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ZIRCALOY-4, URANIUM DIOXIDE, AND MATERIALS FORMED BY THEIR INTERACTION
A LITERATURE REVIEW WITH EXTRAPOLATION OF PHYSICAL PROPERTIES TO HIGH TEMPERATURES

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ZIRCALOY-4, URANIUM DIOXIDE, AND MATERIALS FORMED BY THEIR INTERACTION A LITERATURE REVIEW WITH EXTRAPOLATION OF PHYSICAL PROPERTIES TO HIGH TEMPERATURES

By

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ABSTRACT

The physical properties of UO_2, ZrO_2, UO_2-ZrO_2 solid solutions, ZrO_{2-x}, and Zircaloy-4 have been reviewed. Recommended and extrapolated values of these physical properties are given. The properties covered in this report are, transition temperatures, heat capacities, heat contents, vapor pressures, thermal conductivities and thermal expansion. The temperature ranges and materials covered were geared for use in the analysis of a loss-of-coolant reactor accident.

CONTENTS

FIGURES

TABLES

I. INTRODUCTION

In various portions of the reactor safety program, including the LOFT experiments as originally planned, a knowledge of the high temperature physical-chemical properties of reactor fuel materials is required both for the safety analysis and planning which must precede such tests and for the proper interpretation of the behavior of the core materials during the tests. Since major industrial interest centers on Zircaloy-4 clad uranium dioxide, and the first LOFT core is projected to use this fuel-cladding combination, the pertinent physical-chemical properties of these materials (and compounds which might reasonably be produced by the chemical interaction of these two substances) have been collected for use in the LOFT safety analysis and data interpretation. Temperatures approaching 3000°C may be reached in the fuel elements after the loss-of-coolant accident and it has not always been possible to find experimental values for the desired physical-chemical properties. In a number of cases best estimates have been made by the extrapolation of existing measurements guided by well known physical-chemical principles. Values for the following properties are reported:

1.0 Transition Temperatures

2.0 Thermodynamic Properties

3.0 Equilibrium Vapor Pressure

4.0 Thermal Conductivities

5.0 Thermal Expansion

For greatest utility the information in this report has been arranged in the following manner: Section II, which follows immediately, contains the recommended values for the physical-chemical properties to be used in the aforementioned calculations. In all cases values based on experimental data and estimates are clearly differentiated.

Section III contains the sources of information, alternate presentations of information appearing in Section II, and values for some of the physical properties which are not listed in Section II. Recommendations for further work with these materials are contained in Section IV.

This survey was completed in July 1966 and includes information available from journals published as recently as June 1966 with the exception of one report published in September 1966. Research in this field is active, and pertinent information is appearing frequently; therefore, updating of this document in about two years would be advisable to continue to fulfill the needs of the reactor safety program.

It is expected that a General Electric report "Recommended Property and Reaction Kinetics Data for Use for Evaluating a Light-Water-Cooled Reactor Loss-of-Coolant Incident Involving Zircaloy-4 or 304 ss Clad UO_2", will be shortly published.[1] It is anticipated that the General Electric report will complement this one in several areas, and therefore it is suggested that both documents be used as sources of physical property data.

II. RECOMMENDED VALUES FOR PHYSICAL PROPERTIES

1. TRANSITION TEMPERATURES

1.1	UO_2	
1.11	Melting Point-Unirradiated	2830°C
1.12	Change in Melting Point with Irradiation	-32°C/10,000 MWd/MtU
1.13	Normal Boiling Point	3850°C
1.2	ZrO_2	
1.21	Monoclinic to Tetragonal Transition	1205°C
1.22	Tetragonal to Cubic Transition	2285°C
1.23	Melting Point	2700°C
1.24	Normal Boiling Point	4100°C
1.3	ZrO_{2-x} (See Phase Diagram-Figure 1)	
1.4	UO_2-ZrO_2 Solid Solutions (See Phase Diagram-Figure 2)	
1.41	Eutectic Temperature	2550°C
1.5	Zircaloy-4	
1.51	α - β Transition	~ 950°C
1.52	Melting Point	1850°C

2. THERMODYNAMIC PROPERTIES

2.1 UO_2 (Unirradiated)

2.11 Heat Capacity

2.111 25 to 1200°C

$$C_p = 19.20 + 1.62 \times 10^{-3}T - 3.96 \times 10^{5}T^{-2} \text{ cal/mole-°K} \quad (T \text{ in °K})$$

2.112 1200 to 2830°C

$$C_p = 5.762 + 9.56 \times 10^{-3}T \text{ cal/mole-°K} \quad (T \text{ in °K})$$

2.113 Molten UO_2

$$C_p = 35 \text{ cal/mole-°K}^{*}$$

2.12 Enthalpy

2.121 25 to 1200°C

$$H^{\circ}_{T}-H^{\circ}_{298} = -7125 + 19.20T + 0.81 \times 10^{-3}T^{2} + 3.96 \times 10^{5}T^{-1} \text{ cal/mole} \quad (T \text{ in °K})$$

2.122 1200 to 2830°C

$$H^{\circ}_{T}-H^{\circ}_{298} = 3934 + 5.762T + 4.78 \times 10^{-3}T^{2} \text{ cal/mole} \quad (T \text{ in °K})$$

2.123 ΔH (fusion) $\approx$ 28.5 Kcal/mole

2.124 Molten UO_2 above 2830°C

$$H^{\circ}_{T}-H^{\circ}_{298} \approx 35T-12{,}300 \text{ cal/mole} \quad (T \text{ in °K})^{*}$$

2.125 ΔH (vaporization) (See text under vapor pressure)

2.2 ZrO_2

2.21 Heat Capacity

2.211 Monoclinic ZrO_2 (25°C to 1205°C)

$$C_p = 16.64 + 1.80 \times 10^{-3}T - 3.36 \times 10^{5}T^{-2} \text{ cal/mole-°K} \quad (T \text{ in °K})$$

2.212 Tetragonal ZrO_2 (1205 to 1727°C)

$$C_p = 17.8 \text{ cal/mole-°K}$$

2.213 Tetragonal and Cubic ZrO_2 (1727 to 2700°C)

$$C_p = 5.056 + 6.372 \times 10^{-3}T^{*}$$

---

*Estimated

2.22 Enthalpy

2.221 Monoclinic ZrO_2 (25 to 1205°C)

$$H^\circ_T - H^\circ_{298} = 16.64T + 0.90 \times 10^{-3}T^2 + 3.36 \times 10^5 T^{-1} - 6168 \text{ cal/mole} \quad (T \text{ in } ^\circ K)$$

2.222 Monoclinic to Tetragonal Transition

$$\Delta H = 1420 \text{ cal/mole}$$

2.223 1205°C to 1727°C

$$H^\circ_T - H^\circ_{298} = 17.80T - 4268 \text{ cal/mole} \quad (T \text{ in } ^\circ K)$$

2.224 Tetragonal ZrO_2 (1727 to 2285°C)

$$H^\circ_T - H^\circ_{298} = 8480 + 5.056T + 3.186 \times 10^{-3}T^2 \text{ cal/mole} \quad (T \text{ in } ^\circ K)^*$$

2.225 Tetragonal to Cubic Transition

$$\Delta H_T \approx 3 \text{ kcal/mole}^*$$

2.226 Cubic ZrO_2 (2285 to 2700°C)

$$H^\circ_T - H^\circ_{298} \approx 11500 + 5.056T + 3.186 \times 10^{-3}T^2 \text{ kcal/mole} \quad (T \text{ in } ^\circ K)^*$$

2.227 Heat of Fusion of ZrO_2

$$\Delta H \approx 20.8 \text{ kcal/mole}^*$$

2.228 Molten ZrO_2

$$H^\circ_T - H^\circ_{298} \approx 4400 + 24T \text{ kcal/mole} \quad (T \text{ in } ^\circ K)$$

2.229 ΔH (vaporization). (See text page 18)

2.3 UO_2-ZrO_2 Solid Solutions (See text pages 12 and 13)

2.4 ZrO_{2-x} from x=0 to x=2 (See text page 14)

2.5 Zircaloy-4

---

*Estimated

2.51 Heat Capacities

2.511 α -Zircaloy-4 (25 to 950°C)

$C_p = 7.1 \times 10^{-2} + 1.7 \times 10^{-5}T - 0.89 \times 10^{-3}T^2$ cal/g-°K (T in °K)

2.512 β-Zircaloy-4 (950 to 1850°C)

$C_p = 8.7 \times 10^{-2}$ cal/g-°K

2.513 Liquid Zircaloy-4

$C_p = 8.8 \times 10^{-2}$ cal/g-°K

2.52 Enthalpy

2.521 α-Zircaloy-4 (25 to 950°C)

$H°_T - H°_{298} = 7.1 \times 10^{-2}T + 8.5 \times 10^{-6}T^2 + 0.89 \times 10^3T^{-1} - 24.21$ cal/g (T in °K)

2.522 α - β Transition

$\Delta H = 10$ cal/g

2.523 β-Zircaloy-4 (950 to 1850°C)

$H°_T - H°_{298} = 8.7 \times 10^{-2}T - 20.75$ cal/g (T in °K)

2.524 ΔH (fusion) = 53.7 cal/g*

2.525 ΔH (vaporization) (See text pages 16 and 17)

3. EQUILIBRIUM VAPOR PRESSURES

3.1 UO_2

3.11 Above Solid UO_2

$$\text{Log}\left[P_{UO_2}\ (\text{atm})\right] = 33115T^{-1} - 4.026 \log_{10}T + 22.805$$

