⁹⁰ Mixed oxide pellets have been prepared by cold pressing and sintering the last of these mixed powders 6 hr at 1650°C in helium¹⁹⁰ or a ball-milled mixture of -325-mesh ThO_2 and PuO_2 6 hr at 1600°C in hydrogen.¹⁹¹ Plutonium-thorium oxide solid solutions sinter to higher densities than pure thoria under the same conditions.¹⁹⁰ Sol-gel $(\text{Th,Pu})\text{O}_2$ has been packed into tubular cladding to make several fuel rods for irradiation testing.^{192,193}

3. Crystal Properties

Structure. — The ThO_2 - PuO_2 solid solutions have the cubic fluorite structure of ThO_2 , with plutonium atoms substituted for thorium atoms.¹⁸⁹

Lattice Parameter. — Table 32 gives the values of Mulford and Ellinger.¹⁸⁹ Values by Freshley and Mattys¹⁹⁰ are in good agreement. Both sets are linear in mole fraction.

Color. — Pale green,¹⁸⁹ yellow.¹⁹⁴

4. Thermodynamic Properties

No information is available yet.

5. Change of State

Figure 44 shows the melting point vs composition curve as determined by Freshley and Mattys.¹⁹⁰

Table 32. Lattice Parameters of ThO_2 - PuO_2 Solid Solutions at 25°C

From ref. 189

PuO_2 (mole %)	Parameter (Å)
0	5.598 ± 0.001
15.0	5.568 ± 0.004
26.0	5.5462 ± 0.0004
36.9	5.526 ± 0.001
46.7	5.502 ± 0.001
63.5	5.4693 ± 0.0004
82.5	5.428 ± 0.001
100.0	5.3960 ± 0.0003

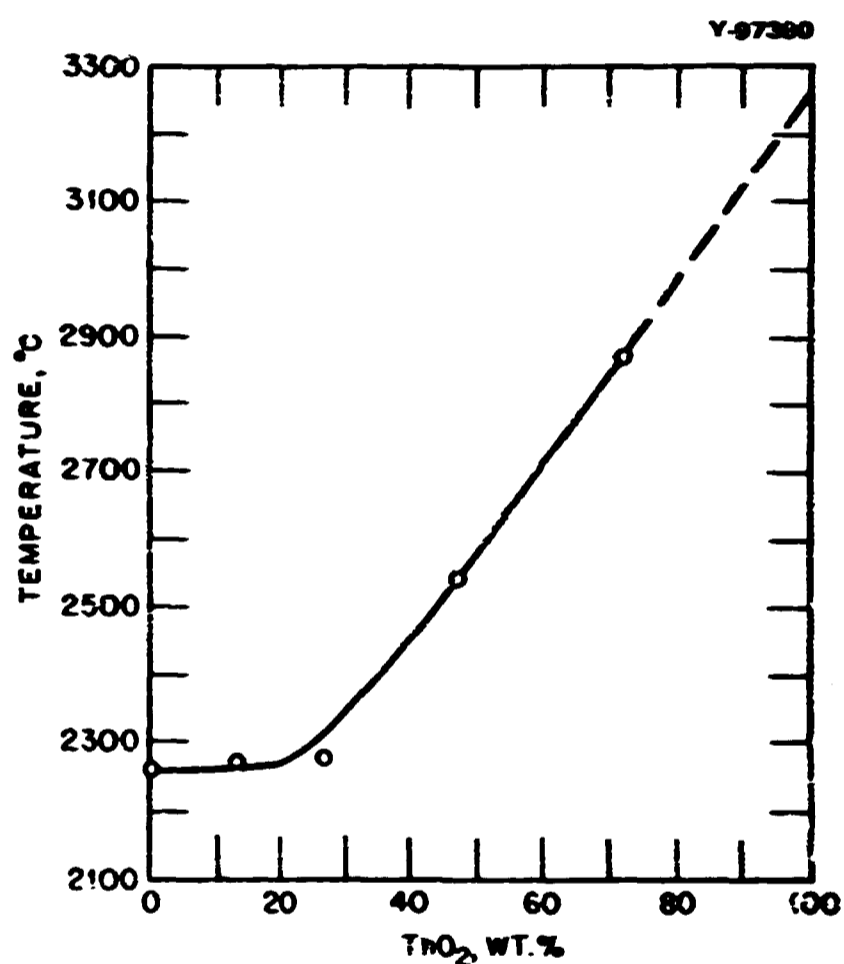


Fig. 44. Melting Point of $(\text{Th,Pu})\text{O}_2$ Solid Solutions. Copied from Freshley and Mattys.¹⁹⁰

6. Electrical and Magnetic Properties

Magnetic Susceptibility. - Table 33 gives Dawson's¹⁸⁸ measurements of the magnetic susceptibility of ThO_2 - PuO_2 solid solutions.

7. Heat and Mass Transport

Jeffs¹⁹⁵ measured heat transport as a function of temperature during irradiation of 96.5% dense $(\text{Th,Pu})\text{O}_2$ containing from 1.1 to 2.7% PuO_2 . The integrated thermal conductivity observed was about the same for the three compositions measured and was consistent with a thermal conductivity that was near $0.05 \text{ W cm}^{-1} (\text{C}^\circ)^{-1}$ at 300 to 400°C and decreased only to about 0.03 to $0.04 \text{ W cm}^{-1} (\text{C}^\circ)^{-1}$ at 1600°C .

8. Mechanical Properties

No information is available yet.

9. Chemical Properties

During irradiation for one month at a linear heat rating of 550 W/cm and an estimated temperature of 1600°C , $\text{Th}-1.1\%$ PuO_2 and $\text{W}-26\%$ Re did not interact.¹²⁶

In 1-hr treatments at 1600°C , $(\text{Th,Pu})\text{O}_2$ microspheres were stable to moist helium, carbon dioxide, and air but were reduced to $(\text{Th,Pu})\text{O}_{2-x}$ and Pu_2O_3 by hydrogen.¹⁹⁶

10. Surface Properties

No information is available yet.

Table 33. Magnetic Susceptibilities of $(\text{Th,Pu})\text{O}_2$
From ref. 188

PuO_2 (%)	Temperature ($^\circ\text{K}$)	Susceptibility per Gram $\times 10^6$
75	90	4.644
	200.5	2.771
	300	2.168
	334.5	2.055
	372	1.942
	411.5	1.852
	446.5	1.793
	521	1.754
	592	1.671
	50.0	90
199		2.034
300		1.614
332		1.490
372		1.436
415		1.410
445		1.374
35.3		90
	200	1.548
	300	1.294
	328.5	1.158
	371	1.117
	411	1.062
	437	1.034
12.1	90	1.205
	201	0.552
	299	0.344
	334.5	0.303
	375	0.260
	414	0.230
	462	0.194
8.82	300	0.280
8.72	300	0.352
4.31	300	0.102
2.19	300	0.056

D. Binary Systems of Thorium Oxide with Nonfuel Oxides

1. Composition

Thoria forms a complete range of solid solutions with other fluorite-structure dioxides; examples reported include the dioxides of cerium,¹⁹⁷ protactinium,¹⁹⁸ uranium (Part B), neptunium,¹⁶³ plutonium (Part C), and americium.¹⁹⁹ Firing in hydrogen can remove

oxygen from the ThO₂-CeO₂ solid solution; no phase change occurs except in cerium-rich compositions at high degrees of reduction. No oxygen is taken up by the ThO₂-NpO₂ solutions,¹⁶³ but ThO₂-PaO₂ solutions can be oxidized to Pa(V) without phase change.^{72,198}

The thoria lattice can accommodate substantial concentrations of rare-earth-type sesquioxides; solubilities are listed in Table 34. Heating ThO₂-Tb₂O₃ solutions in 1 atm O₂ oxidized them to Th_{0.2}Tb_{0.8}O_{1.853} and

Table 34. Solid Solubility of Rare-Earth-Type Sesquioxides in Thoria

Oxide	Temperature (°C)	Solubility		Reference
		(mole % RO _{1.5})	(mole % R ₂ O ₃)	
Am ₂ O ₃	1300	50	33	199
La ₂ O ₃	1000	52	35	200
	1400	48	32	201
	1480	48	32	199
	1800	52	35	202
	1940 ^e ± 10	56	39	202
	Nd ₂ O ₃	1300	50	33
Nd ₂ O ₃	1400	50	33	201
	1500	50	33	199
	Sm ₂ O ₃	1400	60	43
Eu ₂ O ₃	1200	36	22	203
	1300	40	25	203
	1400	47	31	203
	1500	53	36	203
Gd ₂ O ₃	800	32	19	202
	1400	50	33	201
	2000 ^e ± 50	62	45	202
Ho ₂ O ₃	1250	27	15.6	204
	1400	28.5	16.6	204
	1550	35.0	21.2	204
	1700	50.5	33.8	204
Tm ₂ O ₃	1250	10	5.3	205
	1400	11.5	6.1	205
	1550	15.5	8.4	205
	1700	18	9.9	205
Yb ₂ O ₃	1400	10	5.3	203
	1800	18	10	202
Lu ₂ O ₃	1250	7.5	3.9	204
	1400	8.0	4.2	204
	1550	11.0	5.8	204
	1700	12.0	6.4	204
Y ₂ O ₃	1400	25	14	201
	1400	22	12	206
	1500-1600	33	20	207
	1600	35	21	206
	1800	44	28	206
	2000	49	32.5	206
	2200	54	37	206

^eEutectic temperature.

$\text{Th}_{0.8}\text{Tb}_{0.2}\text{O}_{1.964}$ (ref. 208). The compound $\text{ThLa}_2\text{O}_{7.4}$ is stable from about 1150 to 2200°C and ThLa_4O_8 from about 1525 to 2000°C (ref. 202). Phase equilibria for other binary systems with thoria are summarized in Table 35. Several compounds of thoria prepared chemically and unstable at the liquidus are listed in Section 3. Burlese and Lucco Borlera²²⁸ prepared several thorium phosphates and characterized them by x-ray diffraction; none are stable above 1600°C. French *et al.*²²⁹ found that the silicate ThSiO_4 is stable in the tetragonal form below 1225°C and in the monoclinic at higher temperatures.

2. Preparation

Binary solid solutions are generally prepared in the same way as those with urania (Section B2), namely coprecipitation and firing or firing mixed powders at sufficiently high temperatures. The same consolidation methods used for thoria are applicable (Section A2). Heterogeneous ceramics are also prepared similarly, since the other oxide generally has a high melting point. For example, Veevers and Rotsey⁷⁷ mixed beryllia with thoria powder that had been fired at 1700°C, pressed the mixture isotatically at 20 tsi and sintered it 1.5 hr at 1500°C in nitrogen.

Table 35. Phase Data for Systems of Thoria with Various Oxides

Oxide	Solubility in ThO_2		Eutectic		Compound Formed		References
	(mole %)	Temperature (°C)	(mole % ThO_2)	(°C)	Formula	Mp (°C)	
Al_2O_3	Low		20	1920	None		209, 210
B_2O_3	Low		81	1480	ThB_2O_5	1483 ± 5	211
BaO	0.5	1800					212
BeO^a	Low		22	2240	None		213
	<0.1	<2155	30	2155	None		214
	0.05 ^b	1500–2150					196
CaO	10		38	2300	None		215, 216
	8	1800					212
HfO_2	43	1600		~2450	None		217
In_2O_3	3–4	<1400			None		207
MgO	47	1600			None		217
Nb_2O_5	Low		73	1533	$\text{Th}_2\text{Nb}_2\text{O}_9$	1341	218
					$\text{ThNb}_4\text{O}_{12}$	1388	218
$\text{ScO}_{1.5}$	0.8	1750	17	2220	None		219, 220
SiO_2	Low		< 1	1700 ± 10	ThSiO_4	1975 ± 15 ^c	221, 222
SrO	4	1800					212
Ta_2O_5	>5				$\text{Th}_2\text{Ta}_2\text{O}_9$		218, 223
					$\text{ThTa}_4\text{O}_{12}$		218
TiO_2			25	1625			224
V_2O_5					$\text{ThV}_4\text{O}_{12}$	990 ^d	225
					ThV_2O_7	1070 ^d	225
					$\text{Th}_3\text{V}_4\text{O}_{16}$	1300 ^e	225
ZrO_2^f	<2	400–1200	None		None		226, 227

^aSeveral determinations of the ThO_2 - BeO eutectic range from 2100 to 2360°C and 20 to 40 mole % ThO_2 ; the two most recent are quoted.

^bSolubility of ThO_2 in BeO . Ref. 212 gives 0.016 mole % below eutectic, and ref. 213 gives 0.54 mole % at eutectic.

^cIncongruent.

^dMelts with decomposition.

^eDecomposition temperature.

^fContinuous cubic solid solutions can exist metastably up to about 400°C. Also, cubic solid solutions containing up to 82.5 mole % ZrO_2 can be quenched from above 2000°C.

3. Crystal Properties

Structure and Lattice Parameters. — Cubic solid solutions in thoria have the fluorite structure with replacement of some of the thorium atoms by solute atoms. Figure 45 gives lattice parameters of thoria solid solutions with various isomorphous dioxides. The fluorite-structure solid solutions of rare-earth-type sesquioxides in thoria appear to accommodate the different metal-to-oxygen ratio with oxygen vacancies.^{197,206,230} Lattice parameters of such solutions at room temperature are compiled in Fig. 46. Leitner²⁰⁵ gives lattice parameters for the ThO_2 - Tm_2O_3 system at 1250°C and for ThO_2 -7.5 mole % $\text{Tm}_{1.5}$ up to 1250°C . Whitfield *et al.*¹⁹⁷ also give lattice parameters of thoria-ceria solid solutions after various degrees of reduction. Johnson and Curtis²¹⁵ found that dissolution of CaO in the ThO_2 lattice did

Fig. 45. Lattice Parameters of Solid Solutions of Thoria with Other Fluorite-Structure Oxides. Based on: AmO_2 , Radzewitz,¹⁹⁹ CeO_2 , Whitfield *et al.*,¹⁹⁷ NpO_2 , Roberts *et al.*,¹⁶³ PaO_2 , Roberts and Walter.¹⁹⁸

