**THERMAL CONDUCTIVITY VALUES
FOR ADVANCED FUELS**

Interim Report

by

A. Sheth and L. Leibowitz

MASTER

U of C-AUA-USAEC

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

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Chemical Engineering Division

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CHEMICAL ENGINEERING DIVISION
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ABSTRACT

A preliminary examination has been made of existing thermal conductivity and thermal diffusivity data for uranium and plutonium carbides and nitrides. An interim set of recommended values of thermal conductivity is presented for the compounds UC, UN, PuC, PuN, (U,Pu)C, and (U,Pu)N.

This preliminary evaluation is one of a series of reports being prepared within the Advanced Fuels Program of Argonne National Laboratory. The evaluation is an initial part of a more extensive, critical study of existing property data for candidate advanced fuels. The thermal conductivity data presented should be considered as interim values until the rigorous critique, now in progress, is completed.

INTRODUCTION

Two reports in this series, namely, ANL/CEN/AF-100 and ANL-AFP-2, have been published. The former presents a detailed bibliography of properties data on uranium and plutonium carbides and nitrides; the latter lists an interim set of recommended values for heat capacity, enthalpy, vapor pressure, melting point, heat of fusion, and heat of vaporization for UC, UN, PuC, PuN, (U,Pu)C, and (U,Pu)N. As an extension of the past efforts, this report lists an interim set of recommended values of thermal conductivity for the same compounds discussed in ANL-AFP-2.

A critical evaluation of thermal conductivity and thermal diffusivity data of these materials will be made in the near future. As a word of caution, all the literature has not been thoroughly reviewed nor have the available data been critically analyzed; thus, extrapolations should be made carefully and due care should be exercised in using these values in any analyses.

The references that were used are given at the end of the report; however, a detailed bibliography is available in ANL/CEN-AF-100.

Thermal Conductivity of Candidate Advanced Fuels

Interim evaluations have been made for thermal conductivity and thermal diffusivity data for UC, UN, PuC, PuN, (U,Pu)C and (U,Pu)N. In most cases, emphasis was placed on the most recent experimental work or literature assessments. In a few cases, where conductivity data were not available but diffusivity data were available, the conductivity values were calculated using appropriate values for density, thermal expansion coefficient, and heat capacity. In other cases, where tabulated values or satisfactory equations were

not available, the values for thermal conductivity or thermal diffusivity were taken from the available graphical form.

In general, experimental values of thermal conductivity are markedly affected by the following factors:

- (1) Stoichiometry
- (2) Impurities such as oxygen, nitrogen, etc.
- (3) Porosity
- (4) Extent of irradiation
- (5) Fabrication method
- (6) Experimental technique of measurement

In the present report, no attempt was made to include the effects of all these factors; however, an effort was made to specify the characteristics of the samples for which data were obtained, if such information was included in the literature. Values for different candidate fuels are not presented in a consistent way, that is, they were not reduced to a common format such as 100% of theoretical density, stoichiometric composition, etc. To provide data, not only in tabular form but also in equation form, a standard form of a second-order polynomial was fitted to the recommended data using polynomial regression. No attempt was made to determine the optimum form of the equation. These limitations make it advisable to exercise due care in extrapolating the recommended values. The interim recommended sets of thermal conductivity values are given below.

UC. Uranium carbide and similar NaCl-type compounds have many metallic characteristics. At high temperatures, heat transfer is mainly electronic and obeys the Wiedemann-Franz law; therefore, thermal conductivity is proportional to the product of temperature and electrical conductivity. At low temperature, there will also be a large phonon component. Two recent literature reviews, one by Fulkerson and coworkers¹ and another by Washington² were referred to in assessing the available data. Values recommended by Fulkerson¹ cover the temperature range from 127 to 1327°C; these values decrease toward a minimum value and then remain constant. Washington's review,² which is more recent and more thorough, covers the temperature range from 500 to 2400°C and includes the effects of many of the factors listed earlier. Based on these considerations and until a more critical evaluation is made, one should use the equation provided by Washington. The values, which are for stoichiometric UC of 100% theoretical density, were calculated from Eq. 1 and are listed in Table I; the corresponding equation is as follows:

$$K = 0.04774 + 3.1031 \times 10^{-6} (T - 500) \quad 500^{\circ}\text{C} \leq T \leq 2400^{\circ}\text{C} \quad (1)$$

where K = thermal conductivity in cal/sec-cm-°C and T = temperature in °C.