3.12 Above Liquid UO_2

$$\text{Log}\left[P_{UO_2}\ (\text{atm})\right] = 21462T^{-1} + 4.99^{*}$$

---

*Estimated

3.2 ZrO_2

3.21 Solid ZrO_2

3.211 $\mathrm{Log}\left[P_{ZrO_2}\ (\mathrm{atm})\right] = -39{,}778T^{-1} - 3.597\ \mathrm{Log}_{10}T + 21.701$

3.212 $\mathrm{Log}\left[P_{ZrO} \times P_{O_2}^{\frac{1}{2}}\ (\mathrm{atm}\ 3/2)\right] = -61527T^{-1} + 14.17$

3.22 Liquid ZrO_2

3.221 $\mathrm{Log}\left[P_{ZrO}\ (\mathrm{atm})\right] = -31{,}680T^{-1} + 6.542^{*}$

3.222 $\mathrm{Log}\left[P_{ZrO}\ P_{O_2}^{\frac{1}{2}}\ (\mathrm{atm}^{3/2})\right] = -57{,}507T^{-1} + 12.86^{*}$

3.3 Zircaloy-4

3.31 Solid Zircaloy-4

$\mathrm{Log}\left[P_{Zr}\ (\mathrm{atm})\right] = -28{,}899T^{-1} + 5.804$

4. THERMAL CONDUCTIVITIES

4.1 UO_2

4.11 Unirradiated UO_2 (for more detailed information see text page 24)

4.111 Solid UO_2

Temperature °k	Thermal Conductivity, k watts/cm-°C
500	0.0680
1000	0.0370
1500	0.0262
2000	0.0230
2500	0.0280
3000	0.042*

4.112 Liquid UO_2 at 3200°K

$k = 0.05$ watts/cm-°C*

4.12 Irradiated Stoichiometric Solid UO_2

$$k = \frac{38.24}{T+129.4} + 4.788 \times 10^{-3}T^{3} \text{ watts/cm-°C}$$

---

*Estimated

4.2 ZrO_2

ZrO_2 (25 to 2700°C)

$k = 0.0181 + 3.5 \times 10^{-6} T$ (°C) watts/cm-°C

4.3 UO_2-ZrO_2 Solid Solutions (See text page 25)

4.4 Zircaloy-4

4.41 Solid Zircaloy-4

T °C	k watts/cm-°C
200	0.142
400	0.165
600	0.195
800	0.228
1000	0.256
1200	0.308
1400	0.377
1600	0.46*
1800	0.55*

4.42 Liquid Zircaloy-4

1850°C	0.57*

5. THERMAL EXPANSION

5.1 UO_2

5.11 Solid UO_2

5.111 (0 to 2200°C from 0°C)

$$\% \text{ Linear Expansion} = 6.797 \times 10^{-4} + 2.896 \times 10^{-7} T^2 \quad (T \text{ in } °C)$$

5.112 (2200 to 2830°C from 0°C)

$$\% \text{ Linear Expansion} = 0.204 + 3 \times 10^{-4} T + 2 \times 10^{-7} T^2 + 10^{-10} T^3 \quad (T \text{ in } °C)$$

5.12 Melting Point

Increase in volume on melting 9.6%

5.13 Liquid UO_2

$$\% \text{ Linear Expansion} = 3.5 \times 10^{-3}/°C$$

---

*Estimated

5.2 ZrO_2

5.21 Monoclinic ZrO_2 (0 to 1205°C)

% Linear Expansion = $7.8 \times 10^{-4}/°C$

5.22 Monoclinic to Tetragonal Transition

Decrease in volume approximately 7.7%

5.23 Tetragonal and Cubic ZrO_2 (1205 to 2700°C)

% Linear Expansion = $1.302 \times 10^{-3}/°C$

5.3 ZrO_2-UO_2 Solid Solutions (See text page 32)

5.4 Zircaloy-4

5.41 α Form (0 to 950°C)

% Thermal Expansion = $5.6 \times 10^{-4}T + 4 \times 10^{-7}T^2$

5.42 α-β Transition

Decrease in volume approximately 0.5%

5.43 β Form (950 to 1850°C)

% Thermal Expansion = $9.7 \times 10^{-4}/°C$

III. PHYSICAL PROPERTIES OF REACTOR MATERIALS

1. TRANSITION TEMPERATURES

1.1 Uranium Dioxide

Solid uranium dioxide has the face centered cubic structure at all temperatures up to its melting point. [2]

1.11 Unirradiated UO_2

Many different values of the melting point of UO_2 have been reported in the literature, ranging from 2176 to 2880°C. Variations of the recent results indicate that the melting point lies between 2730 and 2880. The large range of reported melting points is probably the result of stoichiometry changes in the UO_2 during the measurements,[3,4] and the higher reported melting points are probably the better determinations.

1.12 Irradiated UO_2

Irradiation of UO_2 of course effects the melting point as a result of the build-up of fission products in the fuel. The results of two determinations of the change in the melting point on irradiation are in disagreement.[8, 10]

The results given in reference 8 indicate an increase in the melting point at low exposures. At higher burn-ups there is a rapid decrease in the melting point to about 2800°C. The melting point was only slightly effected between 5,000 and 50,000 MWd/Mt U. The results given in reference 10 are in disagreement with this work since a constant decrease of 32°C/10,000 MWd/Mt U was observed. The behavior observed in the earlier work at low irradiations may have been the result of changes in UO_2 stoichiometry rather than real changes caused by fission of UO_2. Since more data is available at high burn-ups in reference 10, I recommend the constant decrease in the melting point of 32°C/10,000 MWd/Mt U, although further work is needed to resolve the differences between these two determinations.

1.2 ZrO_2

The reported transition temperatures have been reviewed by Schick[11], and for the monoclinic to tetragonal transition, a temperature of 1478°K is recommended. It has been shown that there is a transition from a tetragonal to a cubic form of ZrO_2 at high temperatures.[12, 13] A temperature of 2285°C is recommended for this transition, which was determined using a high temperature X-ray diffractometer. The recommended melting point is 2700°C.[11]

1.3 ZrO_{2-x} from x = 0 to x = 2

The phase diagram for the zirconium-oxygem system has been reported by Hansen and co-workers.[15] Since the phase diagram does not show the monoclinic, tetragonal, and cubic forms of ZrO_2, the portions of the phase diagram at higher oxygen content, greater than 30 atom percent, is considered to be in doubt; however, the liquidus-solidus curve is probably reasonably accurate. This phase diagram is given in Figure 1.

1.4 Solid Solution of UO_2 and ZrO_2

There is disagreement between workers on the phase diagram for the ZrO_2 and UO_2 system.[5, 16-20] Cohen and Schaner [19] has shown that there is not complete miscibility of the cubic solid solution and tetragonal solid solutions at high temperatures as was suggested by Wolten [16]; indeed there is a high temperature cubic form of ZrO_2.[12, 13] Since Grimes et al have made a fairly extensive study of the lower temperature regions of the ZrO_2-UO_2 system, have incorporated liquidus-solidus curve of Lambertson and Mueller [5], and have used the high temperature results of Cohen and Schaner in their phase diagram, the phase diagram by Grimes et al is recommended. Figure 2 is a copy of this phase diagram with slight modifications. The melting point of the eutectic mixture of UO_2 and ZrO_2 is 2550°C.