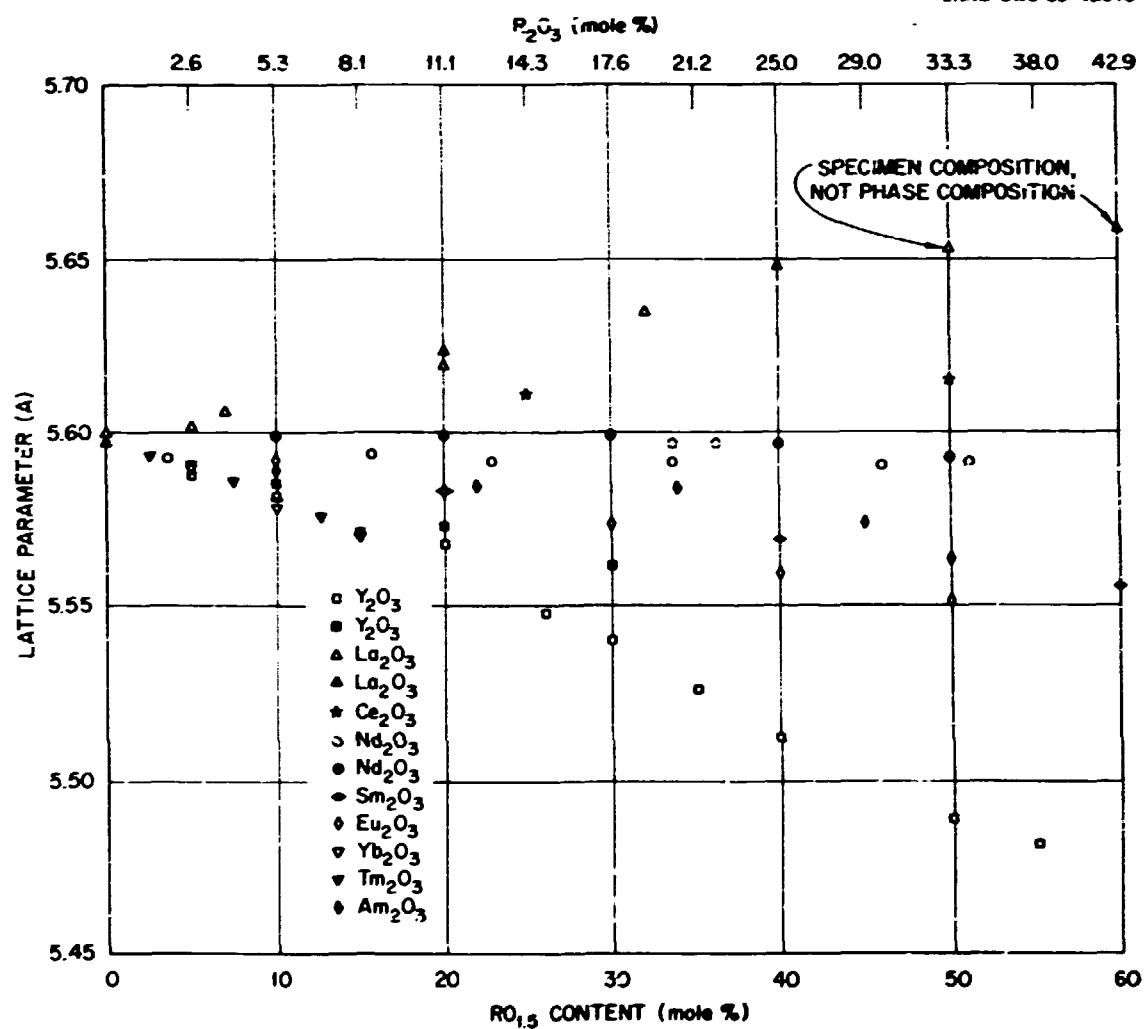
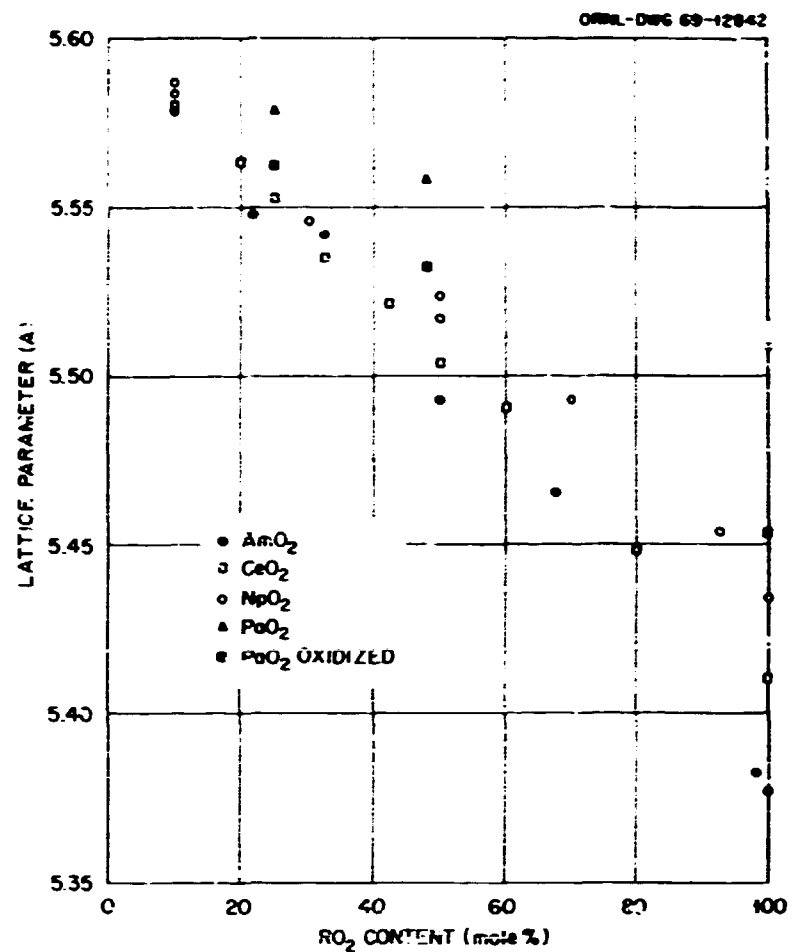


Fig. 46. Lattice Parameters of Solid Solutions of Thoria with Rare-Earth-Type Sesquioxides. Filled points for Y_2O_3 , La_2O_3 , Nd_2O_3 , and Sm_2O_3 are from Brauer and Gradinger.²⁰¹ Other data: Am_2O_3 , La_2O_3 , and Nd_2O_3 , Radzewitz;¹⁹⁹ Y_2O_3 , Subbarao *et al.*,²⁰⁶ Ce_2O_3 , Whitfield *et al.*,¹⁹⁷ values for ThO_2 - CeO_2 solid solutions more than 90% reduced to Ce(III) ; Eu_2O_3 and Yb_2O_3 , Gingerich and Brauer;²⁰³ Tm_2O_3 , Leitner.²⁰⁵

not change the cell size; Möbiss *et al.*²¹² report a very slight decrease. Also, SrO and BaO increased the cell size,²¹² whereas Sc₂O₃ decreased it.²²⁰

Table 36 gives the lattice parameters of several compounds between thoria and other oxides. The literature appears confused on the allotropy in the titanate and molybdate.

Thermal Expansion. — Turner and Smith¹⁵⁸ measured dilatometrically the linear thermal expansion of 20 vol % dispersions of 150- to 200- μ m ThO₂ in BeO. The specimens were mixed, isostatically pressed at 20 tsi, and sintered 1.5 hr at 1500°C in dry nitrogen. The data were fitted by the equation

$$\begin{aligned} \text{Percent expansion} = & 7.73 \times 10^{-4} (t - 20) \\ & + 1.72 \times 10^{-7} (t - 20)^2 + 1.39 \times 10^{-10} (t - 20)^3 \\ & \pm 0.0139, \end{aligned}$$

where t is the temperature in the range 20 to 1000°C.

Richardson²³⁸ found hysteresis in the thermal expansion of slip-cast ThO₂-11% ZrO₂, and Geller²³⁹ found it in dense ThO₂-50% ZrO₂.

Absorption Spectra. — Leitner²⁰⁵ gives infrared absorption spectra of ThO₂-Tm₂O₃ solid solutions.

4. Thermodynamic Properties

No information is available yet.

5. Change of State

Melting Point. — Table 35 gives eutectic temperatures and references to available melting-point-composition data for systems without high solid solubility in thoria. Where extensive solid solubility exists, melting points are quite high and usually unknown. Von Wartenberg and co-workers could not melt thoria-magnesia mixtures²⁴⁰ up to 2500°C or thoria-ceria mixtures²²⁴ up to 2600°C. Ruff *et al.*²⁴¹ report the following melting points for zirconia-thoria:

Thoria, mole %	10	20	25	33	50
Melting point, °C	2695	2705	2720	2755	2795

Table 36. Crystal Data on Binary Compounds of Thoria

Compound	Structure	Lattice Parameters (Å)				Upper Stability Limit (°C)	Reference
		a_0	b_0	c_0	β		
ThGeO ₄	Scheelite	5.140		7.231		1180	231
ThGeO ₄	Zircon	11.531		6.548			231
TaTi ₂ O ₆	Orthorhombic	16.7	14.95	4.1		1300	231
ThTi ₂ O ₆	Tetragonal	7.58		10.45			231
ThTi ₂ O ₆ ^a	Monoclinic	9.89	3.83	7.10	119°30'		199
ThTi ₂ O ₆ ^b	Monoclinic <i>C2/c</i>	10.808	8.580	5.196	115°15'	1300	232
ThB ₂ O ₅ ^c	Monoclinic <i>C2/m</i>	11.554	6.937	10.256	101°28'	900	182
Th ₃ V ₄ O ₁₆	Zircon ^d	7.26		6.474		1300	233
ThNb ₄ O ₁₂	Tetragonal	7.783		7.837		1388	218
ThTa ₄ O ₁₂	Cubic	7.810					218
ThMo ₂ O ₈	Hexagonal <i>P6/m</i>	17.58		6.233		950	234
ThMo ₂ O ₈	Orthorhombic	9.767	10.305	14.36			235
ThMo ₂ O ₈ ^e	Hexagonal	17.60		6.20			236
ThW ₂ O ₈	Orthorhombic	9.72	10.38	14.52			235
CaThO ₃	Monoclinic ^f	8.76	~ a_0	~ a_0	~90°		237
SrThO ₃	Monoclinic ^f	8.86	~ a_0	~ a_0	~90°		237
BaThO ₃	Monoclinic ^f	8.98	~ a_0	~ a_0	~90°		237

^aReported¹⁹⁹ to be the high-temperature form instead of the tetragonal.²³¹

^bReported²³² to be the low-temperature form instead of the orthorhombic.²³¹

^cBaskin *et al.*¹⁸² give optical and other properties of this compound.

^dWith cation vacancies.

^eThouret *et al.*²³⁶ concur with the transformation temperatures of Trunov *et al.*^{234,235} but identify the hexagonal phase as the low-temperature form.

^fVery nearly cubic.

6. Electrical and Magnetic Properties

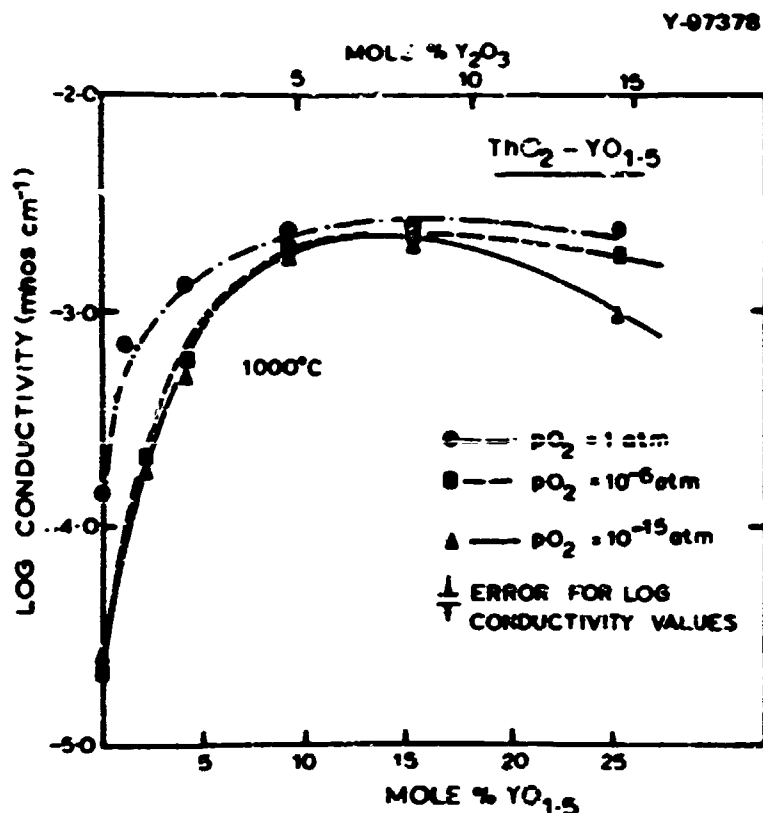


Fig. 47. Composition Dependence of Electrical Conductivity of $\text{ThO}_2\text{-Y}_2\text{O}_3$ Solid Solutions. From Steele and Alcock.⁴⁶ The pressures indicated are 10^5 , 0.1, and 10^{-10} N/m². Copyright by the Metallurgical Society of AIME and reprinted with permission.

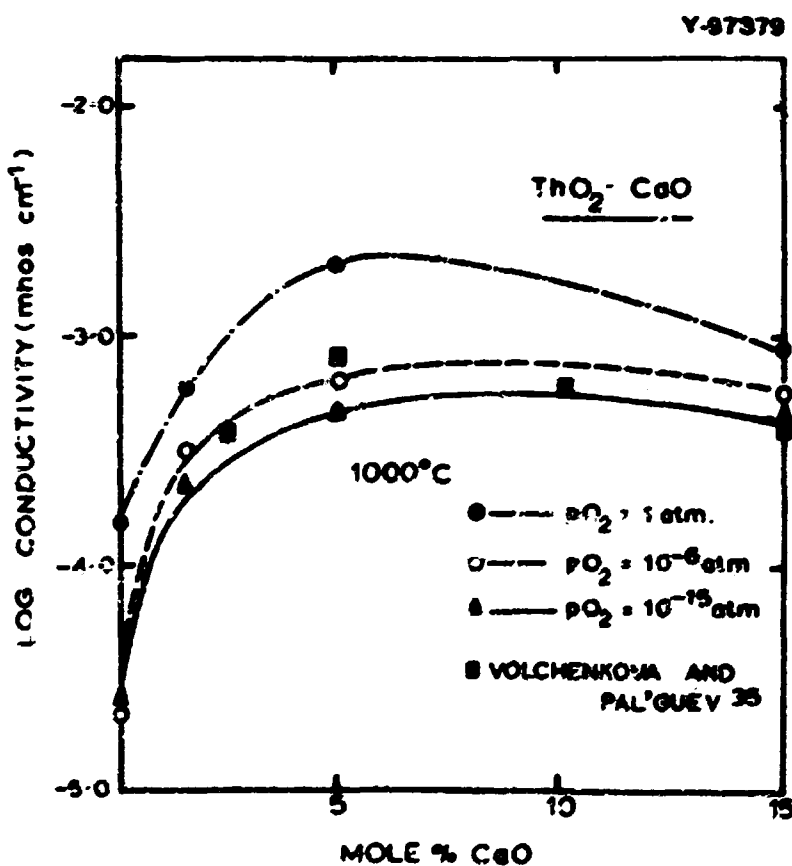


Fig. 48. Composition Dependence of Electrical Conductivity of $\text{ThO}_2\text{-CaO}$ Solid Solutions. From Steele and Alcock.⁴⁶ The pressures indicated are 10^5 , 0.1, and 10^{-10} N/m². Copyright by the Metallurgical Society of AIME and reprinted with permission. A few points are shown from the study of Volchenkova and Pal'guev.²⁴³