According to Washington, the thermal conductivity is reduced in hypostoichiometric fuel, but the extent is uncertain. For 4 wt % C material, he has recommended the equation:

$$K = 0.04058 + 6.9223 \times 10^{-6} (T - 500) \quad (2)$$

TABLE I. Thermal Conductivity of UC^a

Temperature, °C	K, cal/sec-cm-°C
500	0.0477
600	0.0481
700	0.0484
800	0.0487
900	0.0490
1000	0.0493
1100	0.0496
1200	0.0499
1300	0.0502
1400	0.0505
1500	0.0508
1600	0.0512
1700	0.0515
1800	0.0518
1900	0.0521
2000	0.0524
2100	0.0527
2200	0.0530
2300	0.0533
2400	0.0536

^aFor stoichiometric UC of 100% theoretical density, calculated from Eq. 1.

where the terms have the same meaning as given earlier. For other carbon contents, the deviation from the UC value can be considered in proportion to the degree of hypostoichiometry. Washington has also given equations dealing with oxygen additions. Furthermore, the effect of porosity can be included for all compositions as follows:

$$K_p = K_o (1 - P)/(1 + P) \quad (3)$$

where K_p = thermal conductivity of sample with a fractional porosity P , and K_o = thermal conductivity of sample with no porosity ($P = 0$).

UN. For UN, the work reported by Keller,³ Bauer,⁴ and Washington² were examined. The latter two are analytical work whereas the former is experimental. The agreement among all three is quite reasonable; however, the assessment provided by Washington² is recent and satisfies the experimental values reported by Keller³ very well over the entire temperature range. Hence, the data proposed by Washington are recommended. The values are tabulated in Table II, and the corresponding equation for UN of 100% theoretical density is as follows:

$$K = 0.02519 + 4.772 \times 10^{-5} T - 1.4227 \times 10^{-8} T^2 \quad (4)$$

TABLE II. Thermal Conductivity of UN^a

Temperature, °C	K, cal/sec-cm-°C
200	0.0352
400	0.0413
600	0.0475
800	0.0536
900	0.0566
1000	0.0594
1100	0.0614
1200	0.0625
1300	0.0634
1400	0.0640
1500	0.0645
1600	0.0647
1700	0.0649
1800	0.0652

^aFor UN of 100% theoretical density;
for Ref. 2.

with the terms having the same meanings as previously. A few words of caution: the values reported by Washington were in graphical form and were read from it by us to prepare the data in the tabulated and analytical forms in this report. According to Washington, one can use the same equation as was recommended for UC in order to consider the effect of porosity; however, more work is needed to incorporate the effects of the other factors on the thermal conductivity of UN.

PuC. The work on PuC in the literature is very sparse, and the data are fragmentary. Accordingly, an attempt was made to estimate a reliable set of values until a more exact set can be experimentally obtained. The basis for the calculation was set of thermal diffusivity values experimentally measured for a PuC sample of 84% of theoretical density.⁵ The values were read from the smoothed curve representing the experimental data. Using a molecular weight of 249.269 for PuC_{0.87}, the heat capacity values recommended in ANL-AFP-2, room temperature density reported by Kruger^{6,7} and the linear thermal expansion coefficient value provided by Pallmer,⁸ values for thermal conductivity were calculated using the following relation:

$$K = \alpha \cdot \rho \cdot C_p \quad (5)$$

where K = thermal conductivity in cal/sec-cm-°C, α = thermal diffusivity in cm²/sec, C_p = heat capacity in cal/g-°C, and ρ = density in g/cm³. The calculated values of thermal conductivity are tabulated in Table III and the corresponding equation is as follows:

$$K = 0.00918 + 2.181 \times 10^{-5} T - 6.1819 \times 10^{-9} T^2 \quad (6)$$

TABLE III. Thermal Conductivity of PuC^a

Temperature, °C	K, cal/sec-cm-°C
400	0.0167
500	0.0187
600	0.0201
700	0.0215
800	0.0228
900	0.0237
1000	0.0246
1100	0.0256
1200	0.0265
1300	0.0271
1370	0.0275

^a For PuC of 84% theoretical density; calculated using Eq. 5, and diffusivity data of Ref. 5.