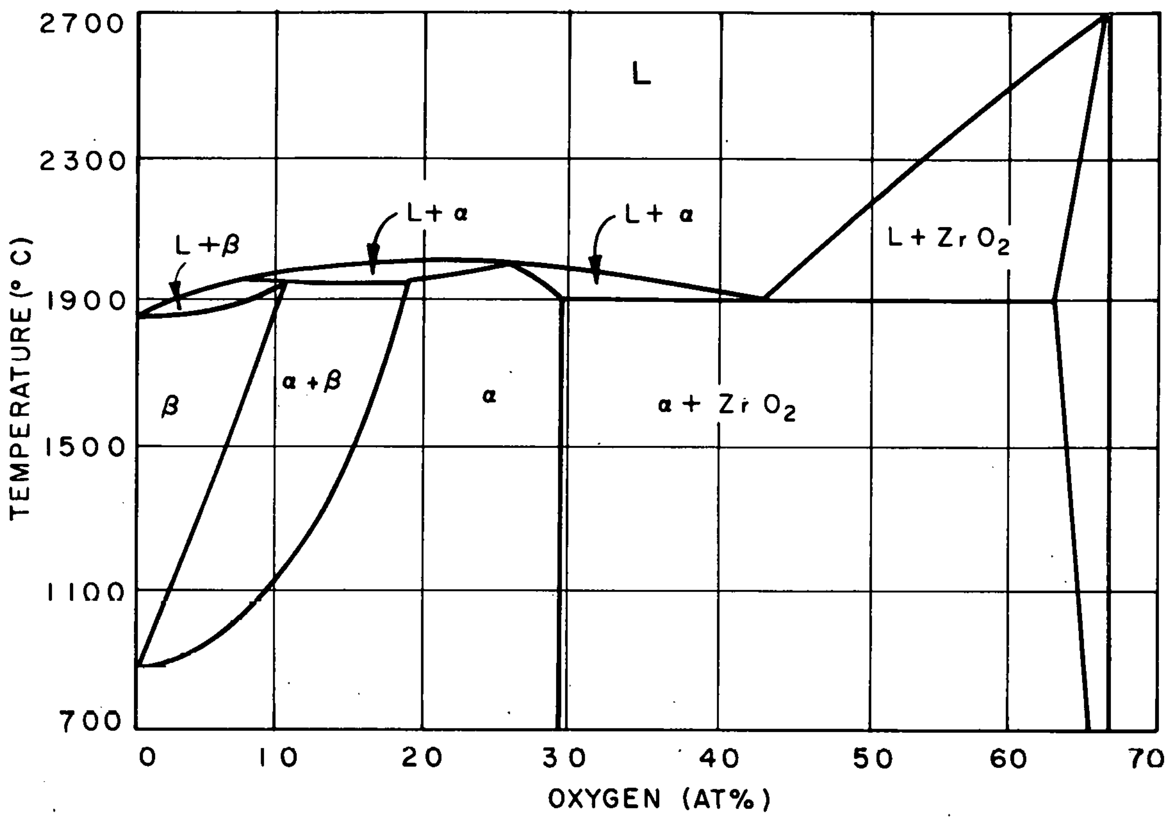

Fig. 1 Zirconium-Oxygen System

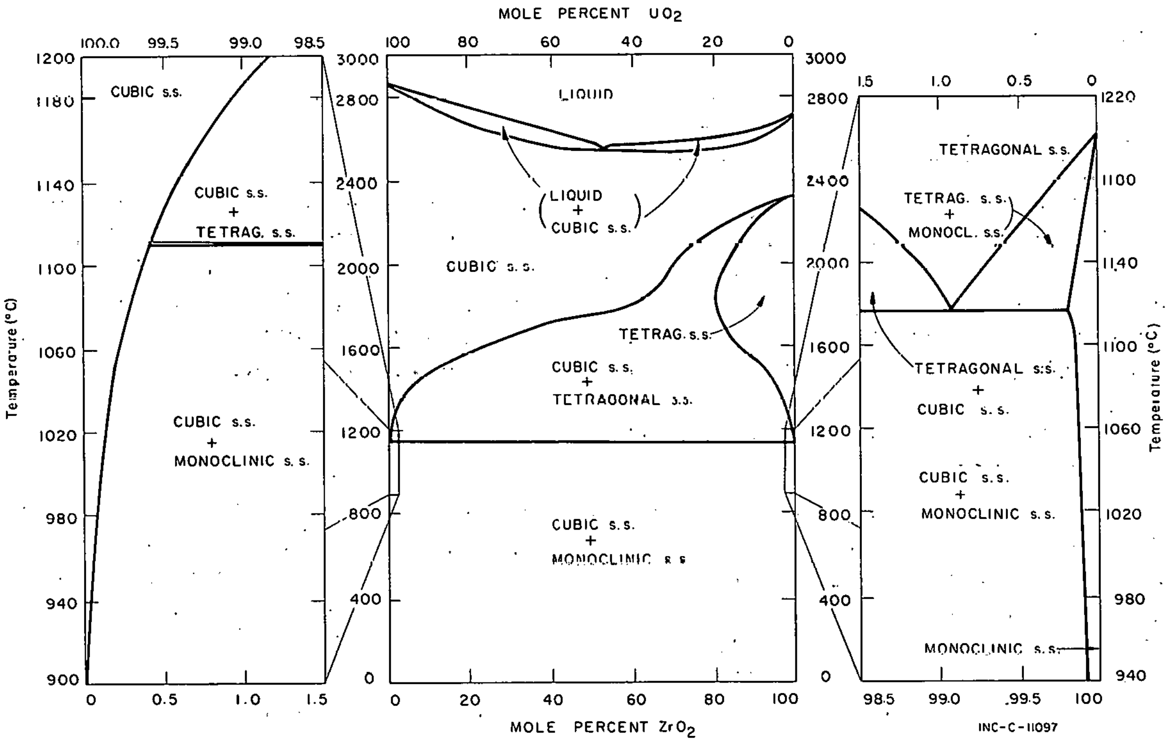

Fig. 2 UO_2-ZrO_2 Phase Diagram

1.5 Zircaloy-4

The transition temperatures of Zircaloy-4 will be different than those listed for pure zirconium. It has been shown that oxygen, nitrogen, hafnium, and tin raise the α to β transition temperature, the other alloying ingredient would lower the transition.[21] Since tin is the major alloying ingredient, it would be expected that the α to β transition would be at a higher temperature than pure zirconium; however, there is some evidence to indicate that the α to β transition temperature is lower than the reported transition point for pure zirconium.[22] A transition point, between 900 and 1000°C, has been reported, and a temperature of 950°C is recommended. The melting point of Zircaloy-4 has been reported to be 1849°C.[23]

2. THERMODYNAMIC PROPERTIES

2.1 UO_2

The heat content of unirradiated UO_2 has been determined above room temperature by three workers.[24-26] The results of Popov et al in the temperature range 160 to 603°C is only in fair agreement with the measurements of Moore and Kelley, in the temperature range 25 to 1190°C. The results of Moore and Kelley are in good agreement with the measurements of Conway and Hein, in the temperature range 900 to 2350°C, at temperatures common to both. The results of Moore and Kelley are recommended in the temperature range 1200 to 2830°C, although there is considerable uncertainty in the extrapolation of heat capacity and enthalpy above 2350°C. The heat of fusion was determined to be 28.5 ± 7.5 kcal/mole by L. N. Grossman from thermal analysis of UO_2 with 2 weight percent Eu_2O_3.[27] The heat capacity of liquid UO_2 was assumed to be the same as that calculated for solid UO_2 at 2830°C.

The thermodynamic properties of irradiated UO_2 are unknown. It is expected that the heat capacity of irradiated UO_2 would be higher than that of unirradiated UO_2, but not significantly higher, since the percent increase in the number of atoms present is not large even at high fuel burn-up.

2.2 ZrO_2

The measurements of the thermodynamic properties of ZrO_2 have been reviewed and are reported by Schick [11], Kelley [28], and in the JANAF tables.[24] Kelley gives equations for the enthalpy and heat capacity of ZrO_2 in the temperature range 25 to 1727°C, and estimated the heat capacity in the temperature range 1727 to 2700°C. The data which Kelley and Schick and the JANAF tables refer to was obtained by the drop calorimetry method. If the transition from monoclinic to tetragonal ZrO_2 is slow, the heat capacity data above 1205°C is probably in error since there was probably only a partial transition of the tetragonal to the monoclinic form on cooling. However, the data does show a sharp transition at 1205°C. The heat of transition from tetragonal to cubic ZrO_2 was estimated to be

3 kcal/mole from the data compiled by H. W. Deem [30] for ZrO_2-UO_2 solid solutions. This is approximately the same as the heat of transition of UO_2 from the tetragonal to the cubic form. The heat of fusion was estimated by Schick to be 25 kcal/mole, and the heat capacity of molten ZrO_2 was estimated to be 24 cal/mole-°K. JANAF gives 20.8 kcal/mole and an estimated heat capacity of 21 cal/mole-°C for molten ZrO_2. At high temperatures for a number of ceramic materials the heat capacity increases with temperature. This is probably because of the expected anharmonicity of vibrations and possible electronic transitions. The higher heat capacity as given by Schick, therefore, seems more reasonable and is recommended. A heat capacity of 24 cal/mole-°C is recommended for liquid ZrO_2. The estimated 20.8 kcal/mole is recommended for the heat of fusion.

2.3 ZrO_2-UO_2 Solid Solutions

H. W. Deem has compiled data on the heat content and heat capacity of various mixtures of UO_2 and ZrO_2 in the temperature range 0 to 2000°C. The following are equations representing the heat capacity of these mixtures:

Composition ZrO_2-10 M/o UO_2

$$C_p = 0.0789 + 8.483 \times 10^{-5} T \quad (273 \text{ to } 727°K)$$

$$C_p = 0.1713 - 7.516 \times 10^{-5} T + 3.279 \times 10^{-8} T^2 \quad (863 \text{ to } 2273°K)$$

Composition ZrO_2-17.5 M/o UO_2

$$C_p = 0.0972 + 2.535 \times 10^{-5} \quad (273 \text{ to } 1292°K)$$

$$C_p = 4.79 \times 10^{-3} + 7.298 \times 10^{-5} T \quad (1481 \text{ to } 2096°K)$$

$$C_p = 0.1475 \quad (2175 \text{ to } 2276°K)$$

$$C_p = 0.1524 \quad (2385 \text{ to } 2487°K)$$

Composition ZrO_2-31.6 M/o UO_2

$$C_p = 9.333 \times 10^{-2} + 1.289 \times 10^{-5} T \quad (273 \text{ to } 1995°K)$$

$$C_p = 0.1192 \quad (2086 \text{ to } 2188°K)$$

$$C_p = 0.1191 \quad (2297 \text{ to } 2380°K)$$

Composition ZrO_2-87.5 M/o UO_2

$$C_p = 1.437 \times 10^{-2} + 1.394 \times 10^{-4} T \quad (273 \text{ to } 474°K)$$

$$C_p = 5.432 \times 10^{-2} + 2.012 \times 10^{-5} T \quad (597 \text{ to } 2273°K)$$

Where C_p = specific heat, cal/g-°K

T = temperature, °K

The following equations give the enthalpy as a function of temperature for various mixtures of ZrO_2 and UO_2:

Composition ZrO_2-10 M/o UO_2

$$H°_T-H°_{298} = 7.89 \times 10^{-2}T + 4.242 \times 10^{-5}T^2 - 27.27 \text{ (273 to 727°K)}$$

$$H°_T-H°_{298} = 50.05 + 0.1713T - 3.758 \times 10^{-5}T^2 + 1.093 \times 10^{-8}T^3 \text{ (868 to 2273°K)}$$