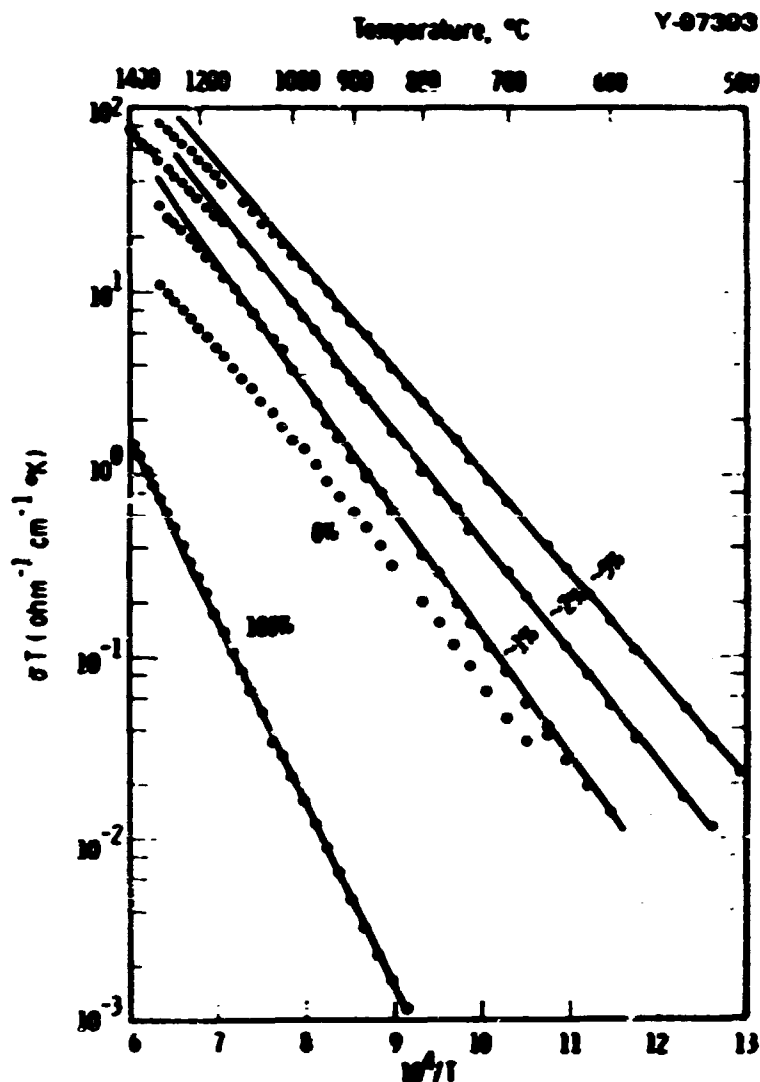


Fig. 49. Effect of Temperature on the Electrical Conductivity in Air of ThO_2 with Low Concentrations of Added Y_2O_3 . Copied from Sabbano *et al.*²⁰⁶ with permission of the American Ceramic Society.

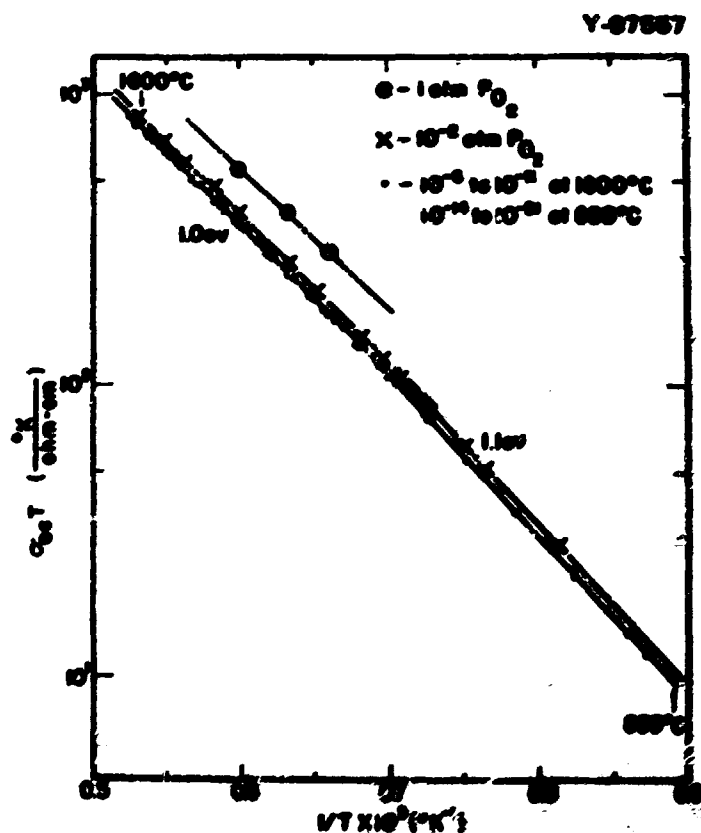


Fig. 50. Effect of Temperature on the Electrical Conductivity of $\text{ThO}_2\text{-12.1 mole \% YO}_{1.5}$. Copied from Winsor *et al.*²⁵⁰ with permission of the American Ceramic Society. Multiply pressures by 10^5 to convert to N/m².

Table 37. Preparation of ThO₂ Defect Solid Solution Specimens for Electrical Conductivity

Reference	Figures	Pressure ^a (atm)	Sintering Conditions	Density (%)
Stein and Alcock ⁴⁶	47, 48	30 ^b	2000°C, vacuum	>99 (ThO ₂ 95)
Subbarao <i>et al.</i> ²⁰⁶	49	10	1400°C, 4 hr 2200°C, 3-7 hr, O ₂	95-99
Wimmer <i>et al.</i> ²³⁰	50	15	2000°C, vacuum	98
Lester and Rapp ⁴⁵	51, 52		2100°C, 2.5 hr, vacuum 1400°C, 5 hr, air	83-95
Rudolph ⁴⁷	53		1500-1600°C	
Hund ^{2,242}	53		1500°C, 5 hr, air	
Volchenkova ²⁴³	48		1550°C, 1 hr, air	

^aAll cold pressed.

^bIsostatic.

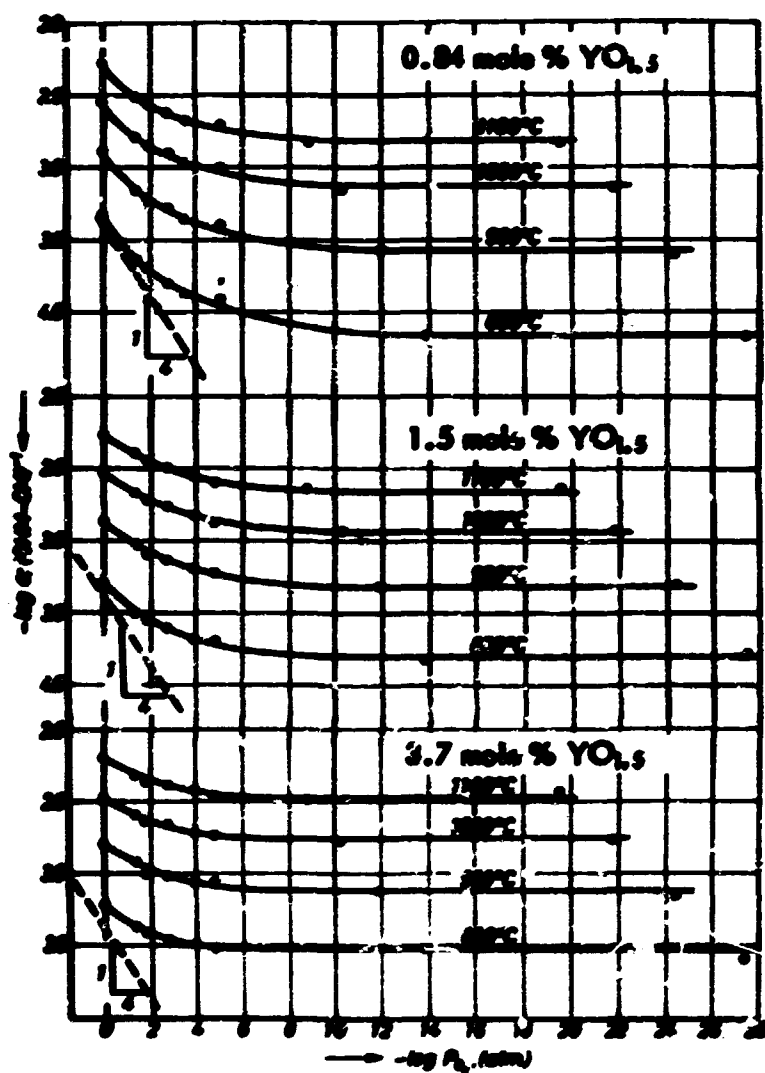


Fig. 51. Effect of Oxygen Activity on the Electrical Conductivity of ThO₂ Containing Low Concentrations of Y₂O₃. Adapted from Lester and Rapp⁴⁵ with permission of Akademische Verlagsgesellschaft.

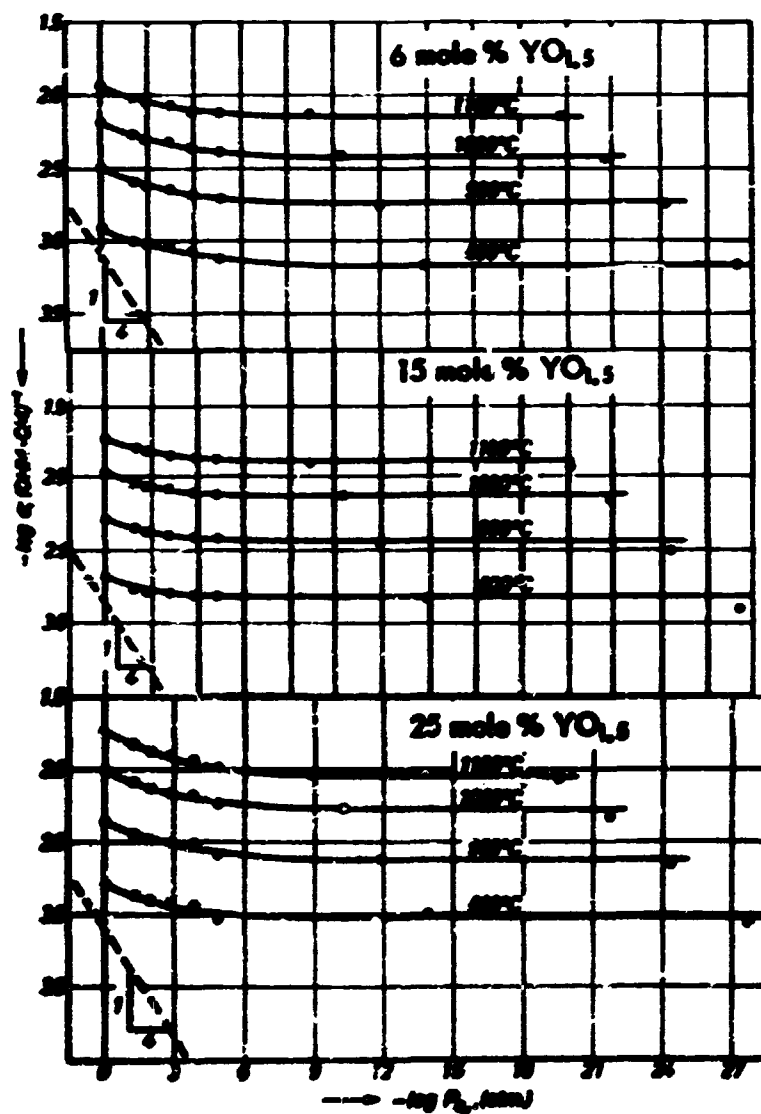


Fig. 52. Effect of Oxygen Activity on the Electrical Conductivity of ThO₂ Containing Higher Concentrations of Y₂O₃. Adapted from Lester and Rapp⁴⁵ with permission of Akademische Verlagsgesellschaft.

Conductivity. — Defect solid solutions of lower-valent oxides in thoria have greater electrical conductivities than thoria. The effect of composition on conductivity is given in Fig. 47 for $\text{ThO}_2\text{-Y}_2\text{O}_3$ and in Fig. 48 for $\text{ThO}_2\text{-CeO}_2$, both taken from Steele and Alcock.⁴⁶ The effect of temperature on $\text{ThO}_2\text{-Y}_2\text{O}_3$ conductivities is given in Figs. 49 and 50. The effect of oxygen activity on $\text{ThO}_2\text{-Y}_2\text{O}_3$ conductivity was determined by Lasker and Rapp⁴⁵ for several compositions and temperatures; the results are given in Figs. 51 and 52. Preparation of specimens for these measurements is summarized in Table 37. Rudolph⁴⁷ found the conductivity of $\text{ThO}_2\text{-2 mole % La}_2\text{O}_3$ over a wide temperature range to depend very little on whether measured in vacuum, oxygen, or hydrogen. Figure 53 gives his results along with older measurements by Hund² at higher lanthanum concentrations and comparable measurements by Hund and Mezger²⁴² on $\text{ThO}_2\text{-Y}_2\text{O}_3$. Steele and Alcock⁴⁶ found the conductivities of $\text{ThO}_2\text{-10 and -15 mole % LaO}_{1.5}$ about 10% higher than those of the Y_2O_3 counterparts. Volchenkova and Pal'guev²⁴³ report conductivities (presumably in air) of $\text{ThO}_2\text{-CaO}$ over the entire range of composition (including heterogeneous regions). The same authors²⁴⁴ also report similar measurements on systems with BeO , MgO , SrO , and BaO .

Thoria doped with Ta_2O_5 shows conductivity remarkably dependent on measurement conditions.^{47,223} Violet to black specimens prepared under reducing conditions showed strongly enhanced conductivity, but heating them in air to 800°C bleached them and reduced the conductivity to that of thoria.²²³ Claudel and Véron²⁴⁵ found a parallel relationship between the effects of heat treatment and measurement atmosphere on the electrical conductivities of ThO_2 and $\text{ThO}_2\text{-1% CeO}_2$ and also on their catalytic activities for the oxidation of carbon monoxide.

7. Heat and Mass Transport

May and Stoute²⁴⁶ in a qualitative comparison showed that 0.1 mole % Y_2O_3 increased the thermal conductivity of thoria.