PuN. Work in the literature on the thermal conductivity of PuN is also very sparse. Some experimental measurements were made at Battelle Memorial Institute.⁹ At the time when those measurements were made, however, reliable data were not available on the heat capacity of PuN and on the change in density as a function of temperature; therefore, the values of thermal conductivity calculated from thermal diffusivity decreased first and after reaching a minimum value kept on increasing, in contrast to normal behavior. Data on thermal conductivity were also reported by Keller.¹⁰ Here, too, thermal diffusivity was measured and the thermal conductivity was calculated by using the heat capacity and the room-temperature density of UN along with the thermal expansion coefficient of PuN; these data showed the normal trend of increasing and levelling off. Based on these facts, the data of Keller¹⁰ are recommended in this interim report until more reliable work is done. The values are tabulated in Table IV and the corresponding equation is as follows:

$$K = 0.01847 + 3.191 \times 10^{-5} T - 2.2659 \times 10^{-8} T^2 \quad (7)$$

(U,Pu)C. The thermal conductivity and thermal diffusivity of (U,Pu)C have been measured by a number of investigators. For the present report, only two recent reviews, one by Washington² and the other by Kerrisk,¹² were considered. According to Kerrisk, the preferred values given by Washington fall below most of the available data in the temperature range 600 to 1600°C. Kerrisk also states that his equations represent all the data better than the function proposed by Washington in the region of steady-state operation. Hence, for the present work it is recommended that Kerrisk's data be used until more critical evaluation is made. His values for (U_{0.8}Pu_{0.2})C of 100% theoretical density are tabulated in Table V and the corresponding equations are as follows:

$$K = 0.03036 + 2.537 \times 10^{-5} T - 6.685 \times 10^{-9} T^2 \quad 100^\circ\text{C} \leq T \leq 1900^\circ\text{C} \quad (8)$$

$$K = 0.0545 \quad T > 1900^\circ\text{C} \quad (9)$$

TABLE IV. Thermal Conductivity of PuN^a

Temperature, °C	K, cal/sec-cm-°C
215	0.024
290	0.026
408	0.028
520	0.029
600	0.030
650	0.029
718	0.029
813	0.030 ^b
535	0.031 ^b

^a From Ref. 10

^b Value not used in fitting the least squares curve.

TABLE V. Thermal Conductivity of (U,Pu)C^a

Temperature, °C	K, cal/sec-cm-°C
100	0.0328
200	0.0352
300	0.0374
400	0.0394
500	0.0414
600	0.0432
700	0.0448
800	0.0464
900	0.0478
1000	0.0490
1100	0.0502
1200	0.0512
1300	0.0520
1400	0.0528
1500	0.0534
1600	0.0538
1700	0.0542
1800	0.0544
1900	0.05443
>1900	0.0545

^a For (U_{0.8}Pu_{0.2})C of 100% theoretical density; calculated from Eq. 8.

In regard to the effect of U/Pu ratio on K, Kerrisk believes that there is not enough information available to differentiate between the thermal conductivity of $(U_{0.8}Pu_{0.2})C$ and $(U_{0.85}Pu_{0.15})C$. In general, the material with higher uranium content should have about 5% higher thermal conductivity, but he thinks that the uncertainties in his equations (about 15%) are greater than the expected 5% difference. To include the effect of porosity, he suggested the use of Eq. 3.

(U,Pu)N. Mixed nitride clearly shows a lower thermal conductivity than UN. It appears that for $(U_{0.8}Pu_{0.2})N$, the conductivity curve has a similar shape to that of UN. In the literature, there are a number of papers dealing with experimental as well as analytical work. Of these, the experimental work reported by Alexander¹¹ and Keller¹⁰ and the analytical review reported by Washington² have been considered in the present evaluation. In the data reported by Washington, no tabulated values or equations were given. In addition, not all the available literature data were used in his review. On the other hand, the experimental work reported by Alexander agreed very well with that reported by Keller. An attempt was made by us to convert Washington's data (read from a graph) to the basis of Alexander's data (from 100% TD to 93% TD) using Eq. 3, but the agreement was poor at the lower and higher temperatures. Hence, it was decided to recommend Alexander's data for $(U_{0.8}Pu_{0.2})N$ of 93% of theoretical density until a more critical evaluation is made. These values are given in Table VI and the corresponding equation is as follows:

$$K = 0.02708 + 1.618 \times 10^{-5} T - 2.4351 \times 10^{-9} T^2 \quad (10)$$

TABLE VI. Thermal Conductivity of $(U,Pu)N^a$

Temperature, °C	K, cal/sec-cm-°C
127	0.029
327	0.032
527	0.035
727	0.038
927	0.040
1127	0.042
1327	0.044 ^b
1527	0.046 ^b
1727	0.048 ^b

^a For $U_{0.8}Pu_{0.2}N$ of 93% theoretical density; from data in Ref. 11.

^b Extrapolated.

Conclusions

This report presents a recommended set of thermal conductivity values for candidate advanced fuels which may be used judiciously until a more thorough evaluation of the available data (now in progress) is completed. Literature data in some cases were fitted to second order polynomials with little or no attempt to optimize the form of the equation. For these reasons, care should be exercised when extrapolating the given values. This preliminary survey of the existing data has revealed some serious gaps and inconsistencies. Both experimental and analytical work are needed to rectify this situation.

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