Composition ZrO_2-17.5 M/o UO_2

$$H°_T-H°_{298} = 30.10 + 0.0972T + 1.268 \times 10^{-5}T^2 \text{ (273 to 1292°K)}$$

$$H°_T-H°_{298} = 72.52 - 4.79 \times 10^{-3}T + 3.649 \times 10^{-5}T^2 \text{ (1480 to 2096°K)}$$

$$H°_T-H°_{298} = -83.21 + 0.1475T \text{ (2175 to 2276°K)}$$

$$H°_T-H°_{298} = -81.66 + 0.1524T \text{ (2385 to 2487°K)}$$

Composition ZrO_2-31.5 M/o UO_2

$$H°_T-H°_{298} = -33.53 + 9.333 \times 10^{-2}T + 6.445 \times 10^{-6}T^2 \text{ (273 to 1995°K)}$$

$$H°_T-H°_{298} = -49.46 + 0.1192T \text{ (2086 to 2188°K)}$$

$$H°_T-H°_{298} = -39.16 + 0.1191T \text{ (2297 to 2430°K)}$$

Composition ZrO_2-87.5 M/o UO_2

$$H°_T-H°_{298} = -10.47 + 1.437 \times 10^{-2}T + 6.968 \times 10^{-5}T^2 \text{ (273 to 474°K)}$$

$$H°_T-H°_{298} = -14.25 + 5.432 \times 10^{-2}T + 1.006 \times 10^{-5}T^2 \text{ (597 to 2273°K)}$$

Where $H°_T-H°_{298}$ = enthalpy, cal/g

T = temperature, °K

It is not certain how reliable the above equations are. Voronov et al, and Grimes et al have pointed out that the differences in the reported phase diagrams are a result of non-equilibrium conditions. The transitions as observed in the enthalpy data reported by Deem, only partially correspond to either the data of Schaner et al, or to that of Grimes et al. It is suspected that the heat capacity of non-equilibrium mixtures of UO_2-ZrO_2 were measured. It would probably be nearly as accurate to estimate the heat capacity of ZrO_2-UO_2 mixtures by multiplying the mole-fraction of each component by the heat capacity of the pure components.

From the heat capacity and from the temperature of the transition or temperature range of the transition obtained from Figure 2, and the heat of transition of the pure components, it would be possible to reasonably estimate enthalpy as a function of temperature for the ZrO_2-UO_2 mixture. The above equations are recommended for the heat capacity and enthalpy of mixtures of ZrO_2 and UO_2 that are near listed compositions. For another composition estimate the heat capacity and enthalpy from the heat capacity and enthalpy of the pure components.

2.4 ZrO_{2-x}

The heat capacity of ZrO_{2-x} for $2 > x > 0$ has not been measured. A reasonable estimate of the heat capacity and enthalpy could be obtained by multiplying the heat capacities of the hypothetical components, ZrO_2 and Zr, by their mole fraction in ZrO_{2-x}.

Zircaloy-4

The heat content and heat capacity of Zircaloy-4 should be very close to that of pure zirconium since the alloying metals are minor components. The composition of Zircaloy-4 is approximately:

Zr	98%
Sn	1.5%
Fe	0.2%
Cr	0.1%

The alloying of components in Zircaloy-4 may change the transition temperatures for Zircaloy-2 and Zircaloy-4 and thus change the heat contents in the temperature region of the α to β transition. The results given in WCAP - (3269) - (3) for Zircaloy-4 are not however in good agreement with the heat content and heat capacity of pure zirconium. The heat content and heat capacity data for pure zirconium should be used.

K. K. Kelley [28] and the JANAF tables [29] have given tables and equations for the heat content and heat capacity of pure zirconium. The recommended heat content and heat capacity of Zircaloy-4 were derived from these references.

3. EQUILIBRIUM VAPOR PRESSURES

The vapor pressure of reactor materials are important properties for reactor safety analyses. Vaporization is undoubtedly an important factor in release of many fission products. Excessive vapor pressure may cause rupture of the cladding material or by vaporization from the surface give access of the fission products within the fuel pins to the surface, where they may be released. The vaporization of a reactor material may also be an important mechanism of heat transfer.

In the case of Zircaloy clad UO_2, and for a loss-of-coolant accident, the vaporization of UO_2 does not appear to be directly important as a heat transfer mechanism except perhaps at temperatures near the melting point. Vaporization would be important indirectly since deposition on and vaporization from the various surfaces will change the emissivity of the fuel pins and thus effect the radiant heat transfer between fuel pins.

The rate of vaporization is dependent on a number of factors. If equilibrium is established, the rate of vaporization is dependent upon the gas flow rate and the vapor pressure of the material of interest. In this case the carrier gas becomes saturated with the vaporizing component. For a material not in equilibrium, the prediction of the rate of vaporization is much more difficult. It is probably dependent upon transport of the vapors from the surface through a thin film of stagnant gas.

In the limiting case of extremely high gas flow rates the rate of vaporization becomes independent of the flow rate and may be given by the following equation which may be derived from the kinetic theory of gases.

$$\text{Rate of Vaporization} = \frac{A\ \alpha\ P}{(2\ \pi\ MRT)^{\frac{1}{2}}}$$

Where A = surface area of material vaporizing
α = the condensation coefficient
P = equilibrium vapor pressure
M = molecular weight of vapor species
T = temperature
R = gas constant

From the experimental pressure measurements for UO_2 it appears that the condensation coefficient is near unity. Since for most simple vaporization processes α is near unity, it may reasonably be assumed the $\alpha = 1$ for Zr and ZrO_2.

3.1 UO_2

A number of measurements of the vapor pressure of uranium dioxide have been made. [31-40] These are in good agreement with the exception of the work by Rehn and Cefola[31], and Smith and Anderson[38], which are higher than the results of other works by respectively about one and three orders of magnitude.

In the effusion study of the vaporization of uranium dioxide, Ackerman et al[33] covered the greatest temperature range, 1600 to 2800°K, of any of the workers. At temperatures above 2000 the apparent vapor pressure of UO_2 from this work shows a positive deviation from that expected for pure UO_2 (g). Ackerman suggested the vapor species U_2O_4 was the cause of this deviation. Later workers have suggested that this increased volatilization was due to either UO_3 or UO. Since at temperatures above 2400°C the UO_2 becomes substoichiometric on vaporization, the proposed mechanisms for increased volatilization at high temperatures was either a loss of atomic oxygen followed by an increase in the volatilization of UO, or vaporization of UO_3. From the oxygen dissociation pressure for

UO_2, given in reference 36, it appears that the partial pressure of UO or UO_3 is much lower than that which would be necessary to account for the increased volatility observed by Ackerman. One possible explanation for this increased volatility, observed by several workers in effusion experiments, is reaction of the tungsten vessels with UO_2 followed by migration of oxygen to the outer surface of the vessels and vaporization of oxygen from the surfaces of the tungsten vessels. Since the surface area of tungsten for the effusion experiments was orders of magnitude greater than the surface area of the cell orifice, even relatively small rates of vaporization of oxygen from the metal surfaces of the effusion cell could fairly rapidly change the stoichiometry of the UO_2 in the effusion cells.

The data given in reference 36 was determined using the transpiration technique. The oxygen content in the transport gas was buffered by using water and hydrogen gas mixtures. Their data is in excellent agreement with the low temperature data of Ackerman et al. The equation given by Ackerman et al for their low temperature data is recommended for the vapor pressure of UO_2.

For the LOFT reactor experiment the gases in the coolant channels might have an important bearing on the volatilization of UO_2. The partial pressure of oxygen in this gas can be related to the partial pressure of the known uranium oxide vapor species. Equations giving the partial pressures of the other possible vapor species as a function of oxygen partial pressure and temperature have been derived from the free energy functions given in reference 41, the high temperature heat capacity given in reference 26, the ΔH°_0 values given in reference 41, and experimental data given in reference 42. The free energy functions were extended to high temperatures using the high temperature heat capacity data, and were fitted to equations of the form $-\frac{\Delta F^\circ_T - \Delta H^\circ_0}{T} = A + BT + CT^2$. The ΔH°_0 values were slightly altered to give better agreement with available experimental data. The changes in all cases were well within the uncertainties in the values for ΔH°_0

A heat of fusion of 28.5 kcal/mole for UO_2 was used to derive equations of the form $\text{Log } K = -AT^{-1} + B$, which give the equilibrium pressures of the various vapor species above molten UO_2, and to derive the heat of reaction for the various vaporization processes from liquid UO_2.

The following equations give the equilibrium vapor pressures for the known vapor species of UO_2 and the heats of vaporization associated with each process:

3.11 Vaporization Processes for Solid UO_2

3.111 For the process $UO_2(s) = UO_2\ (g)$

$$\text{Log}\left[P_{UO_2}\ (\text{atm})\right] = -33115\ T^{-1} - 4.026 \log T + 22.805$$

$$\Delta H_v = 151534 - 8.00\ T \text{ cal/mole}$$

3.112 For the process $UO_2(s) + 1/2\ O_2 = UO_3(g)$

$$\mathrm{Log}_{10}\left[\frac{P_{UO_3}}{P_{O_2}^{\frac{1}{2}}}\ (\mathrm{atm}^{\frac{1}{2}})\right] = -13875T^{-1} + 7.863 - 2.266 \times 10^{-3}T + 3.682 \times 10^{-7}T^2$$

$\Delta H_v = 63{,}492 - 1.037 \times 10^{-2}T^2 + 3.370 \times 10^{-6}T^3$ cal/mole

3.113 For the process $UO_2(s) = UO(g) + \frac{1}{2}\ O_2(g)$

$$\mathrm{Log}\left[P_{UO} \times P_{O_2}^{\frac{1}{2}}\ (\mathrm{atm}^{3/2})\right] = -57900T^{-1} + 15.911 - 2.129 \times 10^{-3}T + 3.345 \times 10^{-7}T^2$$

$\Delta H_v = 264950 - 9.742 \times 10^{-3}T^2 + 3.061 \times 10^{-6}T^3$ cal/mole

3.114 For the process $UO_2(s) = U\ (g) + O_2(g)$

$$\mathrm{Log}\left[P_{O_2} \times P_U\ (\mathrm{atm}^2)\right] = -83676T^{-1} + 17.701 - 1.525 \times 10^{-3}T + 2.33 \times 10^{-7}T^2$$