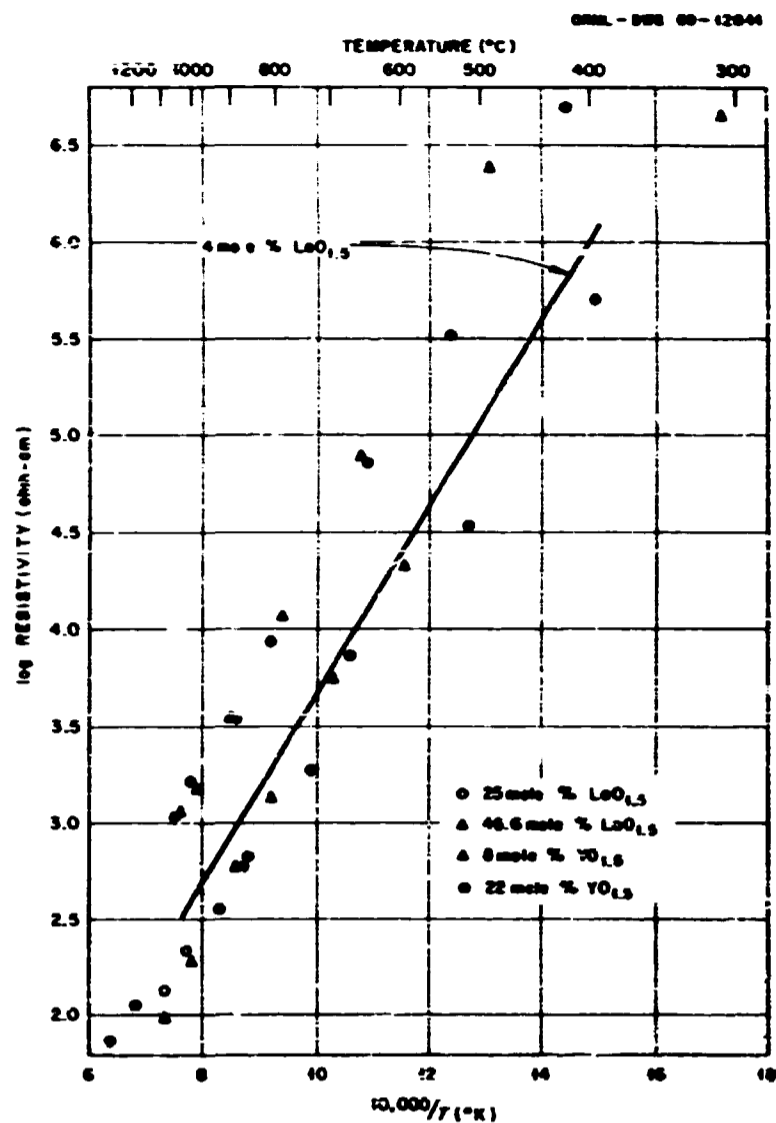


Fig. 53. Electrical Resistivity of $\text{ThO}_2\text{-La}_2\text{O}_3$ Solid Solutions. The line fits measurements of Rudolph⁴⁷ in vacuum, 380 torr O_2 , and 380 torr H_2 . The points are measurements in air by Hund,² Also shown are measurements on $\text{ThO}_2\text{-Y}_2\text{O}_3$ by Hund and Mezger.²⁴²

8. Mechanical Properties

Mechanical properties of thoria containing small concentrations of calcium oxide to aid densification are given in Section A8 with values for pure thoria.

Veevers and Rotsey⁷⁷ measured the modulus of rupture of dispersions of thoria in beryllia as a function of thoria particle size, temperature, and concentration; their data are given in Tables 38 to 40. Their values of Young's modulus for the same material are listed in Table 41.

9. Chemical Properties

Russell *et al.*¹³² found that ThO₂-1% MgO dissolved three to six times as fast as thoria in 13 M HNO₃-0.025 M HF-0.1 M Al(NO₃)₃.

Table 38. Effect of Thoria Particle Size on the Modulus of Rupture of BeO-1.6 vol % ThO₂

Note: 1 psi = 6895 N/m²

Thoria Particle Size (μm)	Porosity (%)	Number Tested	Modulus of Rupture (psi)	Standard Deviation (psi)
5	3.0	5	32,100	1420
10	3.0	5	30,100	1100
15	4.0	5	29,100	4500
33-53	2-7.0	5	25,500	2190
53-63	3.0	5	22,300	1850
104-124	3-4.5	5	20,100	1245
210-250	3-5	5	18,400	1870
300-350	3-7	5	14,300	3520
350-400	2-3	5	16,600	2540
500-600	2-5	5	15,200	2470

10. Surface Properties

No information is available yet.

Table 39. Effect of Temperature on the Modulus of Rupture of BeO-1.6 vol % ThO₂

Thoria particle size 200 μm. Note: 1 psi = 6895 N/m²

Temperature (°C)	Number Tested	Modulus of Rupture (psi)	Standard Deviation (psi)
20	20	18,050	1340
200	20	21,050	1560
400	20	22,100	2840
600	20	22,000	3250
800	20	21,250	2320
1000	20	21,000	2810

Table 40. Effect of Thoria Concentration on the Modulus of Rupture of Dispersions of 200-μm Particles in BeO

Note: 1 psi = 6895 N/m²

Concentration (vol %)	Porosity (%)	Number Tested	Modulus of Rupture (psi)	Standard Deviation (psi)
1.6	4	5	17,950	1180
3.5	3	5	17,100	1850
7.0	5	5	13,550	690
10.0	7	5	12,950	1450
15.0	7	5	9000	1120
20.0	9	5	6950	620

Table 41. Young's Modulus for Dispersions of 200-μm Thoria in Beryllia at Various Temperatures

Concentration (vol %)	Porosity (%)	Young's Modulus (10 ⁶ psi) ^a at -							
		20°C	200°C	400°C	600°C	700°C	800°C	900°C	1000°C
1.6	4.0	51.8	50.9	51.5	50.8	49.8	49.7	49.0	47.7
	4.5	52.1	51.7	51.7	51.0	50.5	48.7	48.2	46.3
	4.0	52.2	51.8	52.8	51.3	51.7	49.3	48.7	45.6
	4.0	51.7	51.0	50.3	50.3	49.5	48.8	48.2	45.8
7.0	9.2	46.1	46.3	46.5	45.1	44.2	43.2	43.5	40.8
	9.2	45.9	46.1	46.1	45.1	45.0	44.5	43.0	39.3
	8.0	47.5	47.5	48.2	47.5	47.0	45.7	44.7	41.8
10.0	4.0	48.5	47.5	47.7	47.3	47.4	46.3	45.6	45.0
	4.5	47.9	47.3	47.3	47.0	45.6	45.6	44.7	44.2
	4.5	47.3	47.0	47.2	47.2	47.2	45.7	44.5	42.7
20.0	12.4	36.5	36.5	36.2	35.4	34.9	34.7	34.2	32.9
	16.0	35.3	35.6	35.7	35.2	34.4	33.3	33.3	31.6
	15.0	35.8	35.7	35.8	35.8	35.0	34.9	34.1	33.7

^a1 psi = 6895 N/m².

E. Ternary and More Complex Systems of Thorium Oxide

1. Composition

Information on the phase equilibria for various systems is summarized below.

ThO₂-UO₂-BeO. - Reeve and Murray²⁴⁷ detected no reaction between ThO₂-UO₂ solid solutions and beryllia, either by x-ray diffraction or microstructural observation. Mixed ThO₂-UO₂ in any proportion formed a eutectic with 60 to 80% BeO at about 2100°C.

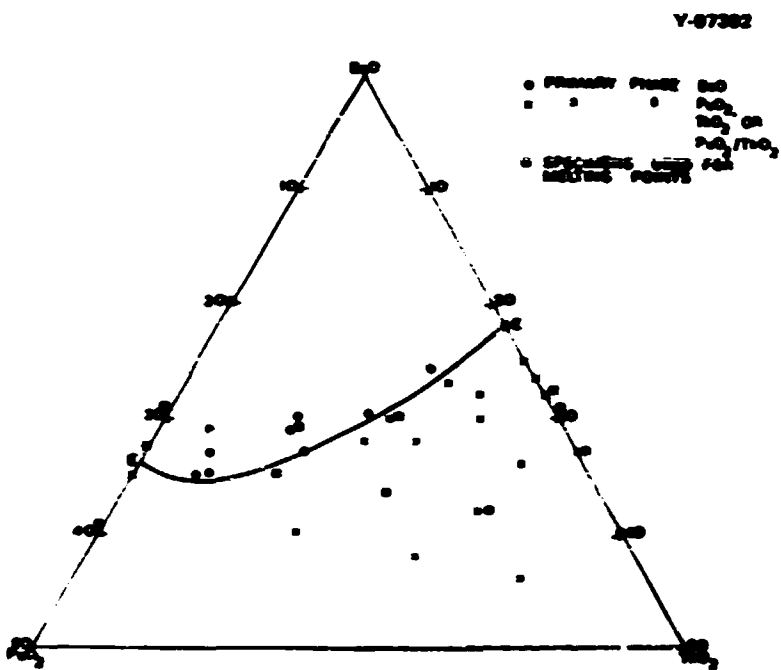


Fig. 54. Location of the Eutectic Valley in the System ThO₂-PuO₂-BeO. Compositions are in mole %. From Hough and Moxley.²¹³ Copyright by North Holland Publishing Company and reproduced with permission.

ThO₂-PuO₂-BeO. - Less than 0.05 mole % of the solid solution ThO₂-50% PuO₂ dissolved in BeO at temperatures up to the solidus.¹⁹⁶ The eutectic temperature varies nearly linearly from 2240°C for thorium-beryllia to 2135°C for plutonium-beryllia.²¹³ Figure 54 shows the variation of the eutectic composition.

ThO₂-UO₂-ZrO₂. - The solubility of zirconia at 1000 and 1400°C increases gradually from about 1% in pure thorium to about 8% in pure uranium.²⁴⁸

ThO₂-UO₂-SiO₂. - Lungu²²² has measured the solid-liquid equilibrium in silica-rich compositions. Mumpton and Rey²⁴⁹ found that ThSiO₄ dissolves up to 20 mole % of the hypothetical USiO₄ at 1000°C.

Unfueled Systems. - Geller *et al.*²¹⁶ present a fusion diagram for ThO₂-Al₂O₃-BeO. The ThO₂-BeAl₂O₄ eutectic is at 1810°C and 53% Al₂O₃, 13% BeO; a ternary eutectic is at about 1795°C and 40% Al₂O₃, 20% BeO. From melting data in the system ThO₂-BeO-MgO, Lang *et al.*²⁵⁰ report a eutectic in the molar proportions 1:10:5 at 1797°C. Grebenchikov²⁵¹ characterized a compound ThBe₂Si₂O₈ melting at about 1700°C; he lists x-ray diffraction peaks. Paderow and Schusterius²⁰⁷ determined by x-ray diffraction solid solubilities at 1400 to 1600°C in the system ThO₂-CeO₂-In₂O₃-Y₂O₃; the solubility of the In₂O₃-Y₂O₃ solid solution in the ThO₂-CeO₂ solid solution decreases with increasing indium content. LeFlom *et al.*²³³ found complete miscibility between Th₃(VO₄)₄ and CeVO₄ and solubility of Na₃VO₄ in Th₃(VO₄)₄ up to a limiting composition of Th₂Na₂(VO₄)₃. Figures 55 and 56 give Mark's results²¹⁷ on the system ThO₂-HfO₂-MgO. Keller²¹⁸ found complete solid solubility between ThNb₄O₁₂ and ThTa₄O₁₂.

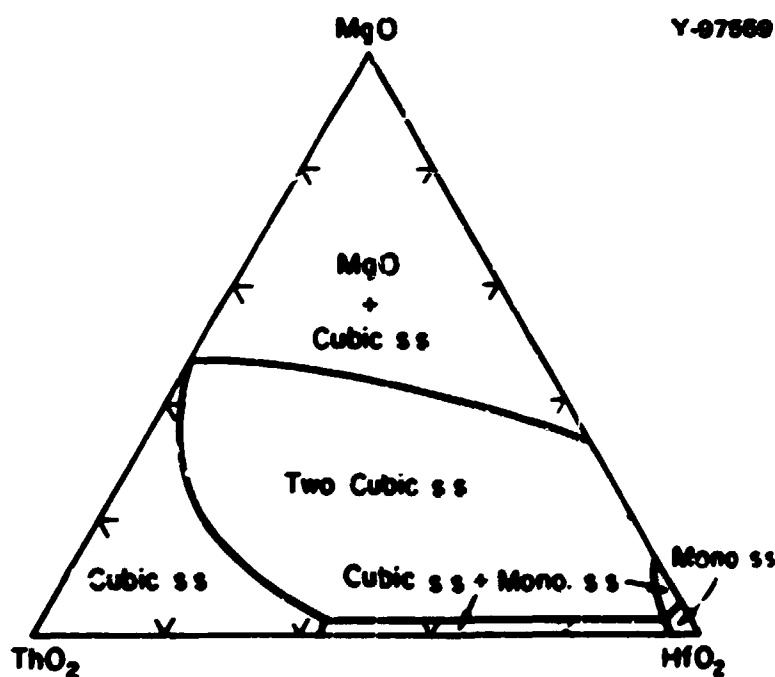


Fig. 55. Stability Fields at 1600°C in the System ThO₂-HfO₂-MgO. ss = solid solution, mono. = monoclinic. Copied from Mark²¹⁷ with permission of the American Ceramic Society.

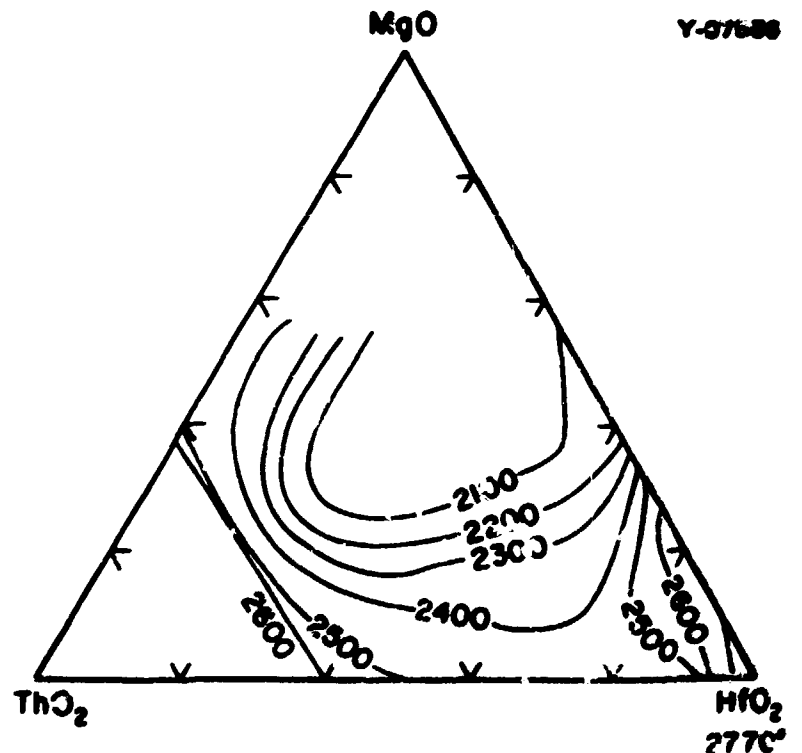


Fig. 56. Apparent Melting Temperatures in the System ThO₂-HfO₂-MgO. Copied from Mark²¹⁷ with permission of the American Ceramic Society.

Mumpton and Roy²⁴⁹ found that ThSiO₄ dissolves 6 ± 2 mole % ZrSiO₄ at about 1000°C. Ruff *et al.*²⁵² studied systems of ThO₂ and MgO or CaO with 50% or more ZrO₂; their data indicate ternary eutectics near 33% CaO, 17% ThO₂ at about 2200°C and near 30% MgO, 25% ThO₂ below 2100°C.

2. Preparation

Preparation of complex systems is by essentially the same methods used for the simpler systems (Section D2).

3. Crystal Properties

Crystal Structure. — Table 42 summarizes available crystal structure information on the systems described in Section 1.

Optical Properties. — Ruff *et al.*²⁵² report that the materials ZrO₂-17.5% ThO₂-5% MgO or CaO are very clear, colorless, and hard with index of refraction 2.21.

Thermal Expansion. — For 20 vol % ThO₂-9% UO₂ dispersed in beryllia, Turner and Smith's report¹⁵⁸ dilatometric values:

$$\text{Percent expansion} = 7.31 \times 10^{-4}(t - 20) + 1.72 \\ \times 10^{-7}(t - 20)^2 + 3.92 \times 10^{-11}(t - 20)^3 \pm 0.0076,$$

where t is the temperature in the range 20 to 1000°C.

Sylvania-Coming¹⁵⁷ reports the mean coefficient to 800°C to be 10×10^{-6} for both ThO₂-6.4% UO₂-1.0% Y₂O₃ and ThO₂-20% UO₂-1.0% Y₂O₃. Burdick *et al.*²⁵³ report 1.11% linear expansion from room temperature to 1200°C for BeO-4.3% Al₂O₃-5.7% ThO₂-2.0% TiO₂.

4. Thermodynamic Properties

No information is available yet.

5. Change of State

No information is available yet.

6. Electrical and Magnetic Properties

Geller²³⁹ compared relative electrical conductivities of resistors made of thorium-base binary and ternary ceramics; Fig. 57 shows his results. Ullmann²⁵⁴ found the electrical conductivity of ThO₂-6.2 mole % CaO-1.2% Al₂O₃-1.4% SiO₂ much lower than that of ThO₂-20 mole % YO_{1.5} over a temperature range.

Table 42. Crystal Structures of Thorium Ternaries

Material	Structure Type	Reference
ThBe ₂ Si ₂ O ₈	Feldspar	251
(Th,Zr)SiO ₄	Thosite	249
(Th,U)SiO ₄	Thosite	249
Th(Nb,Ta) ₄ O ₁₂	Tetragonal	218
Th ₃ (VO ₄) ₄ -CeVO ₄	Zircon with vacancies	233
Th ₃ (VO ₄) ₄ -Na ₃ VO ₄	Zircon with vacancies	233

7. Heat and Mass Transport

Scholes²⁵⁵ measured the thermal conductivity of beryllia-base ceramics containing equal weights of thorium and alumina and various magnesia contents. Over the range 55 to 150°C, the conductivity decreased with increasing content of the additives.

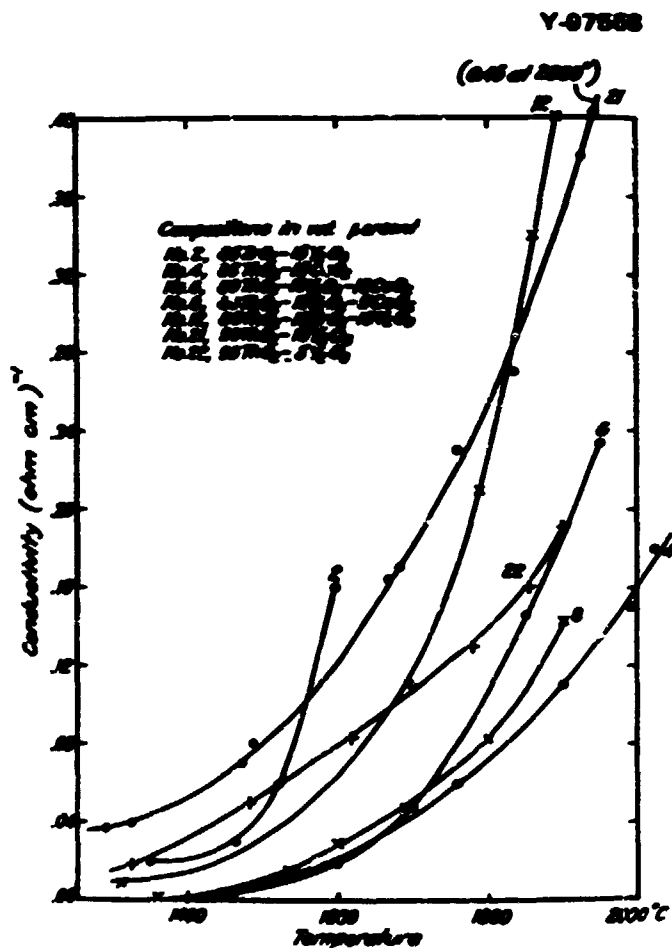


Fig. 57. Relative Electrical Conductivities of Several Thorium-Base Ceramics. Distribution of temperature and current flow do not permit quantitative use of the results. Copied from Geller.²³⁹

8. Mechanical Properties

Veevers and Rotsey²⁵⁶ measured mechanical properties of (Th,U)O₂ dispersions in beryllia. Their dispersoid was prepared two ways. The separate oxides were mixed, ground together, fired, and reground. Also, a thorium-uranium mixture was precipitated from solution, dried, calcined, and ground. The dispersions were prepared in the same way as thoria-beryllia dispersions (Section D2, ref. 77). The effect of particle size of both oxide types on modulus of rupture is given in Table 43. The temperature and composition dependences are in Table 44. Figure 58 shows values of Young's modulus.

Sylvania-Coming¹⁵⁷ found for ThO₂-6.4% UO₂-1.0% Y₂O₃ and ThO₂-20% UO₂-1.0% Y₂O₃ elastic moduli about the same as those of similarly prepared ThO₂ and ThO₂-5% UO₂. Compressive strengths of the ceramics were substantially less. Burdick *et al.*²⁵³ measured several tensile properties of BeO-5.7% ThO₂-4.3% Al₂O₃-2.0% TiO₂. Lang *et al.*²⁵⁰ give ranges of values for several mechanical properties of ceramics in the ThO₂-BeO-MgO system.

Table 43. Effect of (Th,U)O₂ Particle Size on the Modulus of Rupture of 1.7 vol % Dispersions of ThO₂-9% UO₂ in Beryllia at 20°C

Taken from Veevers and Rotsey²⁵⁶

(Th,U)O ₂ Particle Size (μm)	Porosity (%)	Number Tested	Modulus of Rupture (psi) ^a	Standard Deviation (psi) ^a
Coprecipitated (Th,U)O ₂				
3-5	1.5	9	26,700	2460
10-15	1.5	8	25,500	2650
15-20	1.5	14	32,000	3918
25-35	1.5	9	30,700	3350
53-63	1.5	9	32,400	2360
104-124	1.5	9	24,500	3810
210-250	2.5	5	22,600	2540
250-300	2.5	9	21,800	3480
300-400	2.0	8	22,600	2000
450-500	2.0	16	19,600	2559
Mixed UO ₂ -ThO ₂				
~5	3.5	8	29,700	3362
35-53	4.0	8	26,100	3267
152-211	4.0	9	18,500	1351
422-600	3.5	8	15,100	1282

^a1 psi = 6895 N/m².

Table 44. Modulus of Rupture of (Th,U)O₂ Dispersions in Beryllia Based on Veevers and Rotsey²⁵⁶

UO ₂ in Dispersoid (%)	(Th,U)O ₂ in BeO (vol %)	Particle Size (μm)	Modulus of Rupture ^a (1000 psi) at -									
			20°C	200°C	250°C	400°C	500°C	600°C	700°C	750°C	800°C	1000°C
Mixed Oxide												
9	1.7	35-53	26.1	26.0		26.8		27.0			27.3	30.7
		151-211 ^b	18.5	18.5		20.4		20.9			23.6	23.5
			24.1	23.3		24.8		24.3			27.0	27.4
		422-600	15.1	16.7		19.4		18.9			17.0	20.6
Coprecipitated Oxide												
9	1.7	5	25.6	26.0		22.8		24.2			26.1	24.6
		50	25.8	27.8		22.5		24.7			25.2	24.0
		200	18.4	20.2		19.6		20.9			20.5	18.2
9	1.7	200	20.4			22.5			20.0			19.5
		5.0	19.1		18.7		19.0			17.9		17.5
		10.0	15.8		16.2		15.2			15.2		14.4
		20.0	11.5		10.1		10.2			8.4		8.2
25	1.2	50	22.6	24.8		24.3		24.0			23.6	25.0
9	1.7	200 ^c	13.7					18.5				
			16.1					19.5				
0, 50 ^d	1.7	200 ^c	16.6					17.5				
			17.4					19.7				

^aEach value is the average for 8 to 12 specimens; 1 psi = 6895 N/m².

^bThe extreme average values from five batches of (Th,U)O₂ are given.

^cThe extreme average values from three batches of (Th,U)O₂ are given.

^dTwo kinds of particles were dispersed to give an overall dispersoid composition of Th-9% UO₂.

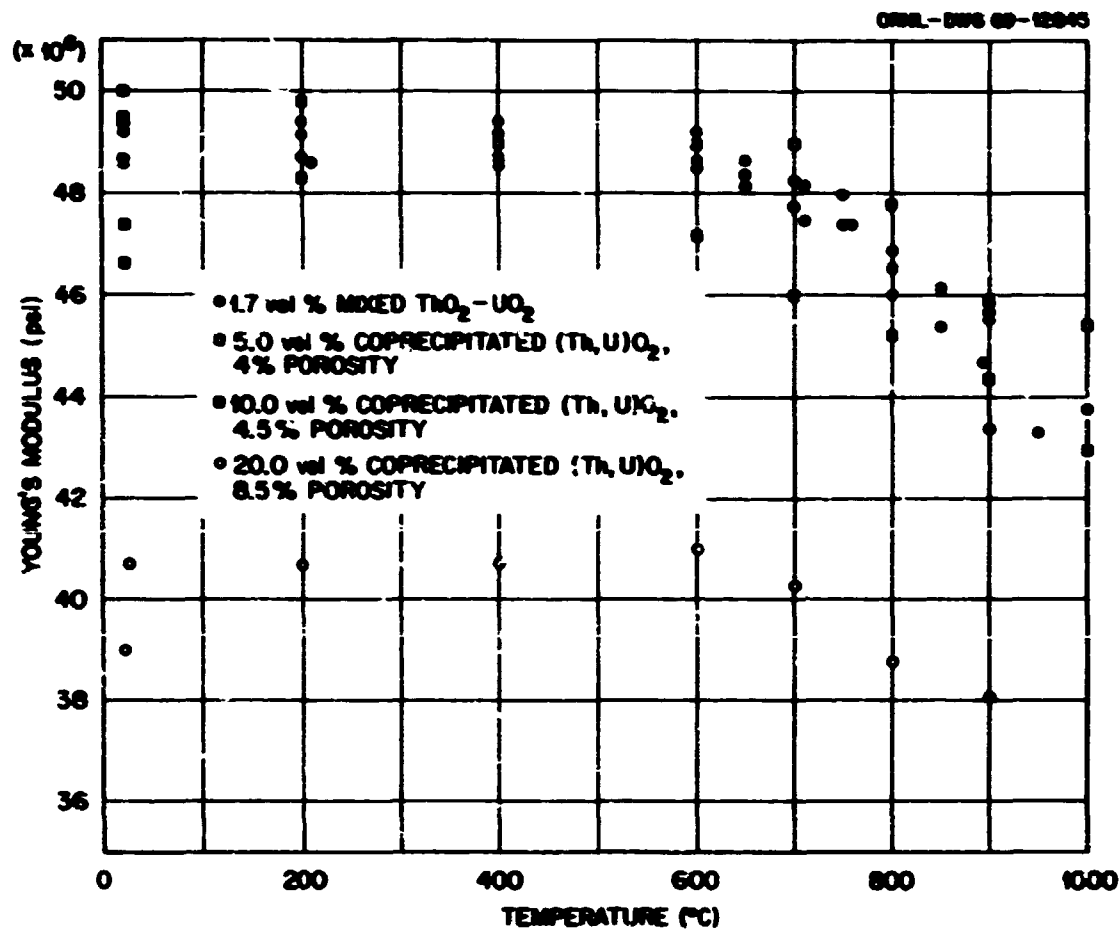


Fig. 58. Young's Modulus of Dispersions of ThO_2 -9% UO_2 in Beryllia. Based on data of Vescey and Rotney.²⁵⁶ To convert: 1 psi = 6895 N/m².

9. Chemical Properties

Incorporating 1.0% Y_2O_3 did not affect the resistance of $(\text{Th}, \text{U})\text{O}_2$ to steam at 336°C and 2000 psi (ref. 157).

10. Surface Properties

No information is available yet.

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METALS AND CERAMICS DIVISION

THORIUM CERAMICS DATA MANUAL

Volume II - Nitrides

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for the
U. S. ATOMIC ENERGY COMMISSION

Volume II. Nitrides

ABSTRACT

Physical, chemical, and mechanical properties of thorium nitrides, alone and in combination with other nitrides and other thorium compounds, are collected from the literature through January 1970 (55 references). The thorium-nitrogen phase equilibrium is reviewed.

This volume will include the following divisions: system information, thorium mononitride systems, and Th_3N_4 systems. The carbonitrides are substitution products of the mononitride and will be covered with it. The oxynitride and nitride-halides are covered under Th_3N_4 systems.

SYSTEM INFORMATION

The thorium-nitrogen phase diagram, taken from Benz *et al.*,¹ is shown in Fig. 1. The only stable compounds shown are ThN and Th_3N_4 . The

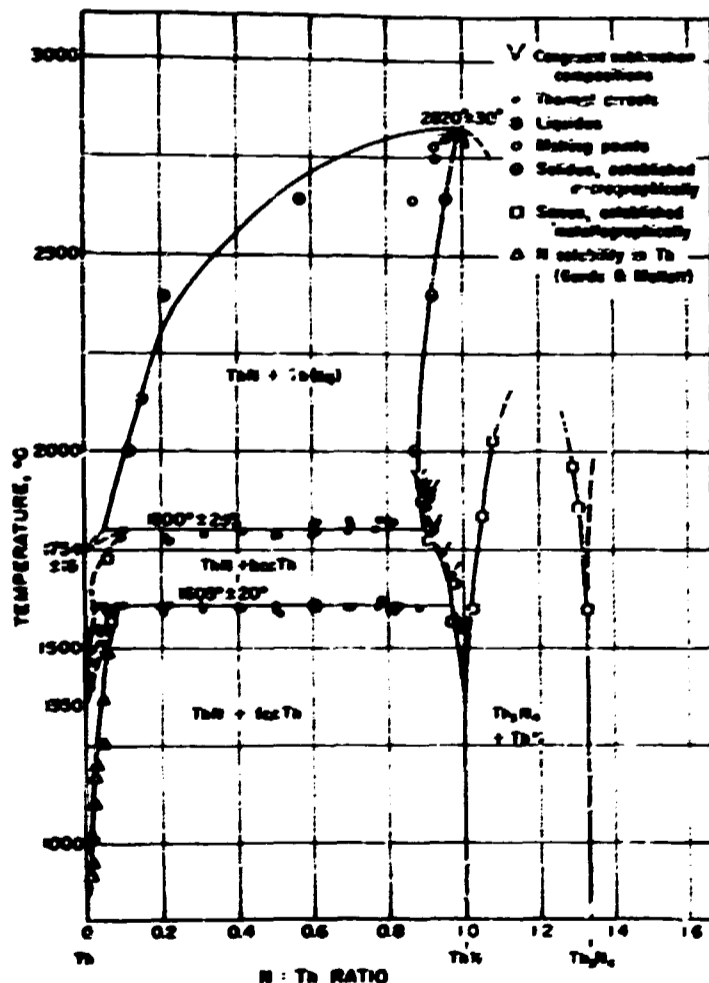


Fig. 1. The Thorium-Nitrogen Phase Diagram. From R. Benz, C. G. Hoffman, and G. N. Rupert.¹ Copyright by the American Chemical Society and reprinted with permission.

reported^{2,3} Th_2N_3 has been identified⁴ as the oxynitride $\text{Th}_2\text{N}_2\text{O}$. This compound is formed from heating ThN and ThO_2 in nitrogen. The equilibrium nitrogen pressure over liquid thorium and ThN is reported by Olson and Mulford⁵ over the range 2416 to 2790°C to be

$$\log p \text{ (atm)} = 8.086 - 33,224/T + 0.958 \times 10^{-17} T^5,$$

or

$$\log p \text{ (N/m}^2\text{)} = 13.092 - 33,224/T + 0.958 \times 10^{-17} T^5,$$

where T is in °K. Oxygen contamination greatly increases this pressure. The equilibrium nitrogen pressure over ThN and Th_3N_4 , measured by Aronson and Auskern,⁶ is shown in Fig. 2.