$\Delta H_v = 382{,}900 - 6.98 \times 10^{-3}T^2 + 2.13 \times 10^{-6}T^3$ cal/mole

3.12 Vaporization Process for Molten UO_2

3.121 For the process $UO_2(l) = UO_2(g)$

$$\mathrm{Log}\left[P_{UO_2}\ (\mathrm{atm})\right] = -21462T^{-1} + 4.99$$

$\Delta H_v = 98{,}210$ cal/°mole

3.122 For the process $UO_2(l) + \frac{1}{2}\ O_2 = UO_3(g)$

$$\mathrm{Log}\left[\frac{P_{UO_3}}{P_{O_2}^{\frac{1}{2}}}\ (\mathrm{atm}^{\frac{1}{2}})\right] = -7832T^{-1} + 2.426$$

$\Delta H_v = 35{,}800$ cal/mole

3.123 For the process $UO_2(l) = UO(g) + \frac{1}{2}\ O_2\ (g)$

$$\mathrm{Log}\left[P_{UO} \times P_{O_2}^{\frac{1}{2}} (\mathrm{atm}^{3/2})\right] = -51159T^{-1} + 10.354$$

ΔH_v 234,000 cal/mole

3.124 For the process $UO_2(l) = U(g) + O_2(g)$

$$\mathrm{Log}\left[P_U \times P_{O_2}\ \ (\mathrm{atm}^2)\right] = -76667T^{-1} + 12.954$$

$\Delta H_v = 324{,}000$ cal/mole

3.2 ZrO_2

The vapor pressure of ZrO_2 is much lower than the vapor pressure of UO_2 at like temperatures. The oxygen decomposition pressure, however, is higher.

The ZrO_2 formed by the oxidation of Zircaloy-4 will have a considerable amount of metallic Sn. This Sn will probably be held within the grain boundaries in the ZrO_2, and will slowly diffuse out. The maximum equilibrium vapor pressure of Sn would be that of the pure Sn.

The vapor pressure has been determined in two recent studies. One a mass spectrometric study and the other study a transpiration study using a H_2 and H_2O atmosphere to control the oxygen partial pressure. [43, 44] The two sets of data are in fairly good agreement. The data given for the transpiration experiments were chosen to represent the vapor pressure of ZrO_2, since the stoichiometry of the ZrO_2 was closely controlled. The equation for the vaporization from solid ZrO_2 has been modified to take into account the difference in heat capacity, ΔC_p, between solid and vapor ZrO_2.

The work of Nakata et al[45] is recommended for the vaporization of ZrO from $ZrO_2(s)$. This reaction was studied by the effusion technique, using a mass spectrometer to determine the partial pressure of each vapor species.

A heat of fusion of 20.8 kcal/mole was used to derive equations which give the partial pressures of the important vapor species above liquid ZrO_2 and the heat of reaction for the vaporization reactions of molten ZrO_2.

The following equations give the equilibrium vapor pressure of ZrO_2 and of ZrO as a function of oxygen pressure above solid and liquid ZrO_2:

3.21 Vaporization Processes for Solid ZrO_2

3.211 For the process $ZrO_2(s) = ZrO_2(g)$

$$\mathrm{Log}\left[P_{ZrO_2}\ (\mathrm{atm})\right] = -39778T^{-1} - 3.597\ \mathrm{Log}\ T + 21.701$$

$$\Delta H_v = 182{,}024 - 7.147T \text{ cal/mole}$$

3.212 For the process $ZrO_2(s) = ZrO + \frac{1}{2} O_2$

$$\mathrm{Log}\left[P_{ZrO} \times P_{O_2}^{\frac{1}{2}}\ (\mathrm{atm}^{3/2})\right] = -61527T^{-1} + 14.17$$

$$\Delta H_v = 281{,}548 \text{ cal/mole}$$

3.22 Vaporization Processes for Liquid ZrO_2

3.221 For the process $ZrO_2(l) = ZrO_2(g)$

$$\text{Log}\left[P_{ZrO_2}\ (\text{atm})\right] = -\frac{30594}{T} + 5.76$$

$$\Delta H_v = 140{,}000 \text{ cal/mole}$$

3.222 For the process $ZrO_2(l) = ZrO(g) + \frac{1}{2}\ O_2$

$$\text{Log}\left[P_{ZrO}\ P_{O_2}^{\frac{1}{2}}\ (\text{atm}^{3/2})\right] = -\frac{56{,}970}{T} + 12.64$$

$$\Delta H_v = 260{,}700 \text{ cal/mole}$$

A normal boiling point of 4100°C has been calculated from the above equations. The main vapor species at the boiling point are ZrO and O.

3.3 Zircaloy-4

The tin component in the Zircaloy-4 has a higher vapor pressure than the zirconium, and by virtue of its higher vapor pressure will preferentially vaporize from the alloy. It is difficult to predict the rate of vaporization of Sn above Zircaloy-4 since the Sn will undoubtedly be depleted at the surface of the cladding. The rate of vaporization of Sn would probably be dependent upon the rate of diffusion of Sn to the Zircaloy-4 surface. The vapor pressure of Sn would be approximately equal to its mole fraction at the surface of the Zircaloy-4 times the vapor pressure of pure Sn at that temperature. The rate of vaporization of zirconium from Zircaloy-4 cladding material is easier to predict since it is by far the major component (~ 97%).

The vapor pressure of solid Zr has been determined by the Langmuir technique.[45]

A heat of fusion of 4.9 kcal/mole was used to calculate the vapor pressure of Zr(g) above liquid ZrO_2 and the heat of vaporization of liquid Zr.

The heat of vaporization and the equilibrium vapor pressure of zirconium above solid and liquid Zircaloy-4 are given in the following equations:

3.31 Vaporization from Solid Zircaloy-4

3.311 For the process $Zr(s) = Zr(g)$

$$\text{Log}\left[P_{Zr}\ (\text{atm})\right] = -\frac{31066}{T} + 7.3351 - 2.415 \times 10^{-4}T$$

$$\Delta H_v = 142{,}158 + 1.105 \times 10^{-3}T^2 \text{ cal/g-atom}$$

3.32 Vaporization from Liquid Zircaloy-4

3.321 For the process $Zr(l) \rightleftharpoons Zr(g)$

$$\text{Log}\left[P_{Zr}\ (\text{atm})\right] = -\frac{31083}{T} + 6.830$$

$$\Delta H_v = 142{,}000 \text{ cal/g-atom}$$

A normal boiling point of 4550°C has been calculated from the above equation.

4. THERMAL CONDUCTIVITY

The needs for accurate thermal conductivity data are obvious. Although a number of determinations of the thermal conductivities of the materials of interest have been made, there are still great uncertainties in the thermal conductivities of these materials. A more systematic approach is needed to evaluate the individual components of the thermal conductivity.

4.1 UO_2

Reviews of the earlier determinations of thermal conductivity of UO_2 are presented by Belle [2] and by Seddon [46]. Some of the determinations of the thermal conductivity that are representative of the later high temperature determinations are by Stora et al [47], Nishijima et al [48], Reiswig [49], Coplin et al [50], Feith [51], and Christensen et al[52].

A great number of determinations of the thermal conductivity of UO_2 have been made from room temperature to temperatures approaching the melting point of UO_2. The differences between the results of the many workers in most cases is probably not from experimental errors but from one or more different changes in structure or composition. Some of the changes which appear to be important are:

1. For low temperature results, stoichiometry effects thermal conductivity.[2]
2. Radiation damage effects low temperature thermal conductivity (below 500°C). The lattice damage can be annealed from the irradiated UO_2 if it is irradiated to less than 10^{18} fissions/cm^3. Beyond this exposure the changes in thermal conductivity cannot be annealed from the UO_2.[53]
3. At high temperatures the stoichiometry of UO_2 greatly effects the thermal conductivity. This is probably a result of a change in the amount of the electronic contribution to the thermal conductivity. [54]
4. Thermal cracking of the test specimens seems to have a great effect on thermal conductivity. [47]

The differences between the results of the many workers can be explained by the above effects. The values of thermal conductivity of UO_2 obtained from in-pile measurements are influenced by many of the above-mentioned changes in structure and composition. Radiation damage of the lattice effects the thermal conductivity of the UO_2 at the edges of the fuel pins. The great thermal gradient across the UO_2 in the fuel pins causes cracking of the fuel pins and migration of oxygen from the center of the fuel pin to the outside of the fuel pin. From thermal cycling of fuel rods and from the large thermal gradients present in the irradiated fuel rods, thermal cracking of UO_2 will occur. The thermal cracking of the fuel pins will result in considerable change in thermal conductivity unless the fuel pin is under considerable external pressure.[47] The oxygen migration results in substoichiometric UO_2 in the center of the fuel pins and hyperstoichiometric UO_2 near the surface of the fuel pin. This should result in a decrease in the thermal conductivity near the edges of the fuel pins. The effects of irradiation damage on thermal conductivity of UO_2 at high temperatures is not well known; this, of course, could be a very important factor. Fission products probably have a considerable effect on thermal conductivity of UO_2 in high burn-up fuel.

The above effects are believed to cause the differences between in-pile thermal conductivity measurements and out-of-pile measurements using unirradiated UO_2.

4.11 Unirradiated UO_2

The IAEA Panel on Thermal Conductivity of UO_2 has recommended the measurements of two workers, Stora et al [49] and Godfrey et al [56]. Godfrey et al measured the thermal conductivity in the temperature range -57°C to 1400°C. Due to the change in the properties of the thermocouples at high temperatures only the results given in the temperature range -57 to 1100°C were considered reliable.

Stora et al measured the thermal conductivity of UO_2 in the temperature range 200 to 2400°C. These results are very similar to the results of Godfrey et al. It should be pointed out that in the measurements by Stora et al, by the radial heat flow technique, there were great temperature differences across his sample which could have resulted in oxygen migration to the outer edges of the sample. The stoichiometry of his sample was not measured after the determination so that loss or migration of oxygen from the UO_2 sample could have caused thermal conductivity changes during the experimental runs. The results of Stora et al are, therefore, considered to be of much greater uncertainty above 2000°C, probably by a factor of 2-3 at the highest temperature. The results of Godfrey et al and Stora et al are shown in Figure 3 along with the estimated lattice and electronic contributions to the thermal conductivity. Table I contains the recommended value for the thermal conductivity to the melting point of UO_2.

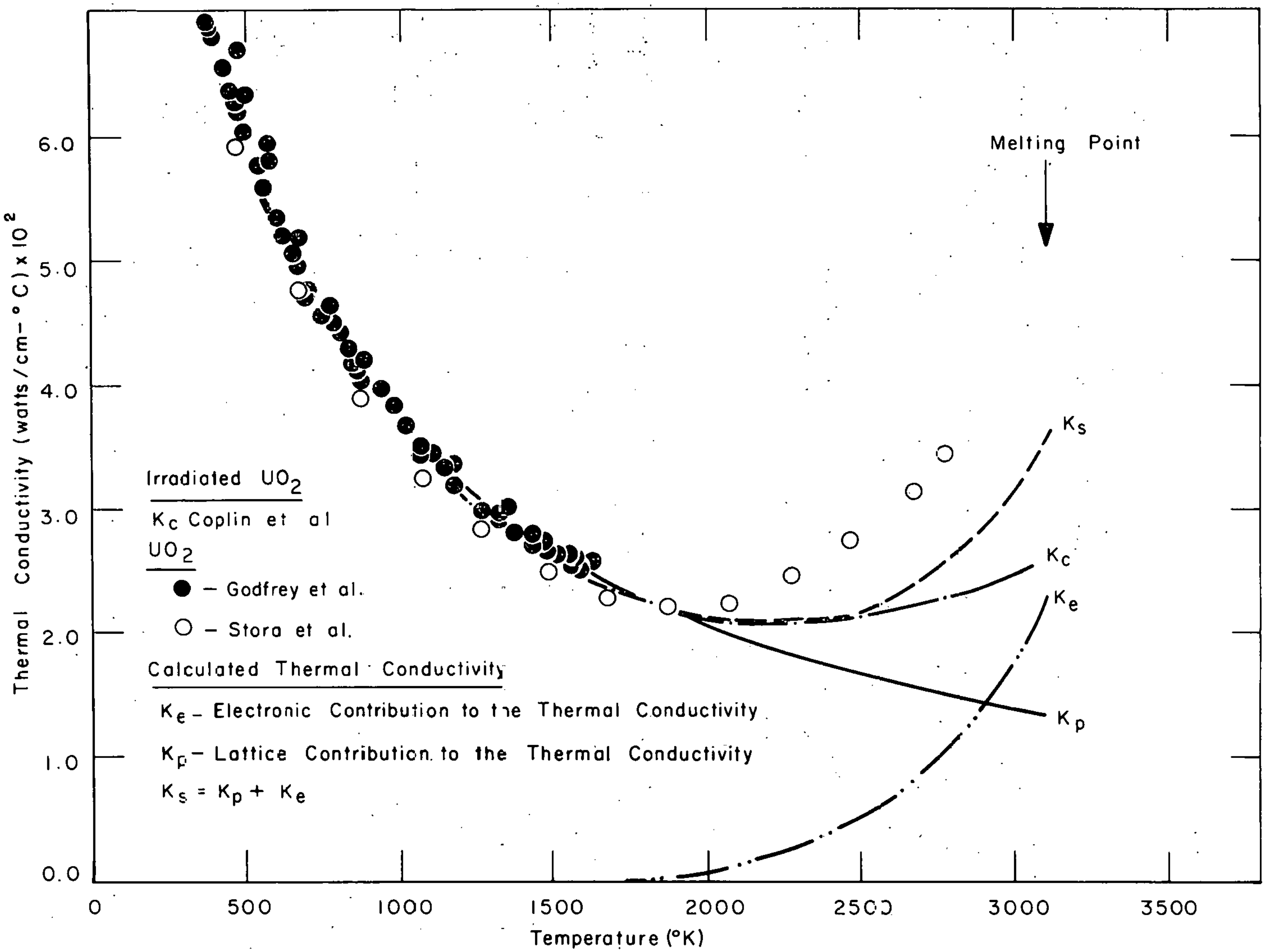

Fig. 3 Thermal Conductivity of UO_2

TABLE I

THERMAL CONDUCTIVITY OF UNIRRADIATED UO_2

Temperature °K	Thermal Conductivity, k watts/cm-°C
500	0.0680
1000	0.0370
1500	0.0262
1600	0.0250
1700	0.0245
1800	0.0240
1900	0.0235
2000	0.0230
2100	0.0230
2200	0.0237
2300	0.0250
2400	0.0264
2500	0.0280
2600	0.0300
2700	0.0323
2800	0.0352*
2900	0.0378*
3000	0.0420*
3100 (s)	0.0485*
3200 (l)	0.050 *

*Estimated

The lattice contribution to the thermal conductivity shown in Figure 3 (page 22) is that recommended by the "IAEA Panel on Thermal Conductivity of UO_2" and is presented below:

$$k\ (\text{lattice}) = \frac{1}{11 + 0.022T} \quad \text{watt/cm-}^{\circ}\text{C} \qquad (T \text{ in } ^{\circ}\text{C})$$

The electronic contribution to the thermal conductivity was calculated for UO_2, assuming UO_2 behaves as a nondegenerate semiconductor. The equation of Drable and Goldsmid[52] was used to calculate the electronic contribution to the thermal conductivity from the electrical conductivity data of Casselton[53], assuming that either the contribution of electrons to the electrical conductivity from migration is much greater than that from migration of holes, or that the contribution to the electrical conductivity from migration of holes is much greater than that from migration of electrons. This would be a minimum electronic contribution to the thermal conductivity for a material behaving as a nondegenerate semiconductor. The sum of the electronic and lattice contributions are in good agreement with the results of Lyons et al up to 2500°C, but lie below the results given by Stora et al.

At high temperatures the lattice contribution to the thermal conductivity could be in considerable error, since the theory predicting lattice contributions to thermal conductivity probably does not hold for highly imperfect lattices or for anharmonic vibrations in the lattice. The prediction of the lattice contribution is not yet possible for highly imperfect crystal lattices or for highly anharmonic vibrations.

Probably the best[58] equation correcting the thermal conductivity for porosity of UO_2 is:

$$k = \frac{k_T\,(1-P)}{1 + P\,(\alpha-1)}$$

where k = thermal conductivity of UO_2

k_T = thermal conductivity of UO_2 at theoretical density

P = is the volume fraction of porosity of the UO_2

α = 1.5 for porosities 0.1 or less

= 2.0 for porosities between 0.1 and 0.15

= 2.4 for porosities between 0.15 and 0.20

= 2.6 for porosities between 0.20 and 0.25

4.12 Irradiated UO_2

The results of Coplin et al[51] are probably the best representation on in-pile thermal conductivity data, if a single expression can represent the thermal conductivity of irradiated UO_2. The following equation represents their data:

$$k = \frac{38.24}{T + 129.4} + 4.788 \times 10^{-13}T^3 \quad \text{watt/cm-}^{\circ}\text{C} \qquad (T \text{ in } ^{\circ}\text{K})$$

4.2 ZrO_2

The ZrO_2 produced from the oxidation of Zircaloy-4 will have as impurities free tin and some other minor constituents. The effects of these components on the thermal conductivity is uncertain; however, the effect is probably small since it has been shown that the addition of free zirconium has little effect on thermal conductivity [61] of yittrium oxide stabilized ZrO_2.

Very little thermal conductivity data is available for pure ZrO_2, but a great deal of information is available for ZrO_2 stabilized with various other oxides.[61-66] The data for pure ZrO_2 probably best represents the thermal conductivity of the material formed by oxidation of Zircaloy-4. The data of Adams[62] has been corrected to zero porosity and is presented by the following equation:

$$k = 0.0181 + 3.5 \times 10^{-6} T \text{ (T in °C) watts/cm-°C (0 to 2700°C)}$$

Since there is no data for pure ZrO_2 above 1300°C, the above equation is recommended to the melting point of ZrO_2. This is probably not a bad estimate since a number of low porosity stabilized zirconia mixtures show a similar dependence of thermal conductivity on temperature at high temperatures. The contribution to the thermal conductivity of convective heat transfer is probably fairly large, since ZrO_2 would be expected to have a fairly high Prandtl number.

4.3 ZrO_2-UO_2 Solid Solutions

The thermal conductivities of ZrO_2-UO_2 solid solutions were calculated from the measured heat capacities and thermal diffusivities of the solid solutions by Deem.[30] These thermal conductivities as a function of temperature are shown in Figures 4, 5, 6, and 7. The thermal conductivities reported by Deem are in fair agreement with thermal conductivities calculated from in-pile data.[66]

4.4 Zircaloy-4

There have been four determinations of the thermal conductivity of Zircaloy-4.[67-70] The results given by Young[67], Feith[69], and Scott[70] appear to be more in line with results for Zircaloy-2[70-73] and should probably be used for the thermal conductivity of Zircaloy-4. The results given in reference 67-70 are shown in Figure 8. The recommended thermal conductivity of Zircaloy-4 is given in Table II.