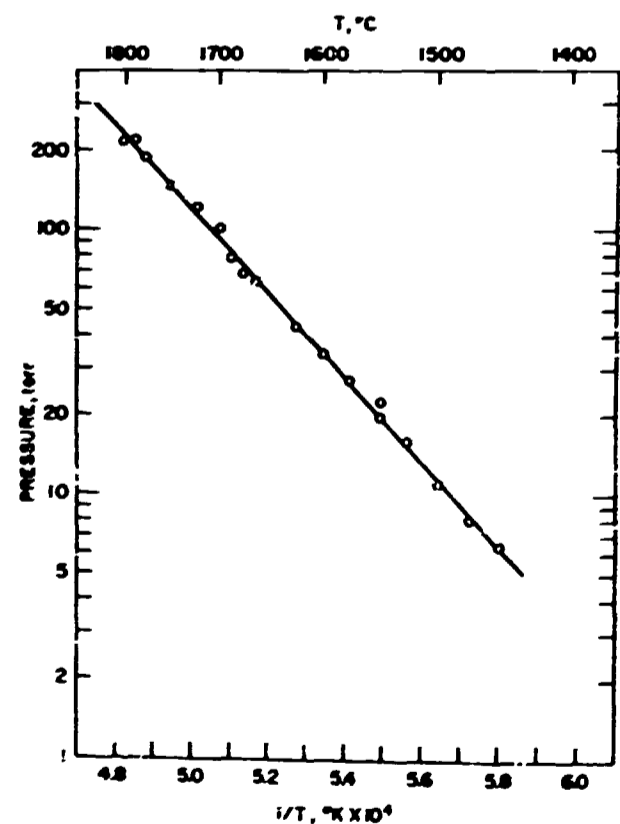


Fig. 2. Nitrogen Pressures over ThN- Th_3N_4 . From S. Aronson and A. B. Auskern.⁶ Copyright by the American Chemical Society and reprinted with permission.

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THORIUM MONONITRIDE SYSTEMS

A. Thorium Mononitride

1. Composition

Benz *et al.*^{1,7} have measured the following limiting compositions of the ThN phase.

	Temperature (°C)	N:Th Atom Ratio
Thorium-rich limit	1576	0.97
	1665	0.96
	1775	0.91
	2000	0.975 ± 0.01
	2100	0.975 ± 0.01
	2645	0.96
Nitrogen-rich limit	1615	1.03 ± 0.03
	1835	1.05
	2065	1.08

At lower temperatures the deviations from stoichiometry are immeasurably small.¹

2. Preparation

Thorium mononitride is generally made as powder from the hydride or metal (usually powdered by hydriding and dehydriding) by heating in nitrogen or from the hydride and ammonia. Synthesis below 1000°C gives Th₃N₄; this is decomposed to ThN at higher temperatures. Benz *et al.*¹ prepared specimens by cold and hot pressing. Olson and Mulford⁵ induction

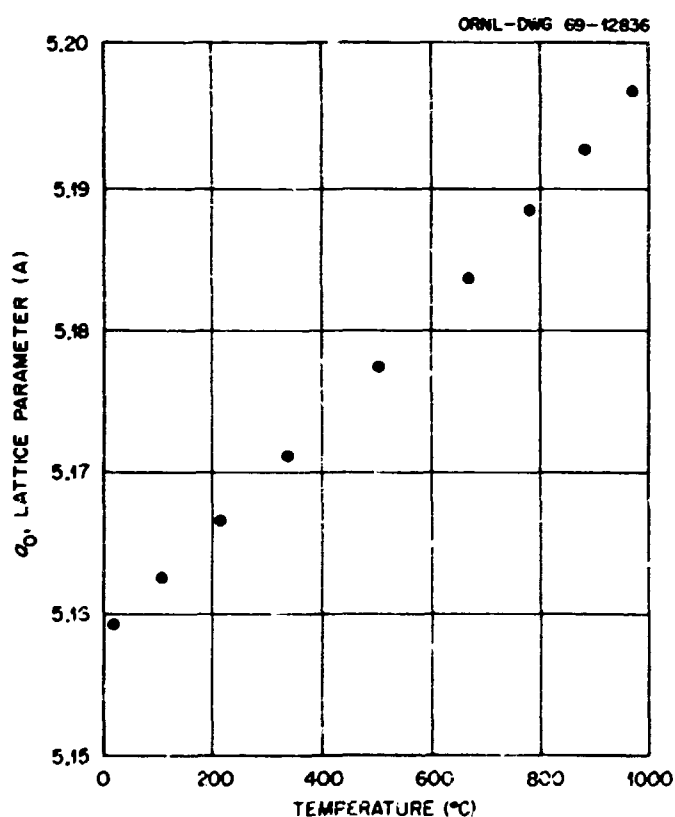


Fig. 3. Temperature Variation of the Lattice Parameter of ThN. Based on Street and Waters.⁸

melted thorium under 2 atm N₂ at 2000°C to get ThN ingots.

3. Crystal Properties

Structure. — Face-centered cubic NaCl type.

Lattice Parameter and Thermal Expansion. — Values of the room-temperature lattice parameter of carefully prepared ThN range from 5.155 to 5.162 Å. Most investigators^{5, 7-9} report close to 5.159. The value most precisely reported is 5.16190 ± 0.00015 by Venard *et al.*¹⁰ Measurement to 900°C by Street and Waters⁸ are shown in Fig. 3; they derive a mean coefficient of expansion of $(7.39 \pm 0.042) \times 10^{-6}/^\circ\text{C}$ over the range measured. Aronson *et al.*⁹ made x-ray diffraction measurements over the range 800 to 1300°C; Fig. 4 compares their expansion values for ThN and some other thorium compounds studied in the same work. The coefficient of expansion of ThN corresponding to these results is $8.2 \times 10^{-6}/^\circ\text{C}$ over the range 800 to 1300°C. The data of Aronson *et al.* and Street and Waters agree reasonably well in the region of overlap.

Color. — Golden yellow,⁵ green-yellow.¹¹

Density. — The density corresponding to $a_0 = 5.159$ is 11.901 g/cm³.

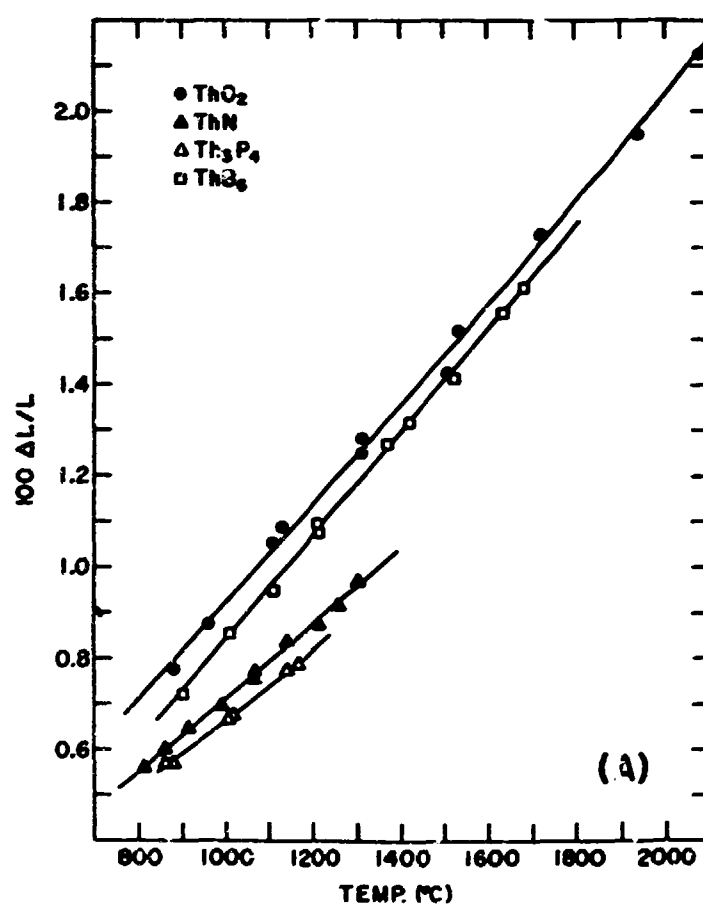


Fig. 4. Thermal Expansion of ThN. Copied from S. Aronson *et al.*⁹ with permission of the American Ceramic Society. Similarly measured expansions of other thorium compounds are included for comparison.

4. Thermodynamic Properties

Aronson and Auskern⁶ estimated the heat and entropy of formation of ThN to be

$$-\Delta H_{298}^{\circ} = 90.6 \text{ kcal/mole} = 379 \text{ kJ/mole}$$

and

$$-\Delta S_{298}^{\circ} = 23.5 \text{ cal mole}^{-1} (\text{°K})^{-1} \\ = 98.3 \text{ J mole}^{-1} (\text{°K})^{-1}$$

From the latter, Aronson and Ingraham¹² take the entropy of ThN at 298°K as $12.2 \pm 2 \text{ cal mole}^{-1} (\text{°K})^{-1}$ or $51 \pm 8 \text{ J mole}^{-1} (\text{°K})^{-1}$, which they compare with values they calculate from a vibrational model. Gingerich¹³ estimates the heat of sublimation as $203.1 \pm 10 \text{ kcal/mole}$, or $849 \pm 42 \text{ kJ/mole}$. Venard and Spruiell¹⁴ estimate the standard free energy of formation to be -51.1 kcal/mole , or -214 kJ/mole , at 1000°C.

5. Change of State

Thorium mononitride melts congruently under sufficient nitrogen pressure. Reported melting points are $2820 \pm 30^{\circ}\text{C}$ under 2 atm ($2 \times 10^5 \text{ N/m}^2$) N_2 by Benz *et al.*,¹ 2820 ± 35 under 2.6 atm ($2.6 \times 10^5 \text{ N/m}^2$) N_2 by Benz,⁷ and $2790 \pm 30^{\circ}\text{C}$ at slightly under 1 atm ($1 \times 10^5 \text{ N/m}^2$) N_2 by Olson and Mulford.⁵ The melting point is lowered by impurities;^{1,5} one mechanism may be by eutectic formation, since Blum and Guinet¹⁵ report that ThN forms a eutectic with 15% ThO_2 , a frequently found impurity in ThN. Also, melting under too little nitrogen lowers the melting point with loss of nitrogen.¹ Chiotti² found melting at 2630°C under helium.

Solid-gas equilibria are given under "System Information."

6. Electrical and Magnetic Properties

Auskern and Aronson¹¹ measured several electrical properties of ThN specimens pressed in vacuum at 5000

psi (35 MN/m^2) and 1275°C and then annealed in vacuum 13 hr at 1800°C to a density of 9.95 g/cm^3 . The results are shown in Fig. 5. The second Hall effect specimen was annealed only 4 hr at 1800°C but reached a density of 10.6 g/cm^3 .

Aronson and Auskern¹⁶ measured the magnetic susceptibility of three ThN specimens at -190 , -76 , and 22°C ; values ranged from 1.65 to $1.84 \times 10^{-7} \text{ emu/g}$, and the decrease with increasing temperature was less than the difference among specimens. Raphael and de Novion¹⁷ found a susceptibility of $1.42 \times 10^{-7} \text{ emu/g}$, constant over the range 4 to 300°K . However, Didchenko and Gortsema¹⁸ found ThN diamagnetic.

Measuring the nuclear magnetic resonance of ^{14}N in ThN, Kuznietz¹⁹ found a positive Knight shift of $(10.7 \pm 1.5) \times 10^{-4}$.

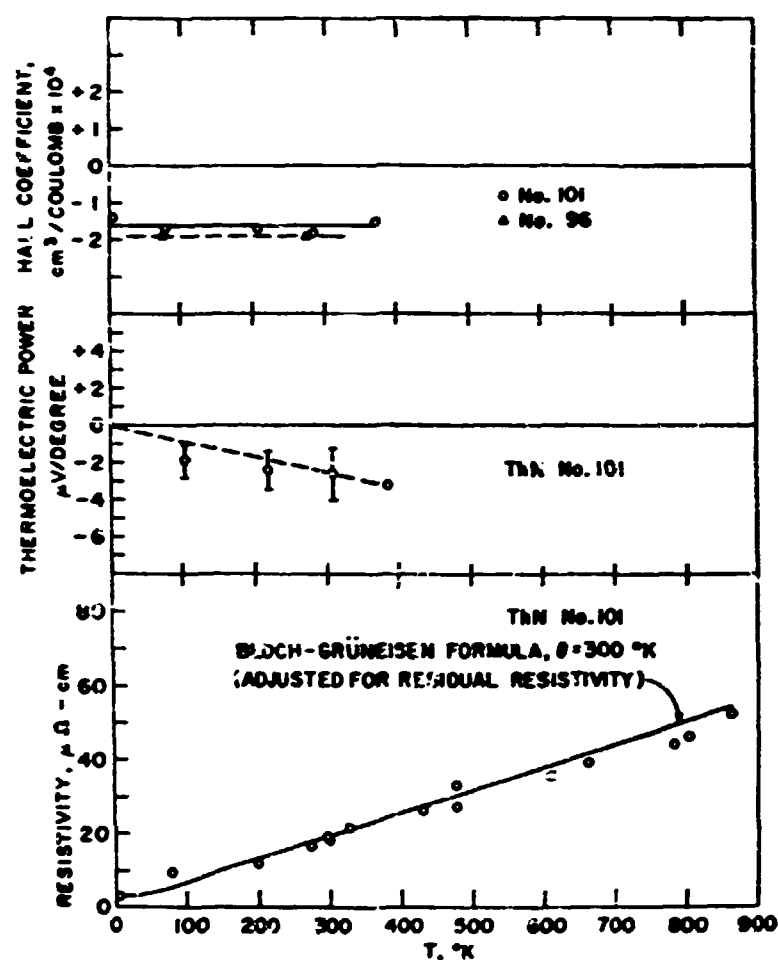


Fig. 5. Hall Coefficient, Thermoelectric Power, and Electrical Resistivity of ThN as Functions of Temperature. Reprinted with permission from A. B. Auskern and S. Aronson,¹¹ copyright by Pergamon.

7. Heat and Mass Transport

From the electrical conductivities measured by Auskern and Aronson¹¹ and the Lorentz equation, Weaver²⁰ has estimated the electronic portion of the thermal conductivity of ThN. His results are compared in Fig. 6 with the thermal conductivities of several nuclear fuel materials.

8. Mechanical Properties

No information is available yet.