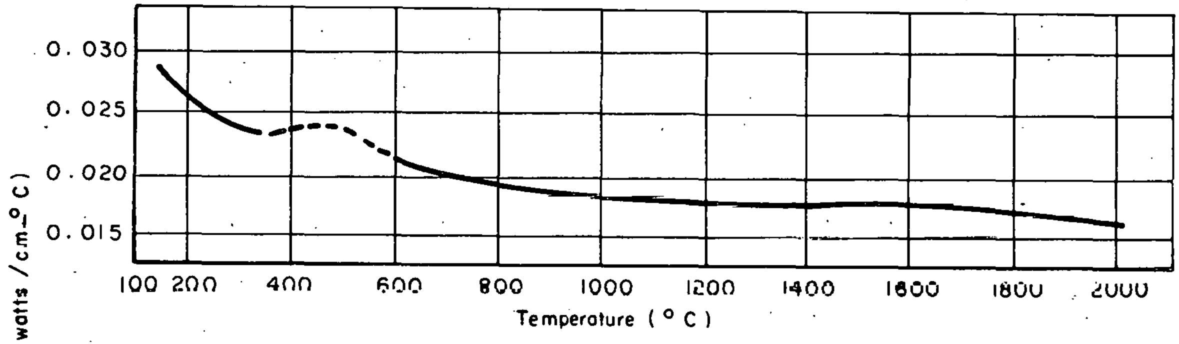

Fig. 4 Thermal Conductivity of ZrO_2-10 m/o UO_2 as a Function of Temperature

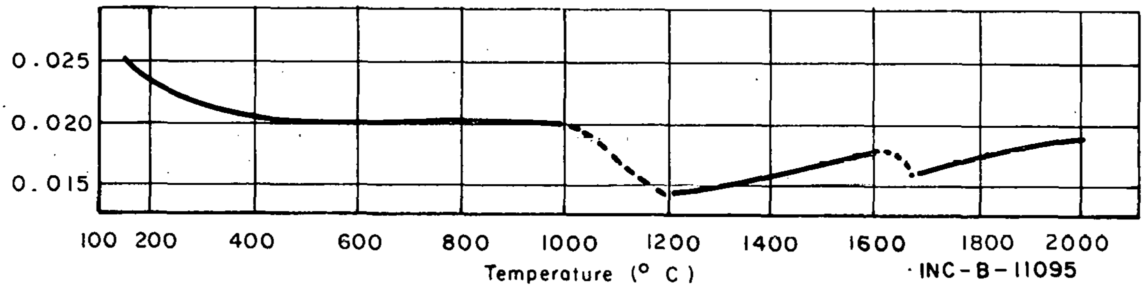

Fig. 5 Thermal Conductivity of ZrO_2-17.5 m/o UO_2 as a Function of Temperature

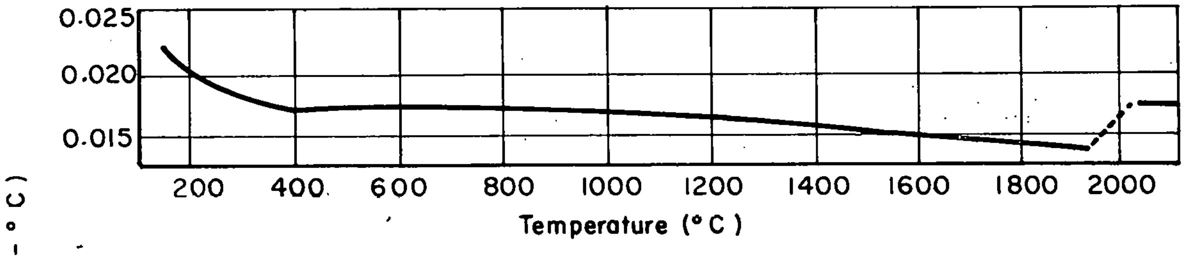

Fig. 6 Thermal Conductivity of ZrO_2-31.5 m/o UO_2 as a Function of Temperature

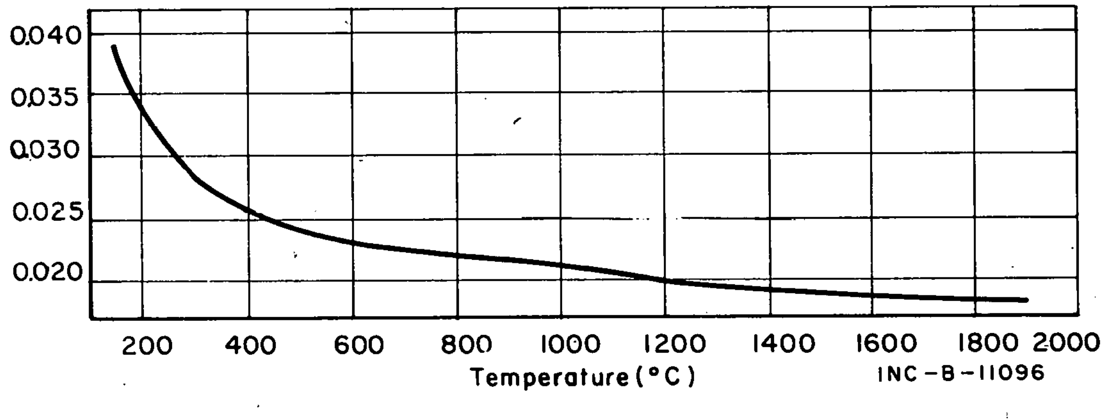

Fig. 7 Thermal Conductivity of ZrO_2-87.5 m/o UO_2 as a Function of Temperature

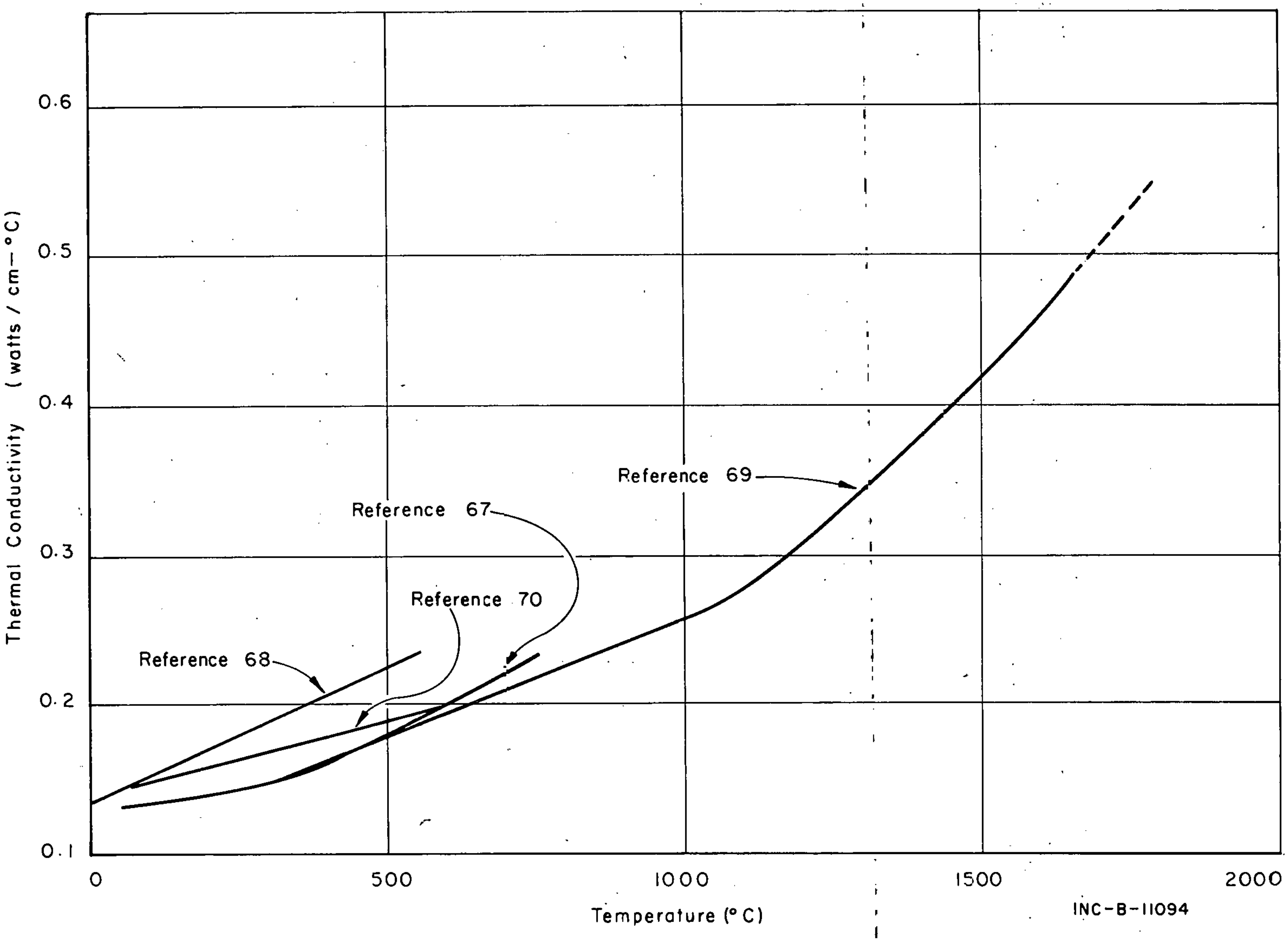

Fig. 8 Thermal Conductivity of Zircaloy-4

TABLE II

THERMAL CONDUCTIVITY OF ZIRCALOY-4

T °C	k watts/cm-°C	T °C	k watts/cm-°C
100	0.138	1000	0.256
200	0.142	1100	0.279
300	0.152	1200	0.308
400	0.165	1300	0.340
500	0.180	1400	0.377
600	0.195	1500	0.416
700	0.216	1600	0.46*
800	0.228	1700	0.50*
900	0.242	1800	0.55*
		Molten (1850)	0.57*

*Estimated

The variation in results shown in Figure 8 is probably the result of differing oxygen content and differing mechanical treatment. The thermal conductivity estimated from the electrical resistivity by the Wiedemann-Franz law gives considerably lower thermal conductivity than that reported by Feith[68] at high temperatures; however, the electrical conductivity data used was for zirconium containing 1.8% hafnium. Since there was little change in oxygen content in the Zircaloy-4 during the determination, the thermal conductivity values are probably reasonably good; however, the results above 1000°C should be considered much less accurate than the lower temperature results.