9. Chemical Properties

Olson and Mulford⁵ report that ThN ingots exposed to air acquire a black film within minutes and that the

powder reacts readily with air to form ThO_2 . Chiotti³ reports that the powder can be readily handled in air but disintegrates in a short time in moist air and burns vigorously when ignited. Also, ThN reacts with water and is readily attacked by nitric acid.³ Aronson *et al.*⁹ found that above 1300°C , ThN reacted with the residual vapors in a vacuum system at 5×10^{-4} torr (0.07 N/m^2), apparently with gradual substitution of carbon to form ThC and ultimately ThC_2 .

10. Surface Properties

No information is available yet.

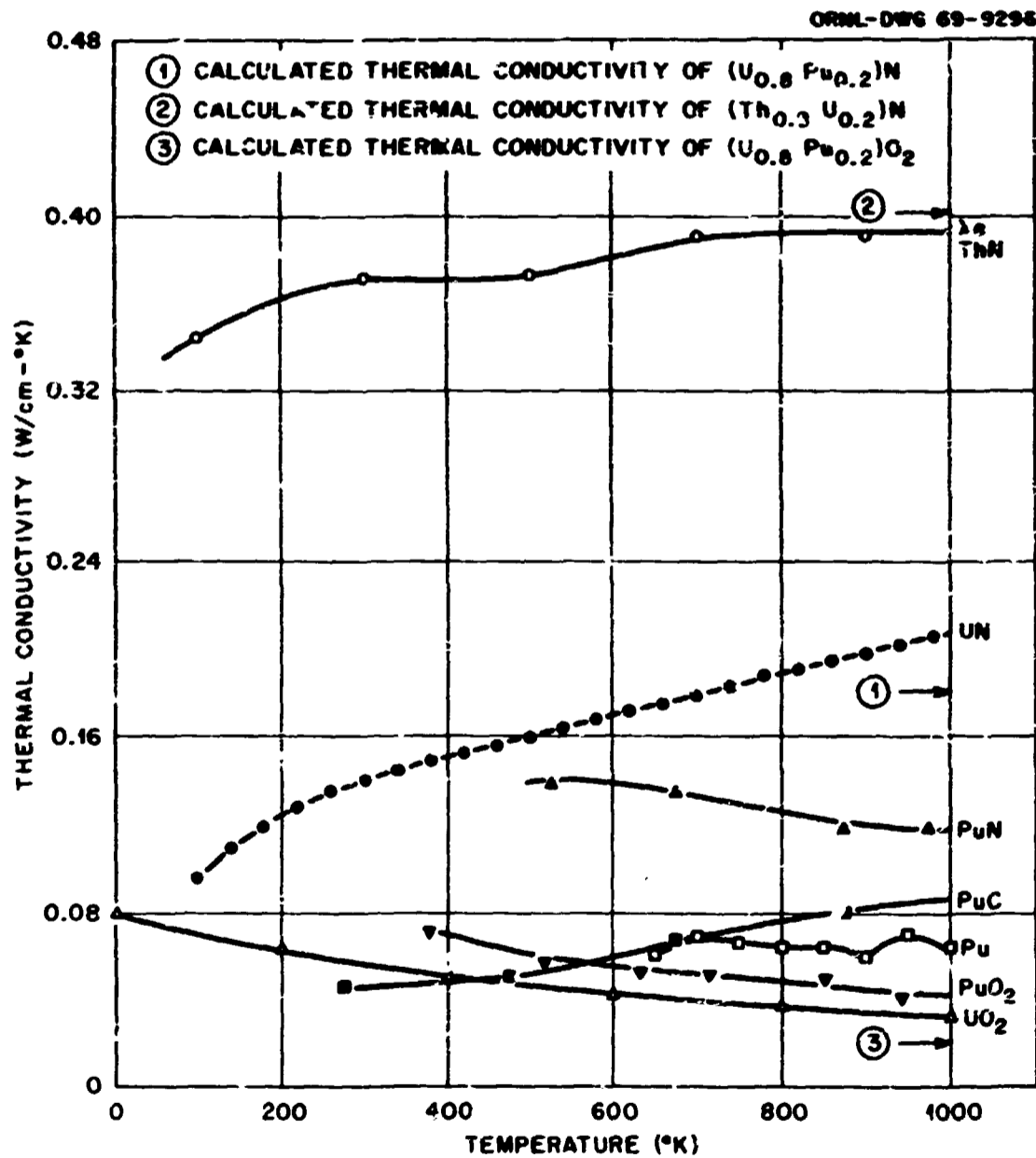


Fig. 6. Estimated Electronic Thermal Conductivity of ThN. Calculated by Weaver²⁰ from electrical resistivity. Thermal conductivities of several nuclear fuel materials are shown for comparison.

B. Thorium-Uranium Mononitrides

1. Composition

Thorium and uranium mononitrides form a continuous series of solid solutions. Equilibria between the mixed nitride phase and the component metals at 1000°C were determined by Venard and Spruiell.¹⁴ Their equilibrium diagram is Fig. 7. The greatest hypostoichiometry was for the composition $\text{Th}_{0.944}\text{U}_{0.056}\text{N}_{0.866}$, which exists at 1000°C in equilibrium with both metals. No information was obtained on the nitrogen-rich composition limits.

2. Preparation

Coarse (Th,U)N powders were prepared from arc-melted thorium-uranium alloys by two hydride-dehydride cycles, reaction with flowing nitrogen at 400 to 800°C, and decomposition to (Th,U)N at 1450 to 1500°C under vacuum.¹⁴

3. Crystal Properties

Lattice parameters for (Th,U)N were determined by Venard *et al.*¹⁰ and are shown in Table 1. "Agreement with Vegard's law is quite good."¹⁰

4. Other Properties

No information is available yet.

C. Thorium Plutonium Mononitrides

Pardue *et al.*²¹ prepared a mononitride from Pu-20% Th, isostatically pressed it at 1540°C and 10,000 psi (70 MN/m²), and heated it 48 hr in flowing nitric gas at 1720°C. Its lattice parameter was 4.980 ± 0.001 Å, and its evaporation loss was 0.0296 g/cm² in 5 hr at 1550°C.

Table 1. Lattice Parameters of (Th,U)N From Venard *et al.*¹⁰

Mole % ThN	Lattice Parameter (Å)
0	4.89034 ± 0.00025
10.24	4.91561 ± 0.00015
20.40	4.95712 ± 0.00086
30.54	4.97434 ± 0.00079
40.60	5.00608 ± 0.00105
50.90	5.03219 ± 0.00043
60.64	5.06339 ± 0.00115
70.56	5.08531 ± 0.00060
80.38	5.10826 ± 0.00019
90.24	5.13461 ± 0.00046
100.00	5.16190 ± 0.00015

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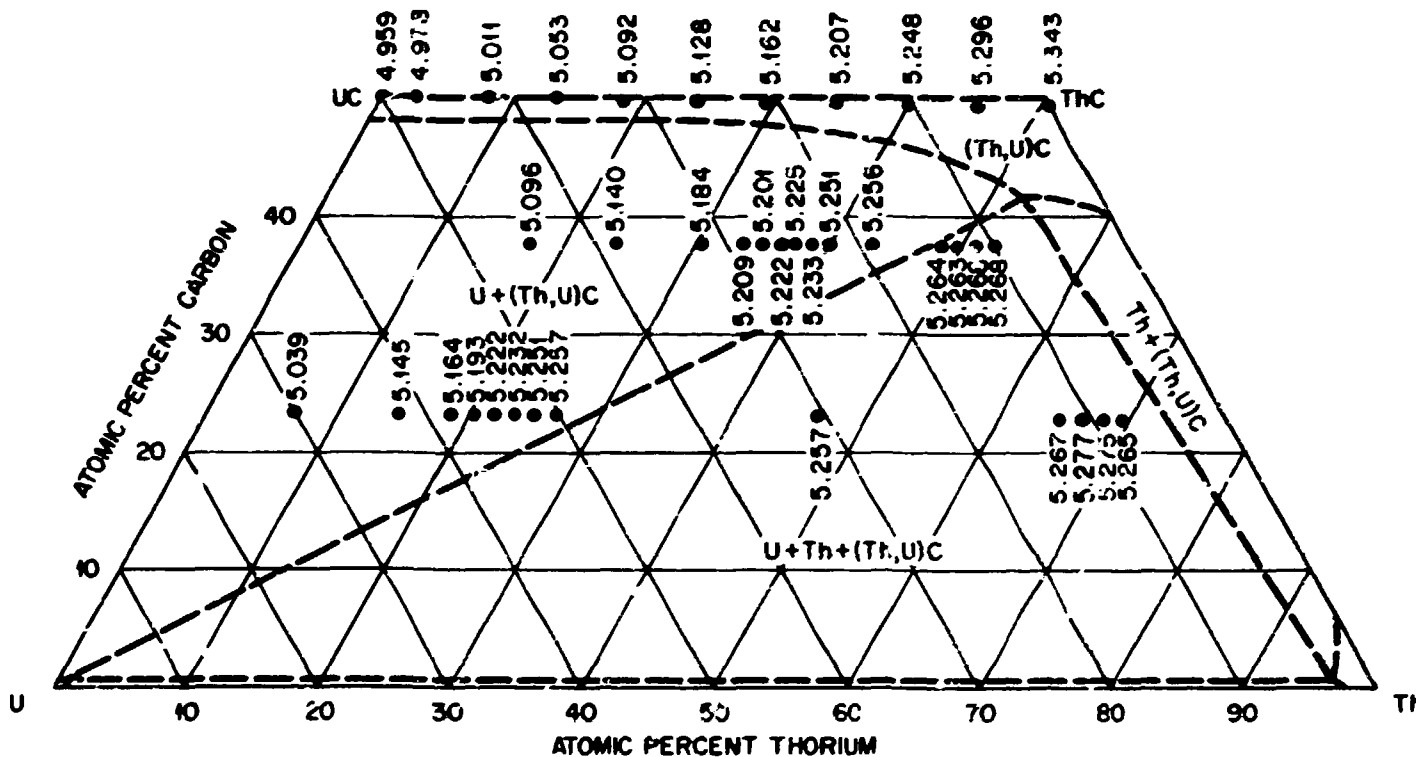


Fig. 7. Phase Equilibria in the Th-U-N System at 1000°C. From Venard and Spruiell.¹⁴ Copyright by North-Holland Publishing Company and reproduced with permission. Lattice parameters are shown for (Th,U)N for several overall compositions.

D. Binary Systems with Nonfuel Nitrides

No information is available yet.

E. Ternary and More Complex Systems with Other Nitrides

No information is available yet.

F. Thorium Carbonitrides

1. Composition

Street and Waters¹⁹ found complete solid solubility between ThN and ThC. Hypostoichiometric compositions are possible^{16,23} when carbon is substituted for some of the nitrogen in ThN, but the limits are not yet known.

2. Preparation

Carbonitrides have been made by heating cold-pressed pellets of the mixed carbide and nitride at 1600°C (ref. 22) or 2000°C (ref. 7). Hypostoichiometric solid solutions have been made^{16,23} by heating mixtures of ThN, thorium, and carbon in vacuum at 1700 to 1800°C. Samples for electrical measurements²³ were hot pressed at 1300°C and 5000 psi (35 MN/m²) in vacuum and then annealed in vacuum at 1800°C for 5 to 17 hr.

Table 2. Melting Points of Th(C_xN_y) Solid Solutions
From Benz⁷

Composition	Lattice Parameter (Å) ^a	Melting Point (°C) ^b	Nitrogen Pressure	
			(atm)	(N/m ²)
				× 10 ⁵
ThC _{0.97}	5.346	2500		
ThC _{0.80} N _{0.21}	5.310	2670	0.01 ± 0.005	0.01
ThC _{0.70} N _{0.28}	5.305	2720	0.05 ± 0.01	0.05
ThC _{0.57} N _{0.39}	5.276	2810	0.18 ± 0.03	0.18
ThC _{0.48} N _{0.49}	5.262	2850	0.30 ± 0.04	0.30
ThC _{0.47} N _{0.47}	5.241	2910	(1.5) ^c	(1.5) ^c
ThC _{0.34} N _{0.56}	5.225	2910	(2.0) ^c	(2.0) ^c
ThC _{0.28} N _{0.63}	5.220	2920	(2.0) ^c	(2.0) ^c
ThC _{0.1} N _{0.9} ^d	5.188	2875		
ThN _{1.00}	5.158	2820	2.6 ± 0.6	2.6

^a±0.001 Å.

^b±35°C.

^cProbably below true equilibrium pressure, since the composition, measured after melting, shows loss of nitrogen.

^dNominal.

3. Crystal Properties

Street and Waters²² found linear variation of the lattice parameter with composition from 5.338 Å for ThC to 5.158 Å for ThN. Benz⁷ found parameters in agreement with those of Street and Waters; both worked with a material close to stoichiometric. For hypostoichiometric materials Auskern and Aronson²³ found agreement with measured parameters and linear interpolation between values for ThN and ThC_x, with x chosen to fit the composition. Their values are:

ThC _{0.778} N _{0.106}	5.320 Å
ThC _{0.625} N _{0.275}	5.288 Å
ThC _{0.537} N _{0.389}	5.266 Å
ThC _{0.461} N _{0.489}	5.246 Å
ThC _{0.203} N _{0.738}	5.197 Å
ThC _{0.029} N _{0.937}	5.165 Å

4. Thermodynamic Properties

Benz⁷ gives the following for the relative internal free energies of mixing of ThC and ThN in the solid and liquid states:

$$\begin{aligned} \Delta G^M(s) &= 7.2 [X_{\text{ThN}}^{(s)}(T - 3090) + X_{\text{ThC}}^{(s)}(T - 2770)] \\ &+ RT [X_{\text{ThN}}^{(s)} \ln X_{\text{ThN}}^{(s)} + X_{\text{ThC}}^{(s)} \ln X_{\text{ThC}}^{(s)}] \\ &- (13,000 \pm 7,000) X_{\text{ThN}}^{(s)} X_{\text{ThC}}^{(s)} \text{ cal/mole} \\ &= 30 [X_{\text{ThN}}^{(s)}(T - 3090) + X_{\text{ThC}}^{(s)}(T - 2770)] \\ &+ RT [X_{\text{ThN}}^{(s)} \ln X_{\text{ThN}}^{(s)} + X_{\text{ThC}}^{(s)} \ln X_{\text{ThC}}^{(s)}] - \\ &- (54,000 \pm 29,000) X_{\text{ThN}}^{(s)} X_{\text{ThC}}^{(s)} \text{ J/mole;} \end{aligned}$$

$$\begin{aligned} \Delta G^M(l) &= RT [X_{\text{ThN}}^{(l)} \ln X_{\text{ThN}}^{(l)} + X_{\text{ThC}}^{(l)} \ln X_{\text{ThC}}^{(l)}] \\ &- (6,600 \pm 7,000) X_{\text{ThN}}^{(l)} X_{\text{ThC}}^{(l)} \text{ cal/mole} \\ &= RT [X_{\text{ThN}}^{(l)} \ln X_{\text{ThN}}^{(l)} + X_{\text{ThC}}^{(l)} \ln X_{\text{ThC}}^{(l)}] \\ &- (28,000 \pm 29,000) X_{\text{ThN}}^{(l)} X_{\text{ThC}}^{(l)} \text{ J/mole;} \end{aligned}$$

the X 's are mole fractions.

5. Change of State

Melting points and equilibrium nitrogen pressures given by Benz⁷ for carbonitride solid solutions are listed in Table 2. Note the maximum.

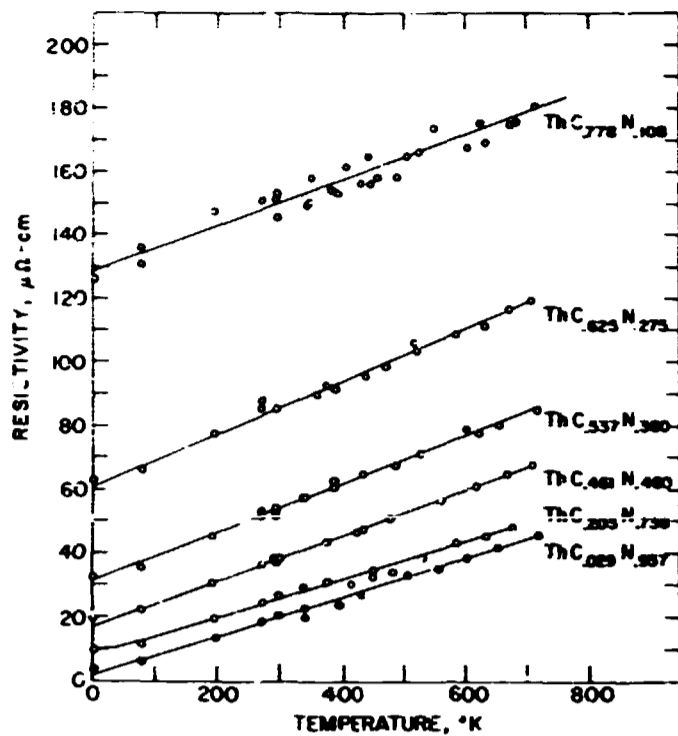


Fig. 8. Electrical Resistivity of Thorium Carbonitrides. Values have been corrected to zero porosity by multiplying by $(1 - P)/(1 + P/2)$, where P is the pore fraction. Copied from A. B. Auskern and S. Aronson²³ with permission; copyright by American Institute of Physics.

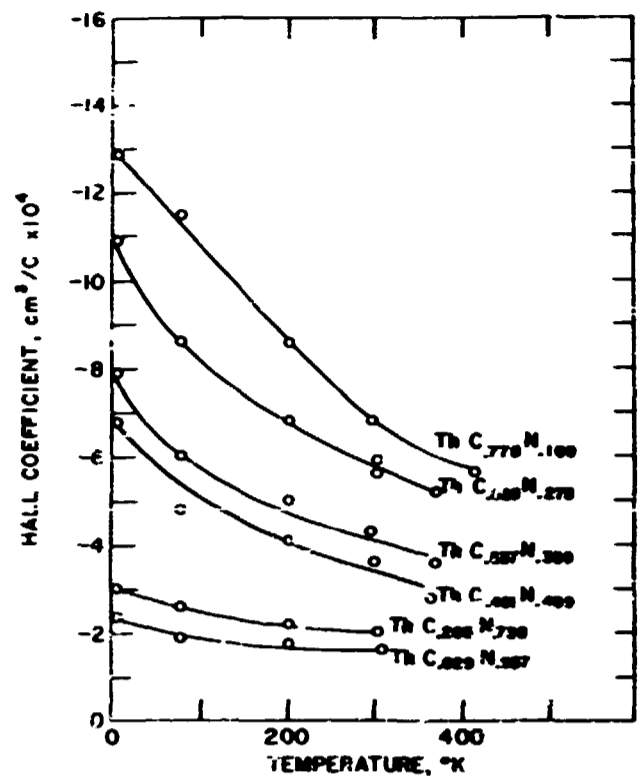


Fig. 9. Hall Coefficient of Thorium Carbonitrides. Values have been corrected to zero porosity by multiplying by $1 - P$, where P is the pore fraction. Copied from A. B. Auskern and S. Aronson²³ with permission; copyright by American Institute of Physics.

6. Electrical and Magnetic Properties

Several electrical properties of hypostoichiometric carbonitrides were measured by Auskern and Aronson.²³ The resistivity, Hall coefficient, and thermoelectric power are given in Figs. 8–10 respectively. The same authors²⁶ magnetic susceptibility values are listed in Table 3.

Table 3. Magnetic Susceptibilities of Thorium Carbonitrides From Aronson and Auskern¹⁶

Composition	Lattice Parameter (Å)	Susceptibility (emu/g) at –		
		22°C	–76°C	–190°C
		$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$
ThC _{0.775} N _{0.113}	5.320	14.6	14.6	15.2
ThC _{0.625} N _{0.275}	5.288	13.5	13.6	13.9
ThC _{0.459} N _{0.489}	5.246	14.2	14.2	14.5
ThC _{0.202} N _{0.734}	5.197	15.6	15.9	16.0
ThC _{0.206} N _{0.749}	5.199	14.6	14.7	14.8
ThC _{0.251} N _{0.936} ^a	5.164	18.2	18.6	18.8

^aCompiler's note: This composition appears to be in error; a carbon subscript of 0.03 to 0.06 would be more consistent with other information in the paper.

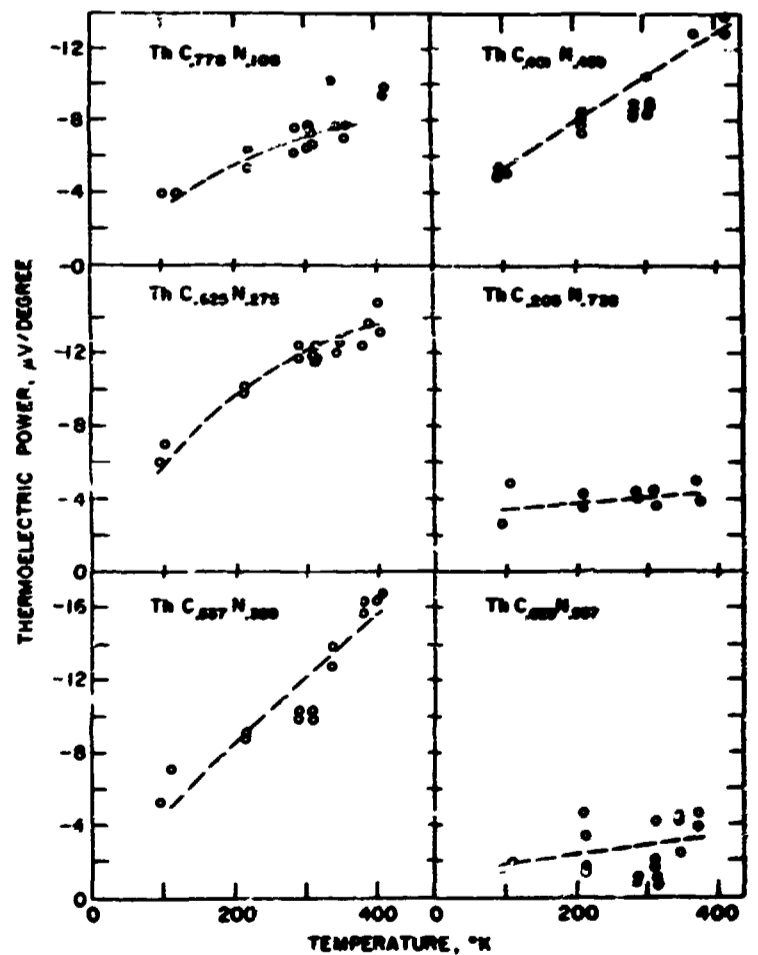


Fig. 10. Absolute Thermoelectric Power of Thorium Carbonitrides. Copied from A. B. Auskern and S. Aronson²³ with permission; copyright by American Institute of Physics.

7. Heat and Mass Transport

No information is available yet.

8. Mechanical Properties

No information is available yet.

9. Chemical Properties

Benz⁷ melted carbon-rich carbonitrides on tantalum and other carbonitrides on tungsten without evidence of interaction. Askern and Aronson²³ found no interaction with molybdenum dies during hot pressing with 30 min contact at 1300°C.

10. Surface Properties

No information is available yet.

Th₃N₄ SYSTEMS

Systems with other nitrides (parts B through E) have not been studied. Compounds between Th₃N₄ and oxide and halides are briefly described in Parts F and G.

A. Th₃N₄

1. Composition

Below 1000°C Benz *et al.*¹ report Th₃N₄ stoichiometric; at higher temperatures they found the following metal-rich limits on the nitrogen-to-thorium atom ratio:

1603°C	1.33 ± 0.03 under 33 torr N ₂ (4400 N/m ²)
1760°C	1.31 under 255 torr N ₂ (34,000 N/m ²)
1960°C	1.28 under 920 torr N ₂ (123,000 N/m ²)

2. Preparation

The first Th₃N₄ characterized^{24,25} was synthesized from the elements, and this is still the usual method.^{6,11} Conditions can vary widely. Benz *et al.*¹ obtained Th₃N₄ from the hydride and nitrogen at 200 to 900°C. Benz and Zachariasen⁴ reacted ThN with 0.13 atm (1.3 × 10⁴ N/m²) N₂ at 1320°C. Düsing and Huniger²⁶ precipitated Th₃N₄ from thorium vapor and nitrogen. Specimens for electrical measurements¹¹ have been hot pressed at 1340 to 1400°C in 1 atm (1 × 10⁵ N/m²) N₂.

3. Crystal Properties

Benz and Zachariasen⁴ find for Th₃N₄ a rhombohedral structure, space group $R\bar{3}m$, with parameters $a_0 = 9.398$ Å and $\alpha = 23.78^\circ$, with the corresponding hexagonal cell having $a_0 = 3.871$ Å, $c_0 = 27.385$ Å. A metastable monoclinic form is reported by Juza and Gerke²⁷ with $a_0 = 6.95$, $b_0 = 3.83$, $c_0 = 6.20$ Å, and $\beta = 90.7^\circ$.

The color of Th₃N₄ has been described as yellow-maroon,^{24,25} maroon,⁶ dark maroon,¹¹ dark brown, almost black,²⁸ and black.²⁶ Chiotti³ describes his higher nitride as reddish brown, but he called it Th₂N₃ and may have had Th₂N₂O.

4. Thermodynamic Properties

Heat of Formation. — By direct measurement Neumann *et al.*²⁸ obtained $\Delta H_{292}^\circ = -308.4$ kcal/mole = -1290 kJ/mole. From a heat of combustion of 564.8 kcal/mole (2363 J/mole) Neumann *et al.*²⁹ found $\Delta H_{292}^\circ = -312.4$ kcal/mole = -1307 kJ/mole. Brewer *et al.*³⁰ give $\Delta H_{298}^\circ = -310.4$ kcal/mole = -1299 kJ/mole.

Free Energy of Formation. — Brewer *et al.* give $\Delta G_{298}^\circ = -283.6$ kcal/mole = -1187 kJ/mole.

Entropy of Formation. — Brewer *et al.* give $\Delta S_{298}^\circ = -89.6$ cal mole⁻¹ (°K)⁻¹ = -375 J mole⁻¹ (°K)⁻¹.

Heat Capacity. — Sato³¹ gives for 0 to 503°C

$$c_p = 0.04395 + 4.436 \times 10^{-5} t$$

$$- 1.1384 \times 10^{-8} t^2 \text{ cal g}^{-1} (\text{°C})^{-1}$$

$$= 0.2048 + 1.856 \times 10^{-4} t$$

$$- 4.763 \times 10^{-8} t^2 \text{ J g}^{-1} (\text{°C})^{-1}$$

Free Energy Function. — From a Russian compilation, Voitovich³² calculates the following values for $(G - H_{298}^\circ)/T$:

Temperature, °C	298	500	1000	1500	2000
Function, cal mole ⁻¹ (°K) ⁻¹	43.2	45.6	59.5	71.7	82.5
Function, J mole ⁻¹ (°K) ⁻¹	180.7	191.6	248.9	300.0	345.2

5. Change of State

Decomposition pressure data are given under "System Information."

6. Electrical and Magnetic Properties

Auskern and Aronson¹¹ found the resistivity of Th₃N₄ to be very sensitive to heat treatment and to range from 10⁵ to 10⁸ ohm-cm at room temperature. Aronson and Auskern¹⁶ found values of the magnetic susceptibility ranging from 0.3 to 0.6 × 10⁻⁸ emu/g over the range -190 to 22°C.

7. Heat and Mass Transport

No information is available yet.

8. Mechanical Properties

No information is available yet.

9. Chemical Properties^{24,25}

Thorium nitride Th₃N₄ hydrolyzes slowly in cold water, immediately on boiling. It burns in oxygen, less luminously than thorium.

10. Surface Properties

No information is available yet.

F. Th₂N₂O

Benz³³ obtained equilibrium between Th₃N₄, Th₂N₂O, and ThO₂ by heating mixtures of thorium, ThN, and ThO₂ in the range 1550 to 2000°C. At equilibrium the phases present were Th₃N₄ and Th₂N₂O, only Th₂N₂O, or Th₂N₂O and ThO₂, depending on whether the initial mixture contained less than, close to, or more than 25 mole % ThO₂ respectively. The Th₂N₂O phase ranged in composition from ThN_{1.22}O_{0.20} to ThN_{1.0}O_{0.5} at 1500 ± 40°C and ThN_{1.28}O_{0.10} to ThN_{1.0}O_{0.5} at 2000 ± 48°C. The ThO₂ phase showed no variability at 1600°C but extended to approximately ThN_{0.1}O_{1.35} at 2000°C. On cooling, precipitation removed nonstoichiometry from these phases. No solubility of oxygen in Th₃N₄ could be detected. The oxynitride was gray to maroon, depending on grain size. Benz and Zachariassen⁴ give the crystal structure of Th₂N₂O as hexagonal with $a_0 = 3.8833 \pm 0.0002 \text{ \AA}$ and $c_0 = 6.1870 \pm 0.0003 \text{ \AA}$.

Several other complex nitrides have been reported by Benz and Zachariassen.³⁴ They have the Ce₂O₂S-type crystal structure, space group $P\bar{3}m1$; the x-ray diffraction characterization is given in Table 4.

G. Thorium Nitride-Halides

Juza and Sievers³⁵ have prepared and characterized a series of compounds ThNX, where X is F, Cl, Br, or I. All arise from reaction of the appropriate thorium tetrahalide with ammonia or Th₃N₄. The fluoride is insoluble and stable to aqueous reagents; it decomposes in 3 hr at 1320°C or in 15 min at 1550°C. The other compounds have reactivities that increase with the atomic weight of the halogen. The fluoride can dissolve up to 10% ThO₂.

The crystal structures have been worked out in detail.³⁵ The fluoride is rhombohedral, and the others are tetragonal. Two intermediate nitride fluorides, ThN_xF_{4-3x}, were also observed, tetragonal with x from 0.88 to 0.94 and orthorhombic with x from 0.79 to 0.87.

Table 4. Some Complex Thorium Nitrides
From Benz and Zachariassen³⁴

Compound	Lattice Parameter (Å)		Theoretical Density (g/cm ³)
	a_0	c_0	
Th ₂ NOAs	4.041 ± 0.001	6.979 ± 0.002	9.58
Th ₂ N ₂ Se	4.0287 ± 0.0002	7.156 ± 0.001	9.43
Th ₂ NOP	4.0285 ± 0.0003	6.835 ± 0.001	9.08
Th ₂ N ₂ S	4.008 ± 0.001	6.920 ± 0.002	9.04

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