The thermal conductivity of molten Zircaloy-4 would probably not be appreciably higher than that of solid Zircaloy-4 at the melting point since conduction by convection in the molten metal would be expected to be small since metals in general have small Prandtl numbers. A value of the thermal conductivity of molten Zircaloy-4 was estimated by extrapolating the estimates for the thermal conductivity of solid zirconium up to the melting point.

5. THERMAL EXPANSION

5.1 UO_2

A number of measurements of the thermal expansion of UO_2 have been made.[2, 74-76] Most of the measurements are in good agreement. The results of Conway et al[74] are a good representation of the available data and are probably some of the more accurate determinations. The data of Christensen is recommended above 2200°C. The experimental data of

Conway et al are considered to be more accurate than the data of Christensen in the temperature range common to both; however, the coefficient of thermal expansion as a function of temperature, derived from the data of Christensen, is considered to be accurate. The equation given by Christensen has been modified to agree with the equation of Conway et al at 2200°C. The following equations are recommended for the % linear expansion and coefficients of thermal expansion (α) of solid and liquid UO_2:

5.11 Solid UO_2

5.111 0 to 2200°C

$$\%\ \text{Linear Expansion (from } 0^\circ\text{C}) = 6.79 \times 10^{-4}T + 2.896 \times 10^{-7}T^2$$

$$\alpha = 5.797 \times 10^{-4} + 5.792 \times 10^{-7}T \quad (T \text{ in } ^\circ\text{C})$$

5.112 2200 to 2830°C

$$\%\ \text{Linear Expansion (from } 0^\circ\text{C}) = 0.204 + 3 \times 10^{-4}T + 2 \times 10^{-7}T^2 + 10^{-10}T^3$$

$$\alpha = 3 \times 10^{-6} + 4 \times 10^{-9}T + 3 \times 10^{-10}T^2 \quad (T \text{ in } ^\circ\text{C})$$

5.12 Solid to Liquid Transition

Increase in volume on melting 9.6%

5.13 Liquid UO_2

$$\%\ \text{Linear Expansion (from } 0^\circ\text{C}) = -4.74 + 3.5 \times 10^{-3}T$$

$$\alpha = 3.5 \times 10^{-5}/^\circ\text{C} \quad (T \text{ in } ^\circ\text{C})$$

The thermal expansion of UO_2 determined by using an x-ray diffractometer agrees well with the data of Conway et al to temperatures approaching 1200°C.[76] Above 1200°C bulk expansion measurements show considerably greater linear expansion. This difference is possibly due to the presence of Schottky defects at high temperatures.

The above equations represent the isothermal expansion characteristics of unirradiated UO_2. In a reactor, however, there are great thermal stresses in UO_2 fuel under irradiation. The thermal expansion characteristics of UO_2 in a fuel pin under irradiation or under loss-of-coolant accident conditions would probably not follow the isothermal data. The percent thermal expansion would probably be dependent upon other factors such as thermal gradients across the fuel pin, and burn-up. Further work is needed to determine the effect of these variables on the thermal expansion of irradiated UO_2.

5.2 ZrO_2

There have been a number of determinations of the linear thermal expansion of pure ZrO_2 below the monoclinic to tetragonal transition. There is a great amount of information available on various formulations of stabilized ZrO_2. The data of Fulkerson[77] and the data presented in Plenum Press "Handbook of High Temperature Materials" [65] is in good agreement with the thermal expansion data given for a number of formulations of ZrO_2 stabilized with CaO[63]. The following are the thermal expansion characteristics of monoclinic ZrO_2:

$$\% \text{ Linear Expansion (from } 0°C) = 7.8 \times 10^{-4} T \text{ (T in °C)}$$

$$(0 \text{ to } 1205°C)$$

$$\alpha = 7.8 \times 10^{-6}/°C$$

The decrease in volume for the α to β phase transition is about 7.7%.[21.]

The axial thermal expansion has been determined by crystallographic measurements in the temperature range 1205 to 1700°C.[78] These axial expansions in this temperature range for the a and c axis respectively are 0.001235%/°C and 0.001435%/°C.

The following are the recommended thermal expansion characteristics of tetragonal ZrO_2:

$$\% \text{ Linear Expansion (from } 0°C) = 1.302 \times 10^{-3} T \text{ (T in °C)}$$

$$(1205 \text{ to } 2700°C)$$

$$\alpha = 1.302 \times 10^{-5}/°C \quad (1205 \text{ to } 2700°C)$$

5.3 ZrO_2-UO_2 Solid Solutions

The following equations have been derived from data presented in reference 30:

5.31 For ZrO_2-10 M/o UO_2

$$\% \text{ Thermal Expansion (from } 0°C) = 5.9 \times 10^{-4} T \text{ (°C)} \quad (0 \text{ to } 360°C)$$

15% decrease in volume at 360°C

$$\% \text{ Thermal Expansion (from } 0°C) = -0.71 + 1.09 \times 10^{-3} T \text{ (°C)}$$

$$(360°C \text{ to } 2000°C)$$

$$\alpha = 5.9 \times 10^{-6}/°C \quad (0 \text{ to } 360°C)$$

$$\alpha = 1.09 \times 10^{-5}/°C \quad (360 \text{ to } 2000°C)$$

5.32 For ZrO_2 - 17.5 M/o UO_2

% Thermal expansion from 0°C = $1.23 \times 10^{-3} T$ (°C)

$\alpha = 1.23 \times 10^{-5}$ (0 to 2000°C)

5.33 For ZrO_2- 31.5 M/o UO_2

% Thermal expansion from 0°C = $9.5 \times 10^{-4} T + 1.42 \times 10^{-7} T^2$ (0 to 2000°C)

$\alpha = 9.5 \times 10^{-6} + 3.26 \times 10^{-9}$ (0 to 2000°C)

5.34 For ZrO_2- 87.5 M/o UO_2

% Thermal expansion from 0°C = $9.9 \times 10^{-4} T + 1.63 \times 10^{-7} T^2$ (0 to 2000°C)

$\alpha = 9.9 \times 10^{-6} + 3.26 \times 10^{-9} T$ (0 to 2000°C)

5.4 Zircaloy-4

The thermal expansion data of crystal bar zirconium and of Zircaloy-2 are very similar up to the α to β transition.[21, 70, 76] Thermal expansion data on ASTM "H-12" tempered Zircaloy-4 tubing along the radial direction are in very good agreement with that of Zircaloy-2 and crystal bar zirconium; however, expansion of the tubing along the axial direction of tubing does not closely follow the data for Zircaloy-2 or for crystal bar zirconium.[79] This is probably the result of mechanical working of the Zircaloy cladding, and is probably what would be expected for the thermal expansion of Zircaloy-4 along the axial direction of the tubing during a loss-of-coolant accident. The thermal expansion of β zirconium is recommended for the thermal expansion of β-Zircaloy-4. The following are the recommended thermal expansion characteristics of Zircaloy-4:

5.41 For α Zircaloy-4

% Thermal expansion from 0°C = $5.6 \times 10^{-4} T + 3.08 \times 10^{-7} T^2$

(0 to 950°C)

$\alpha = 5.77 \times 10^{-6} + 6.15 \times 10^{-9} T$ (0 to 950°C)

5.42 α - β Transition

Decrease in volume ≈ 0.5%

5.43 For β Zircaloy-4

% Thermal expansion from 0°C = $9.7 \times 10^{-4} T$ (°C) (950 to 1850°C)

$\alpha = 9.7 \times 10^{-6}$/°C (950 to 1850°C)

IV. RECOMMENDATIONS FOR FUTURE WORK

For short time periods after a loss-of-coolant reactor accident, the reactor materials will maintain their original shape, and very little interaction of materials will take place. However, at temperatures greater than 1000°C there will be interaction of cladding materials with water vapor and finally at higher temperatures there will be solid-solid, liquid-solid, gas-solid, liquid-gas interactions that could produce a nearly infinite variety of materials. Obviously all of the possible materials formed could not be characterized. It is, therefore, very important to identify important phases that are formed from interactions of UO_2, Zircaloy-4, Type-304 stainless steel, and water vapor. The physical properties of the most important phases should then be determined.

Within the scope of this report, the following information is lacking for the analyses of possible reactor accidents:

1. Phase diagram Zr-U-O system
2. Heat capacity measurements of
   a. UO_2 from 2350 to 3200°C
   b. ZrO_2 from 2000 to 3200°C
   c. ZrO_{2-x} ($x = 0.5$ to 1.5) 0 to 3200°C
   d. Important phases in Zr-U-O system
3. Vapor pressure measurements
   a. ZrO_{2-x}
   b. Important phases in the U-Zr-O system
4. Thermal conductivity
   a. ZrO_{2-x} to 3000°C
   b. A better understanding of the effects of stoichiometry on the thermal conductivity of UO_2 at high temperatures
   c. Important phases of the U-Zr-O system
5. Thermal expansion (from 0°C)
   a. β-Zircaloy-4 from 1000 to 2000°C
   b. Tetragonal and cubic ZrO_2 from 1800 to 3200°C
   c. ZrO_{2-x} from 1000 to 2500°C
   d. Important phases in the Zr-U-O system

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